Ph.D. Department of Chemistry

Peter Grey

ARGENTIMETRIC AND CHELATE-EXCHANGE TITRATIONS IN NONAQUEOUS SOLVENTS

A B S T R A C T

High-frequency titrimetry was applied to the argentimetric determination of halides and thiocyanate, singly and in mixtures in methanol. The titration graphs were correctly predicted from the high-frequency response curves of the individual electrolytes that participated in the titrations.

Chelate-exchange titrations in low-dielectric constant solvents were conceived and developed to determine (i) the oxinates of Pb,Cu(II),Zn,Cd and In with dithizone; (ii) the dithizonates of the same metals and also of Ag, singly and in certain mixtures, with sodium diethyldithiocarbamate. The overall equilibrium constants for the lead, copper and indium oxinate - dithizone systems in benzene were evaluated.

Spectrophotometric titrations were developed to determine oxine, dithizone and sodium diethyldithiocarbamate in nonaqueous solvents.

Mixed chelates and adducts, $Cu(HDz)_2.H_2Dz$, $Cu(HDz)_2.2H_2Dz$, PbOxHDz, PbOxHDz. HOx, $Pb(HDz)_2.HOx$, $InOx(HDz)_2$, $InOx_2(HDz)$, were discovered in benzene, their formation constants evaluated, and their structures postulated.

The titration graphs of the chelate-exchange titrations were predicted from the measured equilibrium constants.

Ph. D. Department of Chemistry

Peter Grey

Short Title of Thesis:

NONAQUEOUS TITRIMETRY

ARGENTIMETRIC AND CHELATE-EXCHANGE TITRATIONS IN NONAQUEOUS SOLVENTS

by

Peter Grey, B.Sc.

A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy

Department of Chemistry,
McGill University,
Montreal, Quebec

July, 1968

© Peter Grey 1969

ACKNOWLEDGMENTS

I am most grateful to Dr. A. J. Frueh of the Dept. of Geology, McGill University for the X-ray measurements, to Dr. A. S. Ross of the Dept. of Chemistry, McGill University for the loan of a standard thermometer and other equipment, to Dr. Nurjahan Begum for the data of Table 5, to Dr. J. Hicks of Mobil Research and Development Corporation for help in computer programming and statistics, to Mrs. Barbara Banks for typing the manuscript with commendable accuracy, and to the many other people who helped in completing the manuscript.

I thank my fellow students for their help and cooperation, and particularly for those discussions over coffee which generated so many ideas.

I am deeply grateful to my Mother whose devotion made all this possible, and to my wife, Anne, for her unfailing moral support.

I thank the Province of Quebec for financial support.

Finally, but not least, my thanks and gratitude to Professor G. C. B. Cave, my Research Director, for his help and guidance and for the invaluable training he has given me.

Page

PART I

FIRST BOOK

ARGENTIMETRIC TITRATION OF HALIDES AND THIOCYANATE IN NONAQUEOUS SOLVENTS BY HIGH-FREQUENCY TITRIMETRY 1

PART II

SECOND BOOK

CHELATE-EXCHANGE TITRATIONS IN NONAQUEOUS SOLVENTS BY SPECTROPHOTOMETRIC TITRIMETRY 99

APPENDICES

THIRD BOOK

TABLE OF CONTENTS

	Page
Acknowledgments	ii
List of Tables	ix
List of Plates	xviii
List of Figures	xix
List of Appendices	xxvii
List of Symbols	xxx

PART I

I.	INTRODUCTION	2
II.	STATEMENT OF THE PROBLEM AND PLAN OF RESEARCH	4
III.	EXPERIMENTAL	7
	A. APPARATUS	7
	1. The Sargent Model V Chemical Oscillometer	7
	2. The Titration Cells	7
	3. Stirrers	11
	4. The Sargent Cell Compensator	11
	5. Volumetric Glassware	12
	B. REAGENTS	13
	C. PROCEDURES	15
	1. The Titrimetric Procedure	15
	2. Measurement of Response Curves	18
	3. Preparation of Simulated Titration Graphs	19
	D. EXPERIMENTAL RESULTS	20
	1. The Effect of Temperature and Evaporation of Solvent on the Apparent Capacitance of a Solution	20
	2. Titration of Halides and Thiocyanate Solutions	27
	3. The Response Curves	48
IV.	DISCUSSION OF RESULTS	55
	A. INTRODUCTION	55
	B. TITRATION OF SINGLE HALIDES	55
	C. SOLID-SOLUTION FORMATION IN THE TITRATION OF BINARY MIXTURES OF CHLORIDE AND BROMIDE	57

TABLE OF CONTENTS - CONTINUED

	Page
D. THE TITRATION OF BINARY MIXTURES OF THIOCYANATE AND CHLORIDE	63
E. INTERPRETATION OF THE TITRATION GRAPHS	65
1. Introduction	65
2. Interpretation of the Titration Graph of a Single Halide	72
3. Interpretation of the Titration Graph for a Binary Mixture of Sodium Chloride and Sodium Bromide	78
F. MICRO-TITRATIONS	85
1. The Effect of the Addition of Sodium Nitrate	85
2. The Effect of the Cell Compensator	87
V. RANGE OF TITRATABLE CONCENTRATIONS	91
A. CONCENTRATION RANGES FOR THE HALIDES AND THIOCYANATE	91
B. USE OF OTHER SOLVENTS TO VARY THE RANGE OF TITRATABLE CONCENTRATIONS	93
VI. SUMMARY AND CONCLUSIONS	95
VII. SUGGESTIONS FOR FURTHER WORK	97
VIII. CLAIMS OF ORIGINAL WORK	98
PART II	
I. INTRODUCTION	100
II. STATEMENT OF THE PROBLEM AND PLAN OF RESEARCH	103
III. PRELIMINARY SURVEY	108
IV. EXPERIMENTAL	113
A. APPARATUS	113
1. Apparatus for Spectrophotometric Titrations	113
2. Perkin-Elmer Model 350 Ultraviolet, Visible and Near Infrared Spectrophotometer	117
3. Cambridge General Purpose Polarograph	118
4. Eberbach Electro-Analysis Apparatus	119
5. Manual, Controlled-Potential Electrolysis Apparatus	121

TABLE OF CONTENTS - CONTINUED

		Page
6.	Vacuum Sublimation Apparatus	121
7.	Infrared Spectrophotometers	121
8.	Glassware	123
B.	REAGENTS	124
1.	Benzene	124
2.	Chloroform	125
3.	Carbon Tetrachloride	126
4.	Precautions in the Use of the Solvents	126
5.	Diphenylthiocarbazone	126
6.	8-Quinolinol	133
7.	Sodium Diethyldithiocarbamate	135
8.	The Metal 8-Quinolinates	137
9.	Metal Diphenylthiocarbazonates	144
10.	Standard Metal Solutions	152
11.	General Reagents	152
12.	Miscellaneous Reagents	157
C.	PROCEDURES	157
1.	Procedure for Spectrophotometric Titrations	157
2.	Standardization of Dithizone Solutions by Spectrophotometric Titration	162
3.	Standardization of Oxine Solutions by Spectrophotometric Titration	172
4.	Standardization of Sodium Diethyldithiocarbamate Solutions by Spectrophotometric Titration	177
5.	Determination of Molar Absorptivities	183
6.	Procedures for Spectrophotometric Study of Reactions of Lead, Copper and Indium Oxinates with Dithizone in Benzene at 25°C	208
7.	Infrared Spectra: Preparation of Samples and Results	210
8.	X-Ray Diffraction Patterns: Preparation of Samples and Results	220
D.	RESULTS	222

TABLE OF CONTENTS - CONTINUED

	Page
1. Spectrophotometric Titrations	222
(a) Introduction	222
(b) Titration of Metal Dithizonates by Diethyldithiocarbamate	223
(c) Titration of Metal Oxinates with Dithizone	232
2. Statistical Treatment of the Titration Data	245
(a) Introduction	245
(b) Statistical Operations	245
(c) Statistical Treatment of the Data for the Titration of Copper Oxinate with Dithizone in Benzene	258
(d) Statistical Treatment of the Data for the Titration of Indium Oxinate with Dithizone in Benzene	268
(e) Statistical Treatment of the Data for the Titration of Lead, Zinc and Cadmium Oxinates with Dithizone in Benzene	272
(f) Statistical Treatment of the Data for the Titration of Metal Dithizonates in Chloroform with Sodium Diethyldithiocarbamate in Ethanol	274
3. Calculation of Equilibrium Constants	275
(a) The Introduction	275
(b) The Copper System	282
(c) The Indium System	333
(d) The Lead System	370
V. DISCUSSION	417
A. TITRATIONS	417
1. Sourcesof error	417
2. Kinetics	425
3. Application to solvent Extraction	427
B. RANGE OF TITRATABLE CONCENTRATIONS	430
1. Range of Concentration	430
2. Comparison with other Techniques	433
C. REACTIONS OF THE METAL CHELATES	435
1. Introduction	435
2. Dithizone and the Metal Dithizonates	435

TABLE OF CONTENTS - CONTINUED

		Page
3.	Oxine and the Metal Oxinates	439
4.	Interpretation of Absorption Curves	441
5.	Mixed Chelates	443
6.	Adduct Formation	447
7.	The Reaction of Cobalt Oxinate with Dithizone	461
D.	EQUILIBRIUM CONSTANTS	462
1.	Activity Coefficients	462
2.	Formation of the Compound, $H_2Dz.HOx$	463
3.	Dimers	463
4.	Effect of Water	465
5.	Effect of Temperature	467
VI.	SUMMARY AND CONCLUSIONS	469
VII.	SUGGESTIONS FOR FURTHER WORK	472
VIII.	CLAIMS TO ORIGINAL WORK	474
	APPENDICES	1a
	REFERENCES	163a

LIST OF TABLES

Table No.		Page
	PART I	
1	The Change of the Apparent Capacitance for a Fixed Change in Temperature, As a Function of Concentration	25
2	High-Frequency Argentimetric Titration of Halides and Thiocyanate Present Alone in Methanol	28
3	High-Frequency Titrations of Sodium Halides and Thiocyanate Mixtures in Methanol	36
4	Precision of High-Frequency Argentimetric Titrations of Sodium Chloride and Sodium Bromide in Equimolar Mixtures in Methanol	39
5	The Effect of Variation in the Mole Ratio of Chloride and Bromide on the Accuracy of Argentimetric Titrations in Methanol	40
6	The Effect of Variation in the Mole Ratio of Chloride and Thiocyanate on the Accuracy of Argentimetric Titrations in Methanol	41
7	High-Frequency Titrations of Micro Amounts of Halide, Alone and in Their Mixtures, in Methanol	46
8	Comparison of Calculated Errors in the Bromide End Point for Homogeneous and Heterogeneous Solid-Solution Formation With Experimental Titration of Chloride-Bromide Mixtures in Methanol	62
9	Comparison of Predicted, Simulated and Experimental Titration Graphs for the High-Frequency Argentimetric Titration of Sodium Chloride in Methanol	76
10	Comparison of Predicted, Simulated and Experimental Titration Graphs for the High-Frequency Titration of an Equimolar Mixture of Sodium Chloride and Sodium Bromide in Methanol	82
11	Upper and Lower Limits in the High-Frequency Argentimetric Titration of Halides and Thiocyanate in Methanol	92

LIST OF TABLES

Table No.		Page
	PART II	
12	Analysis of Solid Metal Oxinates	140
13	Standardization of Benzene Solutions of Metal Oxinates and Dithizonates	143
14	Analysis of Solid Metal Dithizonates	148
15	Standard Solutions of Metals	153
16	Miscellaneous Reagents	158
17	The Molarity of a Standard Solution of Silver Nitrate in Methanol, as a Function of Time	165
18	The Molarity of a Standard Solution of Silver Nitrate in 1:20 Methanol:Benzene, as a Function of Time	166
19	Molarity of a Standard Solution of Silver Nitrate in 1:20 Methanol:Benzene, as a Function of Time Over a Twelve-Hour Period	167
20	The Accuracy and Precision of the Standardization of a Benzene Solution of Dithizone, by Spectrophotometric Titration with a Standard Solution of Silver Nitrate in 1:20 Methanol: Benzene	171
21	Variation in the Precision of the Spectrophotometric Titration of a Benzene Solution of Dithizone, with a Standard Solution of Silver Nitrate in 1:20 Methanol:Benzene, as a Function of Time .	173
22	The Accuracy and Precision of the Standardization of Benzene Solution of Oxine by Spectrophotometric Titration with a Standard Solution of Copper Nitrate in Ethanol	178
23	The Accuracy and Precision of the Standardization of Ethanol Solutions of Sodium Diethyldithiocarbamate, with a Standard Solution of Copper in Ethanol, by Spectrophotometric Titration	180

LIST OF TABLES

Table No.		Page
24	The stability of Ethanol Solutions of Sodium Diethyldithiocarbamate, over a Period of One Week	182
25	Fluctuations in the Molarity of an Ethanol Solution of Sodium Diethyl-dithiocarbamate,over a Twelve Hour Period	184
26	Comparison of the Absorptivity of Dithizone in Benzene at 618 mu and at 450 mu Determined by Two Different Methods	185
27	The Concentration Ranges used for the Determination of the Molar Absorptivities of Metal Dithizonates in Benzene	198
28	Methods of Analysis for the Liberated Metals after Decomposition of the Metal Dithizonates	200
29	Statistical Treatment of the Data for the Determination of the Absorptivity of Lead Dithizonate at 517 mu in Benzene	205
30	Concentration Ranges used for the Determination of the Absorptivi-ties of Metal Oxinates in Benzene	207
31	Infrared Absorption Frequencies of Oxine, Dithizone and of some Metal Oxinates and Metal Dithizo-nates in the Caesium Bromide Region	218

LIST OF TABLES

Table No.		Page
32	Spectrophotometric Titrations of Silver Dithizonate in Chloroform with Standard Sodium Diethyldithiocarbamate in Ethanol at 25°C	224
33	Spectrophotometric Titrations of Lead Dithizonate in Chloroform with Standard Sodium Diethyldithiocarbamate in Ethanol at 25°C	225
34	Spectrophotometric Titrations of Indium Dithizonate in Chloroform with Standard Sodium Diethyldithiocarbamate in Ethanol at 25°C	226
35	Spectrophotometric Titrations of Zinc Dithizonate in Chloroform with Standard Sodium Diethyldithiocarbamate in Ethanol at 25°C	227
36	Spectrophotometric Titrations of Cadmium Dithizonate in Chloroform with Standard Sodium Diethyldithiocarbamate in Ethanol at 25°C	228
37	Spectrophotometric Titrations of Copper Dithizonate in Chloroform with Standard Sodium Diethyldithiocarbamate in Ethanol at 25°C	229
38	Spectrophotometric Titrations of Binary Mixtures of Metal Dithizonates in Chloroform, with Standard Sodium Diethyldithiocarbamate in Ethanol at 25°C	233
39	Spectrophotometric Titrations of Ternary Mixtures of Metal Dithizonates in Chloroform, with Standard Sodium Diethyldithiocarbamate in Ethanol at 25°C	234
40	Spectrophotometric Titrations of Lead Oxinate with Standard Dithizone in Benzene at 25°C	246
41	Microspectrophotometric Titrations of Lead Oxinate with Standard Dithizone in Benzene at 25°C	247

LIST OF TABLES

Table No.		Page
42	Spectrophotometric Titrations of Cadmium Oxinate with Standard Dithizone in Benzene at 25°C.....	248
43	Microspectrophotometric Titrations of Cadmium Pxinate with Standard Dithizone in Benzene at 25°C.....	249
44	Spectrophotometric Titrations of Copper Oxinate with Standard Dithizone in Benzene at 25°C	250
45	Microspectrophotometric Titrations of Copper Oxinate with Standard Dithizone in Benzene at 25°C	251
46	Spectrophotometric Titrations of Zinc Oxinate with Standard Dithizone in Benzene at 25°C	252
47	Spectrophotometric Titrations of Zinc Oxinate with Standard Dithizone in Benzene at 42.4 0.4°C	253
48	Microspectrophotometric Titrations of Zinc Oxinate with Standard Dithizone in Benzene at 42.4 0.4°C	254
49	Spectrophotometric Titrations of Indium Oxinate with Standard Dithizone in Benzene at 25°C	255
50	Microspectrophotometric Titrations of Indium Oxinate with Standard Dithizone in Benzene at 25°C	256
51	Means and Variances for End Points (i) Estimated by Visual Inspection and (ii) Calculated by the Least-Squares Method, in the Titration of Copper Oxinate with Dithizone, in Benzene.....	259
52	Summary of Results from Analysis of Variance on the Data of the Titration of Copper Oxinate with Dithizone in Benzene at 618 mu and 545 mu	262
53	Values of t for the Test of Significance between the Means of the Amount of Copper Oxinate Found in Titrations with Dithizone at 618 mu and 545 mu	264

LIST OF TABLES

Table No.		Page
54	Summary of Results obtained from Analysis of Variance on the Data of the Titration of Indium Oxinate with Dithizone in Benzene at 505 mu.....	269
55	Comparison of Pooled Variances and Grand Means when Lead, Zinc and Cadmium Oxinates Titrated with Dithizone in Benzene at 618 mu and the Wavelength of Maximum Absorption of the Metal Dithizonate	273
56	Comparison of Pooled Variances and Grand Means when Metal Dithizonates in in Chloroform were Titrated with Sodium Diethyldithiocarbamate in Ethanol at 615 mu and the Wavelength of Maximum Absorption of the Metal Dithizonate	275 i
57	Qualitative Experimental Observations on the Reactions of the Copper Chelates..	283
58	System of Beer's Law Equations for the Calculation of Equilibrium Concentrations in the Copper Oxinate - Dithizone System in Benzene at 25°C.....	292
59	Equilibrium Concentrations and Equilibrium Constant for the Reaction $2\ CuDz + 2HOx = CuOx_2 + Cu(HDz)_2$ in Benzene at 25°C.....	297
60	Equilibrium Concentrations and Equilibrium Constant for the Reaction $CuOx_2 + Cu(HDz)_2 = 2\ CuDz + 2HOx$ in Benzene at 25°C.....	298
61	Equilibrium Concentrations and Equilibrium Constant for the Reaction $CuDz + H_2Dz = Cu(HDz)_2$ in Benzene at 25°C.	301
62	Calculated Apparent Concentration of $Cu(HDz)_2$ as a Function of the Initial Ratio of $(Cu(HDz)_2)_i : (H_2Dz)_i$, in Dry Benzene at 25°C	303
63	Equilibrium Concentrations of $Cu(HDz)_2$ and $Cu(HDz)_2$. H_2Dz in Dry Benzene at 25°C, from which the Absorptivity of $Cu(HDz)_2$. H_2Dz was calculated	307

LIST OF TABLES

Table No.		Page
64	Equilibrium Concentrations and Equilibrium Constant for the Reaction $Cu(HDz)_2 + H_2Dz = Cu(HDz)_2 \cdot H_2Dz$ in Dry Benzene at 25°C	311
65	Equilibrium Concentrations and Equilibrium Constant for the reaction $Cu(HDz)_2 \cdot H_2Dz + H_2Dz = Cu(HDz \cdot 2H_2Dz$ in Dry Benzene at 25°C	313
66	Calculated Equilibrium Concentrations of the Species Present in the Solutions for the Continous Variation Plot of the Reaction of CuDz with H_2Dz in Dry Benzene at 25°C	317
67	Calculated Equilibrium Concentrations of the Species Present in the Solutions for the Continous Variation Plot of the Reaction of CuDz with H_2Dz in "Wet" Benzene at 25°C	318
68	Comparison of Calculated and Experimental Absorbances for the Continous Variation Plots of the Reaction of CuDz with H_2Dz in Undried and Dry Benzene at 25°C	319
69	Analytical Data and Calculated Equilibrium Concentrations of the Species Present in Solution when CuOx was Titrated with H_2Dz in Benzene at 25°C	324
70	Analytical Data and Calculated Equilibrium Concentrations of the Species Present in Solution when $CuOx_2$ was Titrated with H_2Dz at 25°C in Benzene Solutions which contained Onehundredfold Excess of Free Oxine	327
71	Comparison of Calculated and Experimental Absorbances of the Titration Graph of the Titration of $CuOx_2$ with H_2Dz in Benzene at 25°C	328
72	Comparison of Absorbances at 618 mu Calculated for Different Values for K_3^1 and K_2^1, with Experimental Absorbances	343

LIST OF TABLES

Table No.		Page.
73	Comparison of Experimental and Calculated Absorbances of the Continuous Variation Solutions for the Reaction of Indium Oxinate with Dithizone in Benzene at 25°C.....	347
74	Experimental Absorbances, and Absorbances Calculated for Different Values of K_1, at 618 mu	352
75	Coefficients of the Equations of the Curves obtained by Plotting Absorbance at 618 mu versus initial Mole Fraction...	355
76	Calculation of Molar Absorptivities of $InOx(HDz)_2$ and $InOx_2$ (HDz) at 510 mu and 25°C, ...	360
77	Comparison of Calculated and Experimental Absorbances for Solutions of Set B.....	363
78	Analytical Data and Comparison of Calculated and Experimental Absorbances for the Titration of Indium Oxinate with Dithizone in Benzine at 25°C.....	365
79	Calculated Equilibrium Concentrations of Species Present in Solution when Indium Oxinate was Titrated with Dithizone in Benzene at 25°C.....	367
80	Calculated Equilibrium Concentrations of Species Present in Solution when Indium Oxinate was Titrated with Dithizone in Benzene at 25°C, with Fiftyfold Excess of Free Oxine Initially Present	368
81	Equations for the Equilibrium Constant K_3 as a Function of Absorptivity of PbOxHDz at 517 mu for the Reaction $PbOx_2$ + $Pb(HDz)_2$ = PbOxHDz	379
82	Equilibrium Concentrations and Equilibrium Constants for Sets A1 and A2	381
83	Equations for the Equilibrium Constant as a Function of Absorptivity of $Pb(HDz)_2$. HOx at 517 mu for the Reaction $Pb(HDz)_2$ + HOx = $Pb(HDz)_2$. HOx in Benzene at 25°C..	387

LIST OF TABLES

Table No.		Page
84	Equilibrium Concentrations and Equilibrium Constants for Se C	389
85	Equations for the Equilibrium Constant K_4 as a Function of Absorptivity of PbOxHDz.HOx at 517 mu (Set B2) and Equations in Absorptivity only for the Reaction PbOxHDz + HOx = PbOxHDz.HOx in Benzene at 25° C.....	393
86	Equilibrium Concentrations and Equilibrium Constants for Sets B1 and B2	395
87	The system of Linear Beer's Law Equations used for the Calculation of Equilibrium Concentrations in the Lead System.....	401
88	Equilibrium Concentrations and Equilibrium Constants for Sets E1 and E2..	403
89	Calculated Equilibrium Concentrations of Species Present in Solution when $PbOx_2$ was Titrated with Dithizone in Benzene at 25°C, for the case where the Solution Contained Free Oxine, Onehundredfold in excess with respect to the Initial $PbOx_2$ Concentration 410	
90	Comparison of Experimental and Calculated Absorbances for the Titration of $PbOx_2$ with Dithizone in Benzene for the case where the Solution contained Free Oxine, Onehundredfold in Excess with respect to the Initial $PbOx_2$ Concentration 414	
91	Range of Titratable Concentrations for the Titration of Metal Dithizonates and Metal Oxinates	
92	Typical Lower Limits of Determinable Concentrations for Various Instrumental Techniques.....	
93	Adduct - Formation with Copper Chelates	

LIST OF PLATES

Plate No.		Page
1	Sargent Model V Chemical Oscillometer and Accessories	9
2	Spectrophotometric Titration Apparatus .	114

LIST OF FIGURES

Figure No.		Page
	PART I	
1	The Large Titration Cell	10
2	Anomalous Changes of Slope in the High-Frequency Argentimetric Titration of Halide Mixtures in Methanol in an Open Titration Cell	22
3	Changes in Apparent Capacitance and in Temperature of a Solution of Sodium Chloride as a Function of Time in an Open Titration Cell	23
4	Effect of a Fixed Change in Solution Temperature on the Apparent Capacitance of Solutions of Sodium Chloride in Methanol	26
5	Typical Titration Graphs of Argentimetric Titrations of Single Halides in Methanol	29
6	Dependence of the Shape of a Titration Graph on Concentration and Halide Species	30
7	Titration Graphs of the Argentimetric Titration of Strontium Chloride and of Cupric Chloride in Methanol	32
8	Effect of Acid in the Argentimetric Titration of Halide in Methanol	34
9	Typical Titration Graphs of Argentimetric Titrations of Pairs of Halides in Methanol	35
10	Argentimetric Titration of Chloride-Bromide Mixtures in 88% Acetone	43
11	Typical Titration Graphs of Argentimetric Titrations of Mixtures of Several Halides in Methanol	44
12	Titration of Graphs of Argentimetric Titrations of Micro Amounts of Sodium Chloride in Methanol, Close to the Lower Limit of Concentration	47

LIST OF FIGURES - CONTINUED

Figure No.		Page
13	Typical Titration Graphs of Argentimetric of Micro Amounts of Halides in Methanol	49
14	Response Curves of Electrolytes in Methanol, and of Silver Nitrate in Ethanol	50
15	Sections of the Response Curves of Several Electrolytes in Methanol, in the Low Concentration Range	51
16	Low Concentration Region of the Response Curve of Sodium Chloride in Methanol, With and Without the Use of the Sargent Cell Compensator	53
17	Titration Graphs of the Argentimetric Titration of Mixtures of Chloride and Bromide in Methanol ..... (a) The Mole Ratio of Cl:Br was 1:20 (b) The Mole Ratio of Cl:Br was 20:1	64
18A	Transfer Plots for Parallel Capacitance Changes	67
18B	Correlation of Capacitance-Change Titrations to Low-Frequency Conductivity Titrations in Aqueous Solution	68
19	The Specific Conductance of Sodium Halides and Sodium Nitrate Solutions in Methanol as a Function of Molar Concentration at 25°C	70
20	Apparent Capacitance of Methanol Solutions of Sodium Halide and Sodium Nitrate, as a Function of the Specific Conductance at 25°C	71
21(a)	Expanded Response Curves for Sodium Chloride and Sodium Nitrate Solutions in Methanol	73
21(b)	Expanded Response Curves for Sodium Iodide and Sodium Nitrate Solutions in Methanol	73

LIST OF FIGURES - CONTINUED

Figure No.		Page
22	Experimental, Calculated and Simulated Titration Graphs for the High-Frequency Angentimetric Titration of Sodium Chloride in Methanol	77
23	Expanded Response Curves for Solutions of Sodium Chloride, Sodium Bromide and Sodium Nitrate in Methanol	79
24	Experimental, Calculated and Simulated Titration Graphs for the High-Frequency Argentimetric Titration of an Equimolar Mixture of Sodium Chloride and Sodium Bromide in Methanol	83
25	Effect of Addition of Sodium Nitrate to the Titration Solution in the Argentimetric Titration of Micro Amounts of Chloride and Chloride + Bromide in Methanol	86
26	Effect of the Sargent Cell Compensator in the Argentimetric Titration of Micro Amounts of Chloride in Methanol	89
27	Typical Titration Graphs for the Titration of Metal Chelates with 8-Quinolinol or Diphenylthiocarbazone in Chloroform	109
28	Effect of Initial Concentrations of Free Acetylacetone in the Titration of Copper (II) Acetylacetonate with 8-Quinolinol in Chloroform at 410 mμ	111
29	The 3-ml Cell Holder	116
30	The 5-ml Polarographic Cell and H-Cell Assembly	120
31	Circuit Diagram of Controlled-Potential Electrolysis Apparatus	122
32	Molar Absorptivity Curve for Dithizone in Benzene and a Spectral Transmission Curve of a Solution of the Oxidation Product of Dithizone in Benzene	128

LIST OF FIGURES - CONTINUED

Figure No.		Page
33	Percent Purity of Dithizone as a Function of the Number of Ammonia Extractions	131
34	Typical Titration Graphs of the Spectrophotometric Titration of Dithizone Solutions in Benzene with Standard Silver Nitrate Solution in 1:20 Methanol-Benzene	168
35	A Typical Titration Graph of the Spectrophotometric Titration of Oxine in Benzene with a Standard Solution of Copper Nitrate in Ethanol	176
36	A Typical Titration Graph of the Spectrophotometric Titration of an Ethanol Solution of Cupric Nitrate, by an Ethanol Solution of Sodium Diethyldithiocarbamate, at 435 mμ	181
37	The Absorptivity of Dithizone in Benzene at 25°C, as a Function of Wavelength	191
38	Absorptivity of Oxine in Benzene at 25°C, as a Function of Wavelength	194
39	The Molar Absorptivity Curves of the Metal Dithizonates in Benzene at 25°C	202
40	Comparison of the Absorptivity Curves of the Metal Dithizonates in Benzene at 25°C	203
41	Molar Absorptivity Curves for the Metal Oxinates in Benzene at 25°C	209
42	Comparison of the Molar Absorptivity Curves of the Metal Oxinates and Oxine, in Benzene at 25°C	210
43	Infrared Spectra From 14 to 33 Microns of Lead Oxinate, Lead Dithizonate and the 1:1 Molar Mixture of Lead Oxinate and Lead Dithizonate	219
44	X-ray Powder Patterns of Dithizone, Cupric Dithizonate and the 1:1 Molar Mixture of Cupric Dithizonate and Dithizone	221

LIST OF FIGURES - CONTINUED

Figure No.		Page
45	Typical Titration Graphs of Spectrophotometric Titrations of Single Metal Dithizonates in Chloroform at 25°C with a Standard Solution of Diethyldithiocarbamate in Ethanol	231
46	Typical Titration Graphs of the Spectrophotometric Titration of Binary Mixtures of Metal Dithizonates in Chloroform at 25°C, with Sodium Diethyldithiocarbamate in Ethanol	235
47	Typical Titration Graphs of the Spectrophotometric Titration of Ternary Mixtures of Metal Dithizonates in Chloroform at 25°C, with Sodium Diethyldithiocarbamate in Ethanol	236
48	Rate of Attainment of Equilibrium of the Reaction of Copper Oxinate With Dithizone in Benzene at 25°C	238
49	Rate of Attainment of Equilibrium of the Reaction of Zinc Oxinate with Dithizone in Benzene, as a Function of Temperature and Initial Concentration of Free Oxine	239
50	Rate of Attainment of Equilibrium of the Reaction of Cadmium Oxinate with Dithizone in Benzene	240
51	Typical Titration Graphs for the Reaction of Cupric Oxinate with Dithizone in Benzene at 25°C	243
52	Titration Graphs Illustrating the Effect of Initial Free Oxine in the Solution for Titration when Indium Oxinate was Titrated Spectrophotometrically with Dithizone in Benzene at 25°C and 505 mμ	244
53	Correction Curves for the Titration of Copper Oxinate with Dithizone in Benzene .	265
54	Correction Curve for the Titration of Indium Oxinate with Dithizone in Benzene at 505 mμ	271

LIST OF FIGURES - CONTINUED

Figure No.		Page
55	Continuous-Variations Plots for the Reaction of Copper Oxinate with Dithizone at 25°C in Undried Benzene Solutions.....	284
56	Continuous-Variations Plots for the Reaction of Secondary Copper Dithizonate with Oxine in Undried Benzene At 25°C.....	285
57	Comparison of Continuous-Variations Plots at 618, 545 and 445 mu for the Reaction of Secondary Copper Dithizonate with Dithizone at 25°C in Undried and Dry Benzene.....	287
58	Absorptivity versus Wavelength for $Cu(HDz)_2.H_2Dz$ and for $Cu(HDz)_2.2H_2Dz$ at 25°C in Dry Benzene.....	308
59	Comparison of the Calculated and Experimental Titration Graphs of the Titration of Copper Oxinate with Dithizone in Benzene at 25°C.....	329
60	Comparison of Calculated and Experimental Titration Graphs for the Titration of Copper Oxinate with Dithizone at 25°C in Benzene Solutions which contained Onehundredfold Excess of Free Oxine.....	332
61	Comparison of Calculated Continuous-Variations Plots at 618 mu using Different Combinations of K_2^1 and K_3^1 for the Reaction of Indium Dithizonate with Oxine in Benzene at 25°C...	345
62	Comparison of Calculated and Experimental Continuous-Variations Plots at 618 mu for the Reaction of Indium Dithizonate with Oxine in Benzene at 25°C.....	346
63	Comparison of Calculated and Experimental Continuous-Variations Plots for the Reaction of Indium Oxinate with Dithizone in Benzene at 25°C.....	348

LIST OF FIGURES - CONTINUED

Figure No.		Page
64	Comparison of Calculated and Experimental Continuous-Variations Plots for the Reaction of Indium Oxinate with Dithizone in Benzene at 25°C.....	350
65	Comparison of Calculated and Experimental Continuous-Variations Plots for the Reaction of Indium Oxinate with Dithizone in Benzene at 25°C.....	351
66	Sections of Continuous-Variations Plots at 618 mu, using Different Values of K_1, for the reaction of Indium Oxinate with Dithizone in Benzene at 25°C.....	353
67	Experimental Points, Regression Line and 95% Confidence Limits for Part of the Continuous-Variations Plot of Set D.....	357
68	Molar Absorptivity of $InOx_2(HDz)$ and $InOx(HDz)_2$ at 25°C in Benzene versus Wavelength.....	361
69	Comparison of Experimental and Calculated Continuous-Variations Plots for the Reaction of Indium Dithizonate with Oxine in Benzene at 25°C...	364
70	Comparison of Calculated and Experimental Titration Graphs for the Titration of Indium Oxinate with Dithizone in Benzene at 25°C.....	369
71	Continuous-Variations Plot for the Reaction of Lead Oxinate with Dithizone in Benzene at 25°C.....	371
72	Curve of Absorptivity versus Wavelength for PbOxHDz, in Benzene at 25°C.....	382
73	Curve of Absorptivity versus Wavelength for the Oxine Adduct $Pb(HDz)_2.HOx$ in Benzene at 25°C.....	390
74	Curve of Absorptivity versus Wavelength for PbOxHDz.HOx in Benzene at 25°C.....	399

LIST OF FIGURES - CONTINUED

Figure No.		Page
75	Calculated and Experimental Titration Graphs for the Titration of Lead Oxinate with Dithizone in Benzene at 25°C for the Case where the Solution contained Initial Free Oxine, Onehundredfold in Excess with Respect to the Initial Concentration of Lead Oxinate.....	415

LIST OF APPENDICES

Appendix No.		Page
I	Calculation of the First Branch of the Titration Graph for the Argentimetric Titration of an Equimolar Mixture of Chloride and Bromide	2a
II	The Solubility Products of Silver Halides in Some Solvents	5a
III	Solubilities of Some Electrolytes in Selected Nonaqueous Solvents	7a
IV	Wavelength Calibration for Beckmann DU Spectrophotometer	12a
V	Spectrophotometric Titration Apparatus.	13a
VI	Manual, Controlled Potential Electrolysis Apparatus	18a
VII	Vacuum Sublimation Apparatus	20a
VIII	Comparison of the Behaviour of Dithizone in Different Grades of Benzene	22a
IX	Method for the Purification of Dithizone	32a
X	Procedure for the Purification of Oxine	34a
XI	Procedure for the Preparation of Metal Oxinates.....	36a
XII	Approximate Solubilities of Metal Dithizonates and Metal Oxinates in Chloroform, Carbon Tetrachloride and Benzene	40a
XIII	Procedure for the Preparation of Metal Dithizonates	43a
XIV	Method for the Decomposition of the Organic Matter in Metal Chelates	46a
XV	Colorimetric Determination of the Oxinate Radical in a Metal Oxinate ..	48a
XVI	Standard Metal Solutions	50a

LIST OF APPENDICES

Appendix No.		Page
XVII	Reversion Technique	55a
XVIII	Tables of Values for the Molar Absorptivity of Dithizone in Benzene at 25°C as a Function of Wavelength	58a
XIX	Tables of Values for the Molar Absorptivity of Oxine in Benzene at 25°C as a Function of Wavelength	61a
XX	Tables of Values for the Molar Absorptivity of the Metal Dithizonates in Benzene at 25°C as a Function of Wavelength	63a
XXI	Wavelength of Maximum Absorption in the Visible Region of Some Metal Dithizonates in Benzene, Chloroform and Carbon Tetrachloride	71a
XXII	Tables of Values for the Molar Absorptivity of Metal Oxinates in Benzene at 25°C as a Function of Wavelength	73a
XXIII	Wavelength of Maximum Absorption in the Visible Region of Some Metal Oxinates in Benzene and Chloroform ...	79a
XXIV	Preparation of Solutions for the Study of Reactions of Lead, Copper and Indium Oxinates in Benzene	80a
XXV	Statistical Treatment of the Data for the Titration of Copper Oxinate with Dithizone in Benzene	88a
XXVI	Statistical Treatment of the Data for the Titration of Indium Oxinate with Dithizone in Benzene	97a
XXVII	Analytical Data for the Reactions of the Copper Chelates	103a

LIST OF APPENDICES

Appendix No.		Page
XXVIII	Analytical Data for the Reactions of the Indium Chelates	126a
XXIX	Analytical Data for the Reactions of the Lead Chelates	146a

LIST OF SYMBOLS

H_2Dz	Diphenylthiocarbazone (dithizone)
$M(HDz)_n$	Primary metal dithizonate of metal with valency n
MDz	Secondary metal dithizonate of e.g. divalent metal
HOx	8-quinolinol (oxine)
MOx_n	Metal oxinate of metal with valancy n
NaD	Sodium diethyldithiocarbamate
MD_n	Metal dithyldithiocarbamate of metal with valancy n
[ ]	Denotes equilibrium concentration in moles $litre^{-1}$
$(\ )_i$	Denotes initial, stoichiometric concentration in moles $litre^{-1}$
M	Molarity in moles $litre^{-1}$
N	Normality in equivalents $litre^{-1}$
K_1	Concentration equilibrium constant of reaction 1
K_o	Overall concentration equilibrium constant
$(HDz)_T$	Total (stoichiometric) molar concentration of dithizonate ligand
$(Ox)_T$	Total (stoichiometric) molar concentration of oxinate ligand
$(M)_T$	Total (stoichiometric) molar concentration of metal, M
λ_i	Wavelength, i mμ
$a_{\lambda_i,m}$	Molar absorptivity of species m in litre $mole^{-1}$ cm^{-1} at wavelength λ_i
A_{p,λ_i}	Absorbance of chemical solution p at wavelength λ_i for a given path length
b	path length of spectrophotometric cell in cm
S^2	Sample Variance
S	Sample standard deviation

LIST OF SYMBOLS

$\sigma^2_{HO_x}$	Component of population variance due to presence of free oxine
σ^2_{λ}	Component of population variance due to change of wavelength
$\sigma^2_{rep.}$	Component of population variance due to reproducibility
σ^2_{I}	Component of population variance due to interaction between wavelength and presence of free oxine
F	Ratio of the greater variance to the lesser variance in the test for significance of variances
t	Value of the t distribution for the comparison of two means

PART I

ARGENTIMETRIC TITRATION OF HALIDES AND THIOCYANATE IN NONAQUEOUS SOLVENTS BY HIGH-FREQUENCY TITRIMETRY

I. INTRODUCTION

In the present work, methods were developed for the high-frequency argentimetric titration of alkali-metal halides and thiocyanates present alone and in their mixtures dissolved in nonaqueous solvents.

The high-frequency method is a volumetric one in which the solution for titration comprises the dielectric. This dielectric may either be in the inductance coil of an oscillator, or it may be between the plates of a condenser. The coil-type instrument has been described by Jensen and Parrack (1), and the condenser-type instrument by Anderson et. al. (2). The Sargent Model V Chemical Oscillometer used in the present investigation is the condenser type; but the frequency is fixed at five megacycles per second. In operation, calibrated capacitance equal to the capacitance of the cell and contents is added or removed to restore the instrument to its natural frequency.

Volumetric methods for the halides usually are based on the use of silver nitrate as the titrant. In addition to the use of indicators to detect the end point, potentiometric, conductometric and amperometric methods may be used (3).

High-frequency titrations have been reported for the determination of chloride alone in aqueous solutions (4,5) and in other solvents (6), and for the determination of chloride and of sulphate present together in acetone-water solutions (7).

In potentiometric titrations, it is difficult to accurately determine the individual end points in the titration of halide mixtures (8). Low-frequency conductometric titrations of single halides are practicable, but are not satisfactory for the individual determination of halides in mixtures, in aqueous solution or in methanol. With the use of the high-frequency technique these problems were avoided.

In the titration vessel, the condenser plates were on the outside walls of the glass annulus, so that the solution for titration was never in contact with these plates.

The proposed method has been found useful for the direct determination of halides in the nonaqueous phase after solvent extraction (9).

High-frequency titration curves have previously been interpreted in terms of low-frequency conductometric curves (4,10,11). Excellent correlation was found for aqueous solutions. Nonaqueous solutions have not been treated. A new and simpler method for interpreting titration graphs is proposed in the present work. Changes in instrument response were plotted against the total concentration of alkali-metal halide in a given solvent. The resulting "response curves" were different for each halide and were used to predict the slopes of titration graphs.

II. STATEMENT OF THE PROBLEM AND PLAN OF RESEARCH

The argentimetric titration of halides and thiocyanate by visual detection of the equivalence point is limited to the titration of a single halide in aqueous solution. There are many methods, for example solvent extraction of halometallic acids, which require the determination of halides and sometimes mixtures of halides in nonaqueous solutions.

It was the purpose of the present investigation to develop a convenient, accurate and precise argentimetric titration of mixtures of halides in nonaqueous solutions.

Potentiometry has been used for the argentimetric titration of mixtures of halides in aqueous and aqueous-organic solutions, but it has disadvantages: (a) it is not possible in the titration of mixtures of halides to precisely locate the equivalence point of one component from the titration graph; (b) the presence of precipitate or nonaqueous solvent tends to affect the performance of the electrodes; (c) it is inconvenient to have the reference calomel electrode in a separate compartment, joined by a salt bridge.

The use of low-frequency conductometry for the argentimetric titration of mixtures of halides is impracticable, due to the similarity in conductance of the individual halides and thiocyanate and nitrate*. Thus, little or no change of slope in the titration graph occurs when one component of the mixture has been titrated.

---

*From the added titrant, silver nitrate.

The high-frequency conductometric technique is generally well suited for precipitation titrations in nonaqueous solvents. Thus, the titration cell may be constructed so that the solution is not in contact with the electrodes. This method was found in the present work to be sensitive enough to distinguish between the conductances of halides, thiocyanate and nitrate in methanol.

Methanol was chosen as the solvent because (a) it was readily available in a pure and essentially anhydrous state, (b) it is miscible with water and most common organic solvents and (c) it was found that much sharper changes in instrument readings were obtained in the argentimetric high-frequency titration of mixtures of halides in this solvent than in water.

The sodium halides were used. They were appreciably soluble in methanol, so that a wide range of salt concentration could be studied.

First, the argentimetric titration of single halides and thiocyanate in methanol was investigated. Then, the titration of binary, ternary and finally quaternary (chloride + bromide + iodide + thiocyanate) mixtures was studied. Finally, the method was extended to the titration of micro amounts of halides in methanol, by using a 6-ml titration cell and compensating for the capacitance of the cell walls.

The following factors were found to influence the accuracy and precision of the titration procedure, and were

investigated: (a) solvent evaporation and the temperature of the titration solution; (b) solid solution of one silver halide in another; (c) changes in the ionic strength of the sample solution.

By measuring the change in the apparent capacitance of a methanol solution in the titration cell, as a function of the molar concentration of the electrolyte, a response curve was obtained. These curves, measured for individual halides, made it possible to: (a) interpret the shapes of the titration graphs for the titration of single halides and of mixtures of halides; (b) prescribe the best titration conditions such as ionic strength, in order to obtain the sharpest breaks in the titration graphs; (c) prescribe the range of titratable concentrations.

III. EXPERIMENTAL

A. APPARATUS

1. The Sargent Model V Chemical Oscillometer

The Sargent Model V Chemical Oscillometer was used. It is a null-type instrument, with a fixed frequency of 5 megacycles per second.

The titration cell was a capacitor in parallel with standard capacitors, to comprise the resonant circuit of the oscillometer's sine-wave oscillator. After each measured addition of titrant, the apparent capacitance of the filled cell was measured by removing standard capacitances from the resonant circuit, until the frequency of the circuit was restored to its original value. This apparent capacitance is a function of the conductance and the dielectric constant of the solution. The principles of high-frequency titrimetry have been described by Reilley and McCurdy (11), and by Sherrick et. al. (12).

A photograph of the apparatus is shown in Plate 1.

For electrolyte solutions, the reading that was obtained from the instrument was a complex function of both the capacitance and conductance of the solution in the cell. It is hereinafter called "apparent capacitance" and measured as "instrument divisions". The apparent capacitance was measured with a reliability of ± 5 instrument divisions.

2. The Titration Cells

For a titration cell, the closed-type macro cell supplied with the Oscillometer was used. Its diameter was

50 mm, and the overall height was 165 mm. It had an outside-fitting ground-glass cap. For the present work, two holes, 9 mm in diameter, were drilled through this cap. A central hole was for the shaft of a polypropylene stirrer. The other hole was for the delivery tip of a buret. The shaft and the delivery tip were each fitted with a sliding washer of Silicone rubber having a thin smear of Silicone grease, to provide reasonably gas-tight seals at the two holes in the glass cap. A closed-type titration cell has also been used by Hitchcock and Elving, for nonaqueous titrations (13).

The solution for titration was contained in an annulus of 90-ml capacity, which constituted the lower half of the cell. The two outer cylindrical walls of this annulus each had a metal coating, to serve as the plates of the capacitor*. Thus, solutions never were in contact with these plates.

A photograph of a titration cell is shown in Plate 1 and a detailed diagram in Figure 1.

For micro titrations, a 10-ml closed-type cell supplied with the oscillometer was used. It was 15 mm in diameter, and 123 mm in height, constructed like the previously described macrocell, but with an annulus 65 mm deep that held only 5 ml of liquid. The outer walls were plated, to provide

*The electrodes were made by first applying powdered silver in the form of a paste. This paste was baked onto the glass. The electrode area was then rhodium plated. The electrodes were already prepared on the cell by the manufacturer.

PLATE 1

THE SARGENT MODEL V CHEMICAL OSCILLOMETER
WITH ACCESSORIES.

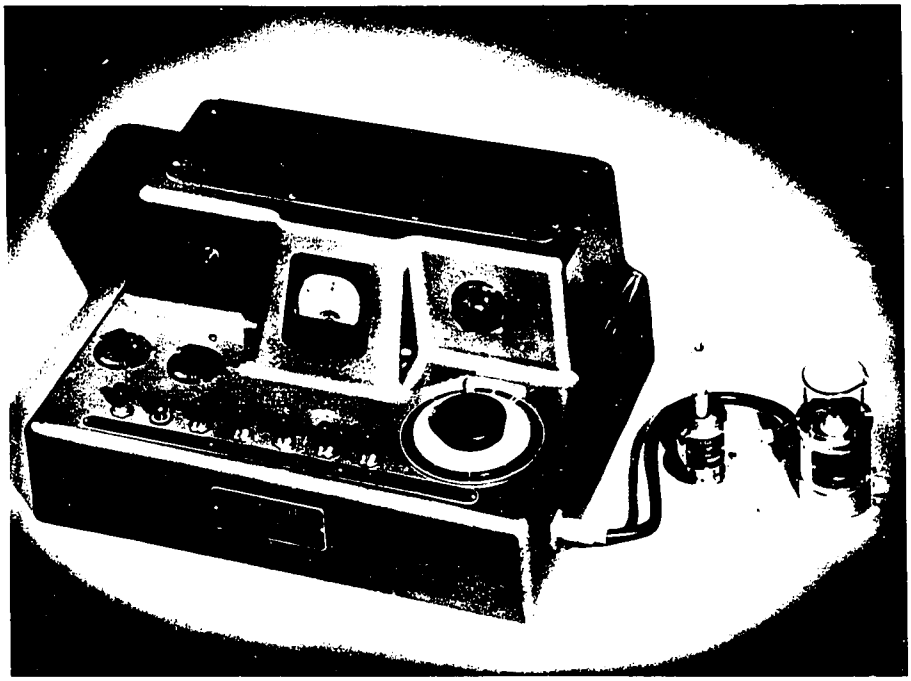
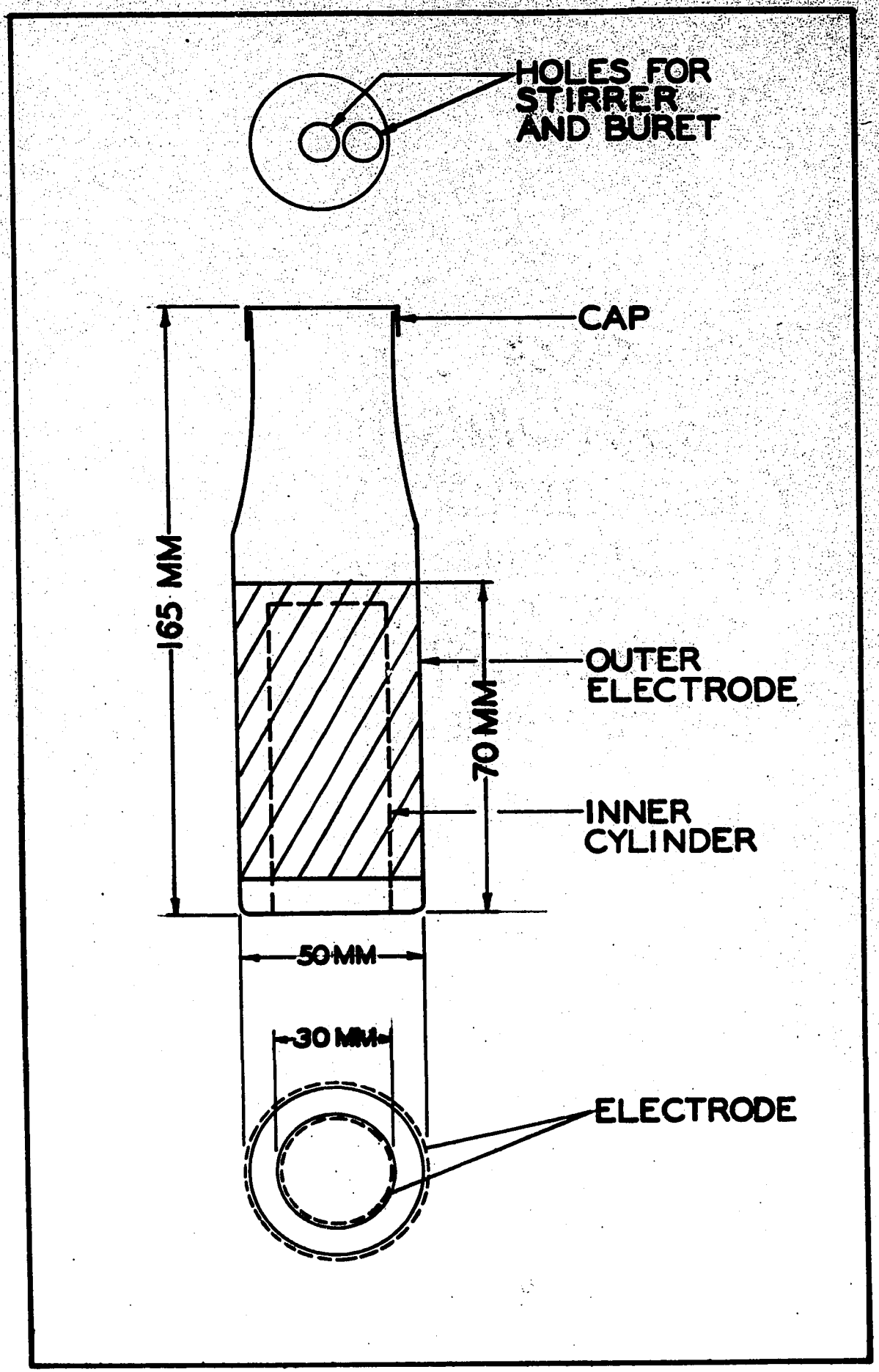


FIGURE 1

THE LARGE TITRATION CELL


HOLES FOR
STIRRER
AND BURET
CAP
165 MM
70 MM
OUTER
ELECTRODE
INNER
CYLINDER
50 MM
30 MM
ELECTRODE

a capacitor. In practice, 6 ml of solution were used for a titration. The standard taper 14/10 stopper supplied with the cell was replaced by a cover that consisted of a 25-mm square of Silicone rubber, 4 mm thick. A thin smear of Silicone grease on the underside of this square provided a reasonably gas-tight seal.

3. Stirrers

With the large titration cell, a polypropylene clover-leaf paddle stirrer, 40 mm in diameter with a 10 mm-diameter shaft, was used. The shaft was inserted directly into a Gallenkamp stirring motor whose speed was controlled by a Variac.

For use with the 10-ml titration cell, a stirrer was constructed from $\frac{1}{8}$" flexible Teflon rod. A paddle of polypropylene was inserted through a $\frac{1}{16}$" diameter hole which had been bored $\frac{1}{8}$" from the end of the rod. The stem of the stirrer was inserted into a drive shaft which was coupled to a stirring motor by means of a rubber loop.

4. The Sargent Cell Compensator

When higher sensitivity was needed, especially for titrations of micro amounts of halides, a Sargent Cell Compensator was coupled in the transmission line ahead of the sample cell. It was a variable inductance calibrated in 0-3000 arbitrary units. It had a variable dial of 0-1500 units divided into units of one. A further 1500 units were connected into the circuit by means of a switch.

The compensator was also equipped with a two-way switch; one position was marked "zero" and the other "test". With the switch in the zero position, the instrument was calibrated against a standard capacitance and not air. This device was used to check for instrumental drift, without removing the cell.

The compensator was used in such a way that its reactance could be adjusted to the capacitive reactance arising from the walls of the titration cell. Its effect was to establish a linear relationship between the dielectric constant of the solution in the cell with the instrument divisions.

A photograph of this accessory is shown in Plate 1.

5. Volumetric Glassware

For titrations at halide concentrations above 4×10^{-4} M, a 50-ml buret was used. The original tip was replaced by a glass tip bent in such a way that it was 8 cm at right-angles to the stopcock, and then 11 cm at right-angles down. The glass stopcock was lubricated with Dow Corning Silicone grease, which was insoluble in the solvents used.

For titrations at halide concentrations below 4×10^{-4} M, a 5-ml Koch micro-buret was used. The tip of the buret as supplied by the manufacturer was a standard ground-glass Luer joint. A 22-gauge Lumbar Puncture hyperdermic needle with a standard Luer joint was attached to this tip. The needle was 3" long and made of stainless steel.

All pipets, burets and volumetric flasks were calibrated to deliver methanol.

B. REAGENTS

1. Absolute Methanol

The absolute methanol was Fisher Certified reagent-grade. The water content was determined by a differential spectrophotometric technique (14) which used the infra-red peak of water at 1.95 microns. Beer's Law was found to be obeyed up to 0.2% water. The water content was found to be 0.03% by weight. A gas chromatogram showed no other impurities.

2. Sodium Chloride

Merck reagent grade sodium chloride was dried at 550°C for four hours before use. It was assayed by a standard method (15) and found to be pure. The dried salt was used as the primary standard in all titrations.

3. Sodium Nitrate

The sodium nitrate was Merck reagent-grade dried at 120°C. Water has been reported to be lost at 115°C (16). The salt begins to decompose into nitrite at 150°C.

The addition of silver nitrate to solutions of sodium nitrate reagent showed no Tyndall cone; halide was presumed to be absent. However, in all titrations where sodium nitrate was used a titration blank was performed on the reagent alone; halide was never found.

4. Silver Nitrate

Nichols reagent-grade silver nitrate was dried at 110°C for four hours and then for 15 minutes at 225°C (the melting point). Its purity was confirmed gravimetrically as silver chloride, by a conventional method (15).

Standard solutions were standardized against the primary standard sodium chloride and were then used as secondary standards.

5. Partial List of Reagents

Reagent	Source, and Purification	Method of Assay
Acetone	Fisher-Certified Reagent Grade	
Ethanol, absolute	Gooderham and Worts, Ltd.	
NaBr	Baker; dried for 4 hours at 550°C	Volumetric for bromide (15)
NaI	Baker; dried for 4 hours at 120°C (550°C caused decomposition)	Gravimetric as AgI
KSCN	Fisher, reagent grade; dried at 120°C	Volumetric for thiocyanate (17)
$SrCl_2$	Fisher, reagent grade; dried for 2 hours at 200°C (loses $6H_2O$ at 183°C (18))	Gravimetric as AgCl
$CuCl_2$	Merck; analytical grade; dried for 4 hours at 140°C (complete dehydration occurs at 131°C (19))	Electrolytic for copper

Partial List of Reagents Continued

Reagent	Source, and Purification	Method of Assay
$FeCl_3 \cdot 6H_2O$	Analar reagent grade. Used without drying	
Nitric Acid*	Nichols, reagent grade	Potentiometric titration gave 70.6% HNO_3; sp. grav. = 1.421
Hydrochloric* Acid	Nichols, reagent grade	Potentiometric titration gave 37.5% HCl; sp. grav. = 1.190

C. PROCEDURES

1. The Titrimetric Procedure

(a) Introduction

The procedures described in this section are general procedures for high-frequency titrimetry. They were used specifically in the present work for the argentimetric titration of halides and thiocyanate in methanol.

(b) For Titrations of Halides and Thiocyanate in the 4×10^{-5} M to 1.0 M Concentration Range

A clean, dry, large titration cell was inserted into the cell holder of the oscillometer. The instrument reading

*Standard solutions of the acid were prepared by dispensing an appropriate volume from a calibrated Koch microburet and then diluting with methanol. By using the con-

was then adjusted to zero by removing from the circuit a capacitance equal to that of the empty cell. Without removing the cell, the required aliquot of one of the standard solutions of halide in methanol was added by pipet. This aliquot was then diluted to 120 ± 1 ml with methanol. This volume provided for satisfactory stirring, as well as bringing the level of the liquid well above the top of the condenser plates of the cell. The polypropylene stirrer was positioned, with its paddles 5 mm above the top of the condenser plates. The ground-glass cap was then slid down the stirrer shaft, into position. The filled buret was positioned. Finally, the two Silicone-rubber washers were positioned at the holes in the cap.

The rate of stirring was not critical. It was adjusted so that the top of the vortex was about 25 mm above the still level of the liquid. The precipitated silver halide was then found not to settle.

After the original solution was stirred, the apparent capacitance was measured, and recorded as instrument divisions. A standard solution of silver nitrate in methanol was added in measured increments. After each addition, the apparent capacitance was read. The additions were continued past the end point. Stirring was continuous throughout the titration.

---

centrated acid the water content of the methanol solution was minimized.

Apparent capacitance (as instrument divisions) was plotted against the volume of titrant added. In general, straight lines could be drawn through the points, and they intersected at the end point.

At the conclusion of the titration, the cell was removed from the holder, washed with acetone and air dried.

(c) For Titrations of Micro Amounts of Halides and Thiocyanate at Less Than 4×10^{-5} M Concentration

The Sargent Cell Compensator was coupled into the transmission line between the cell assembly and the instrument. A clean, dry 10-ml titration cell was inserted into its cell holder. With the switch on the compensator at the "zero" position, the instrument reading was adjusted to zero as described in (b) of this sub-section.

An aliquot of the halide solution in methanol was transferred to the titration cell, and the contents diluted to 6 ± 0.2 ml with methanol. In some cases, particularly at very low concentrations of halide, an aliquot of a 5×10^{-4} M solution of sodium nitrate in methanol was added prior to the final dilution to 6 ml. The purpose was to raise the ionic strength of the solution to a point where the sensitivity of the instrument toward changes in concentrations was sufficient. In cases of such additions, titration blanks for halide in the sodium nitrate were always separately run.

The stirrer was then positioned so that the paddle was about 5 mm above the top of the cell electrodes. The

tip of the buret needle was placed about 5 mm above the level of the still solution. The Silicone-rubber cover was then pressed firmly to the top of the open cell, to form a seal by reason of the applied Silicone grease. The rate of stirring was adjusted to cause the outer edge of the solution to rise about 10 mm in the cell.

The switch of the cell compensator was turned to the "test" position. The compensator was set at 640 dial units. This value gave the maximum instrumental sensitivity, while still keeping the oscillometer readings within the limits of variation of its standard capacitors, for the solutions titrated. Without the cell compensator, breaks were not obtained in the titration graphs for the micro amounts of halide taken in the present work.

The titration was carried out and the end point located in the same way as that described in (b) of this sub-section.

2. Measurement of Response Curves

When the apparent capacitance was plotted for a series of solutions against the logarithm of the molarity of the electrolyte in those solutions, the well-known sigmoid-shaped curve was obtained for every electrolyte studied. Hereinafter this curve is referred to as a response curve.

To obtain a response curve, the large titration cell was filled with 100 ± 0.2 ml of methanol. The 50-ml buret was filled with a 0.05-M standard solution of the electrolyte in methanol. The procedure described under

sub-section 1(b) of this section was then followed. Measured increments of the electrolyte were added to the 100 ml of methanol in the cell and the apparent capacitance recorded. The concentration of the solution of electrolyte in the titration cell was then calculated. The maximum concentration of electrolyte that was obtained by this procedure was 0.01 M. For higher concentrations, standard solutions from 0.02 M to 0.05 M were prepared separately and their apparent capacitances measured.

3. Preparation of Simulated Titration Graphs

To observe (a) the effect of the presence of precipitate, (b) the effect of solid-solution formation in the titration of mixtures of halides and (c) to interpret titration graphs, simulated titration graphs were determined in the absence of a silver halide precipitate. The halide was replaced by nitrate in successive mixtures, with the total concentration of electrolyte remaining constant. After the end point, silver nitrate was added, in excess, to a sodium nitrate solution of the same molarity as the original halide solution.

To simulate the titration graph for a single halide, mixtures were prepared in the large titration cell in which the sodium halide and sodium nitrate mole ratios were varied from 0 to 1. The total concentration of electrolyte was kept constant at 4.17×10^{-4} M. The first reading on each solution was recorded as apparent capacitance, without dilution. Then, a volume of methanol, exactly equivalent to

the volume of 0.01-N silver nitrate that would have been added in a titration, was added. The reading was recorded as apparent capacitance, with dilution. To reproduce the right-hand portion of a titration graph, the same increments of 0.01-N silver nitrate solution that were used in a titration were added to a 4.17×10^{-4} M solution of sodium nitrate. Again the solutions were suitably diluted to give readings with and without dilution.

To determine simulated titration graphs for the titration of binary mixtures of halides, ternary mixtures of two halides and nitrate were prepared in the large titration cell. The mole ratios were varied from 1:1:0 to 1:0:1 to 0:0:2, as in a titration. The total concentration of electrolyte was kept constant at 8.4×10^{-4} M. The same procedure as that described above was carried out to obtain complete, simulated titration graphs, in the absence of silver halide, with and without dilution.

There was some scatter of the points because each measurement of apparent capacitance was made on a separate solution. This necessitated removing the cell, and it was not possible to reproduce its position exactly.

D. EXPERIMENTAL RESULTS

1. The Effect of Temperature and Evaporation of Solvent on the Apparent Capacitance of a Solution

During exploratory argentimetric titrations, using an open titration cell, anomalous changes of slope were observed

in the titration graphs. In these titrations, stirring was intermittent, and the increment of titrant was varied. Figure 2 illustrates the spurious changes of slope in the titration of an equimolar mixture of chloride and bromide. In the titration the increment of titrant was reduced near the expected bromide end point and a change of slope resulted in the titration graph. Similarly, increment size was reduced at the total halide end point. These changes of slope were not constant from titration to titration.

During a titration in a large open cell, the temperature of the solution decreased due to the evaporation of solvent; this contributed to the observed changes of slope. To study the effect, a 8.94×10^{-4} M solution of sodium chloride in methanol was stirred continuously in a large open cell for sixty minutes. The apparent capacitance and temperature of the solution were recorded at suitable time intervals. The results are shown in Figure 3. From Figure 3 it is clear that there were two opposing tendencies, the apparent capacitance was reduced by a reduction in temperature and was increased due to the concentration effect of solvent evaporation. After the expected minimum the latter effect become predominant. When the above experiment was repeated with a closed titration cell the temperature of the solution decreased only 0.4 degrees during a sixty minute period of continuous stirring and the apparent capacitance remained constant. It was then obvious that titrations would have to

FIGURE 2

ANOMALOUS CHANGES OF SLOPE IN THE HIGH-FREQUENCY ARGENTIMETRIC TITRATION OF HALIDE MIXTURES IN METHANOL IN AN OPEN TITRATION CELL

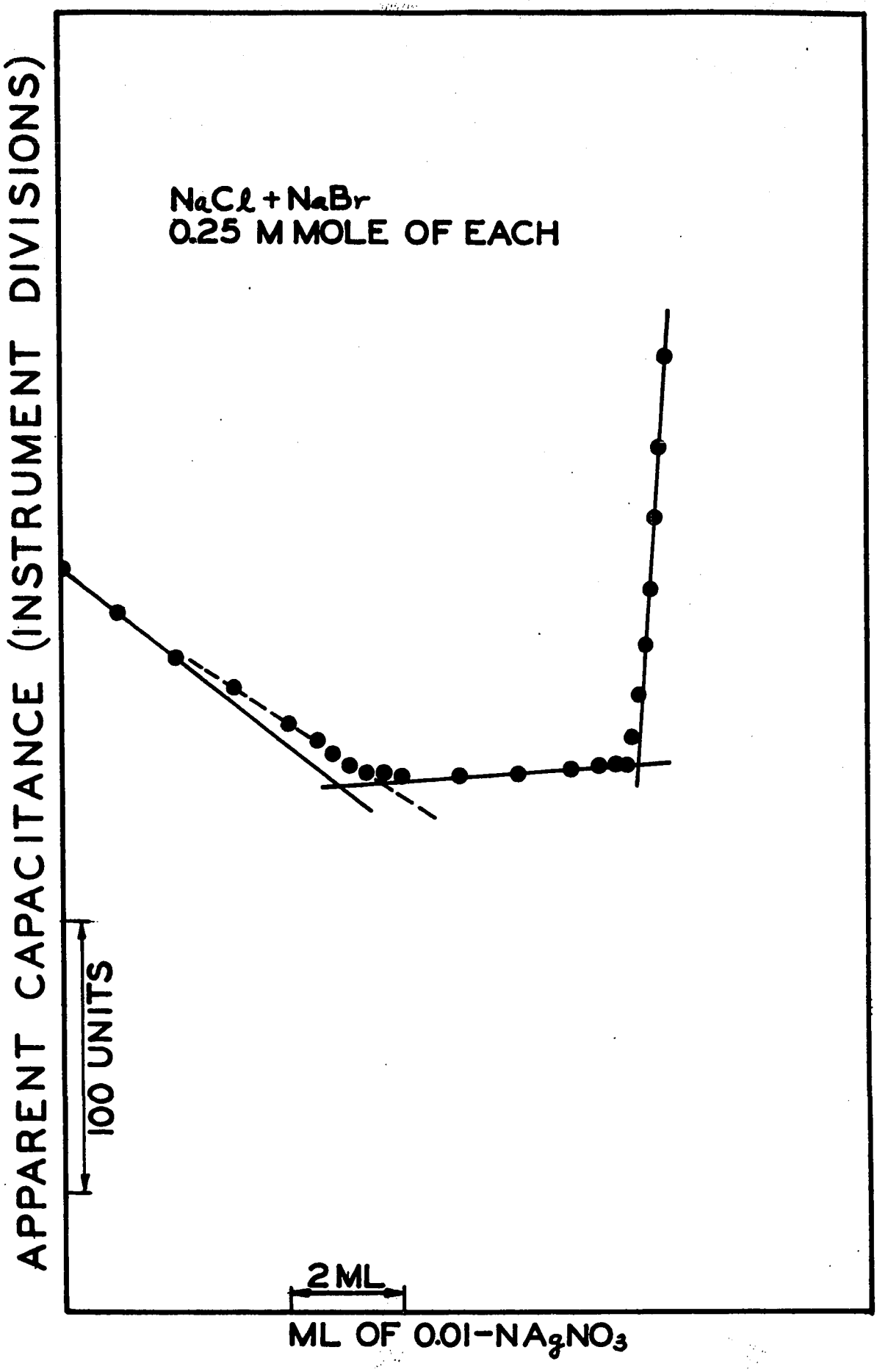
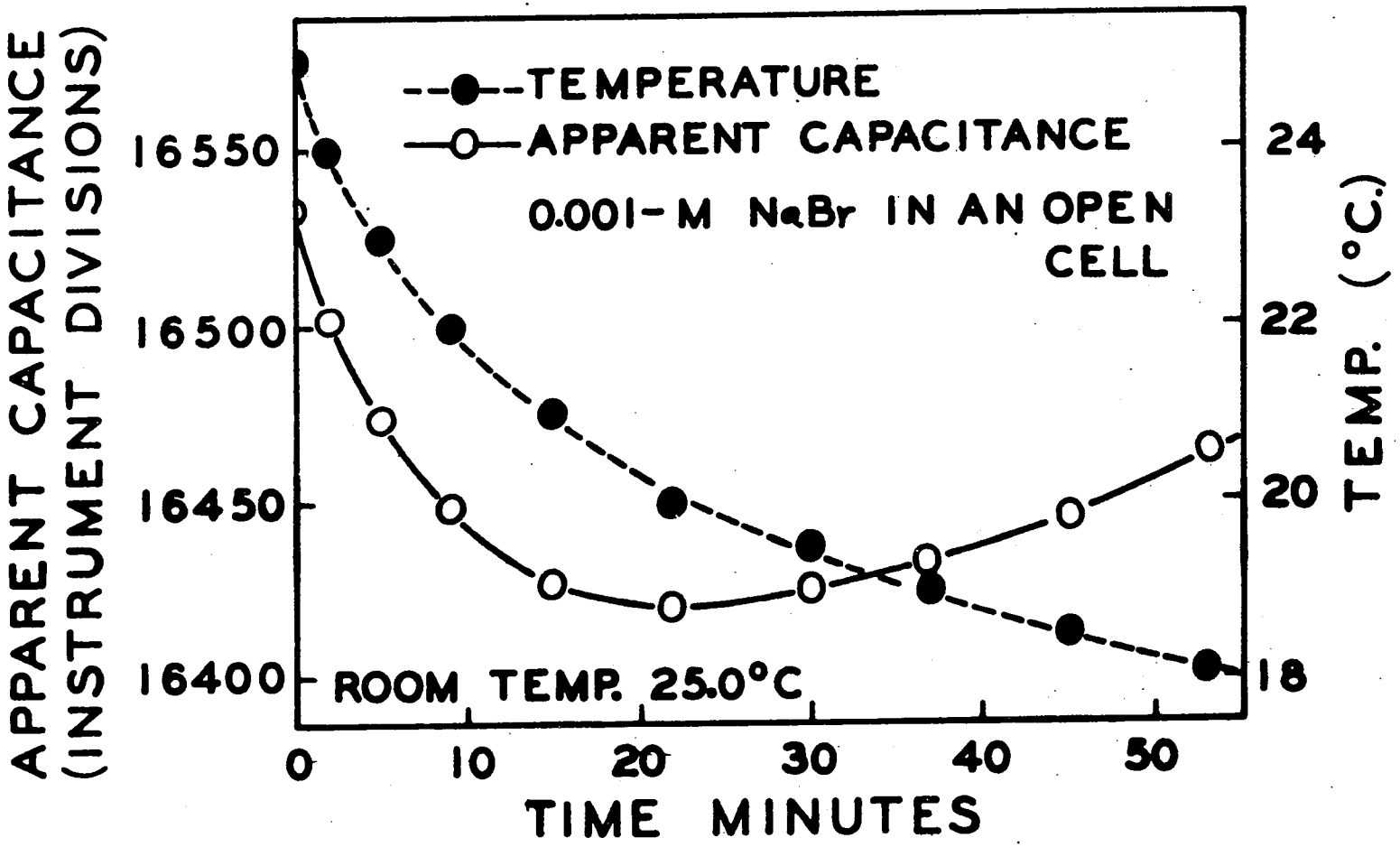

NaCl + NaBr
0.25 M MOLE OF EACH
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
100 UNITS
2 ML
ML OF 0.01-N AgNO3

FIGURE 3

CHANGES IN APPARENT CAPACITANCE AND IN TEMPERATURE
OF A SOLUTION OF SODIUM CHLORIDE
AS A FUNCTION OF TIME IN AN OPEN TITRATION CELL


--●--TEMPERATURE
—○—APPARENT CAPACITANCE
0.001-M NaBr IN AN OPEN CELL
ROOM TEMP. 25.0°C
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
16550
16500
16450
16400
TEMP. (°C.)
24
22
20
18
0
10
20
30
40
50
TIME MINUTES

be performed in a closed titration cell and at a reasonably constant ambient temperature.

The temperature dependence of the apparent capacitance of a solution is a function of the concentration of the electrolyte. This is evident from the data in Table 1 and Figure 4. The explanation for Figure 4 is as follows: Apparent capacitance of a solution is a function both of the capacitance and of the conductance of that solution. The temperature coefficient of dielectric constant, and hence capacitance, is negative. The temperature coefficient of conductance is positive. At very low concentrations of electrolyte conductance is low. In such a case the temperature effect of capacitance predominates over that of conductance and the temperature coefficient of apparent capacitance will be negative. The reverse is true at higher concentrations of electrolyte where the conductance is high. Clearly there will be some concentration of electrolytes at which the temperature dependence of apparent capacitance is zero. This point is shown in Figure 4.

The apparent capacitances of solutions in the small titration cell were much more sensitive to temperature fluctuations than those in the large cell. Therefore, such titrations should be performed either at constant ambient temperature or with the micro cell surrounded by a water-bath.

All titrations with the small titration cell were, in the present work, performed at 25°C and required a period

TABLE 1

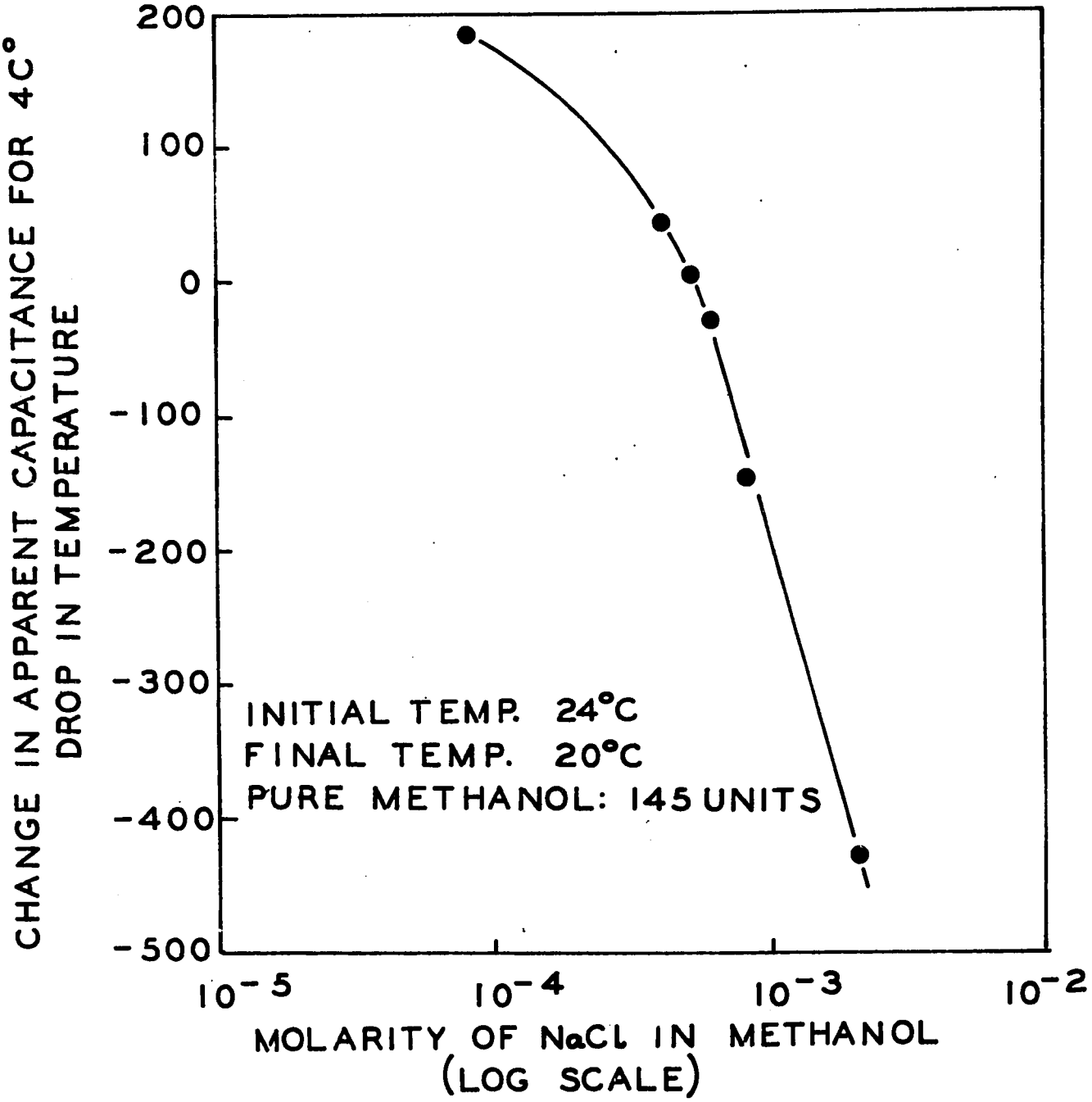
THE CHANGE OF THE APPARENT CAPACITANCE FOR A FIXED CHANGE IN TEMPERATURE, AS A FUNCTION OF CONCENTRATION

Closed titration cell with stirring
Volume of solution in cell = 120 ml
Room temperature = 25°C

Molar Concentration of NaCl in Methanol	Temperature of Solution °C	Apparent Capacitance Instrument Divisions	Change in Apparent Capacitance Instrument Divisions
Absolute Methanol	24	14015	145
	20	14160	
8.34×10^{-5}	24	13840	185
	20	14025	
4.17×10^{-4}	24	14470	45
	20	14515	
5.35×10^{-4}	24	14745	7
	20	14752	
6.25×10^{-4}	24	15065	- 28
	20	15037	
8.34×10^{-4}	24	16280	-145
	20	16135	
2.08×10^{-3}	24	20983	-428
	20	20555	

FIGURE 4

EFFECT OF A FIXED CHANGE IN SOLUTION TEMPERATURE
ON THE APPARENT CAPACITANCE OF SOLUTIONS
OF SODIUM CHLORIDE IN METHANOL


200
100
0
-100
-200
-300
-400
-500
CHANGE IN APPARENT CAPACITANCE FOR 4C° DROP IN TEMPERATURE
INITIAL TEMP. 24°C
FINAL TEMP. 20°C
PURE METHANOL: 145 UNITS
10^{-5}
10^{-4}
10^{-3}
10^{-2}
MOLARITY OF NaCl IN METHANOL
(LOG SCALE)

not exceeding 5 minutes. Tests showed that during that period the ambient temperature did not change. It was observed that the response curves were steeper at 18°C than they were at 25°C. Consequently it is possible that temperatures lower than 25°C would have provided sharper end points. This matter was not pursued partly because the temperature coefficient of the apparent capacitance was a function of the concentration of the electrolyte thus introducing an additional complication.

2. Titration of Halide and Thiocyanate Solutions

(a) Determination of Single Halides in Methanol

(i) Titration of sodium halides

Standard solutions, about 5 x 10^{-3} M in sodium chloride, sodium bromide, sodium iodide and potassium thiocyanate, were prepared by dissolving the dried salts in methanol. Aliquots ranging from 1.0 to 20.0 ml were dispensed by pipet into the titration cell. These solutions, after dilution to 120 ml, were titrated with standard 0.01-N silver nitrate solution in methanol. Replicate titrations were performed for each halide. The results are given in Table 2 and typical titration graphs are in Figure 5.

The slopes of the titration graph were found to depend not only on the kind of halide (Figure 5) but also on the concentration of halide present. This dependence is illustrated in Figure 6. The shape of a titration graph was found, by tests in which sodium nitrate was added to

TABLE 2

HIGH FREQUENCY ARGENTIMETRIC TITRATION OF HALIDES AND THIOCYANATE PRESENT ALONE IN METHANOL

Initial Volume of solution in titration cell: 120 ml
Normality of standard $AgNO_3$ in methanol : 1.029×10^{-2} N
Concentration of each halide taken : 50 µmole

Halide	Mean Halide Found µmole	Number of Samples	Standard Deviation
NaCl	50.1	3	0.2
NaBr	51.1	4	0.1
NaI	50.6	3	0.2
KSCN	51.2	3	0.3

FIGURE 5

TYPICAL TITRATION GRAPHS OF ARGENTIMETRIC TITRATIONS OF SINGLE HALIDES IN METHANOL

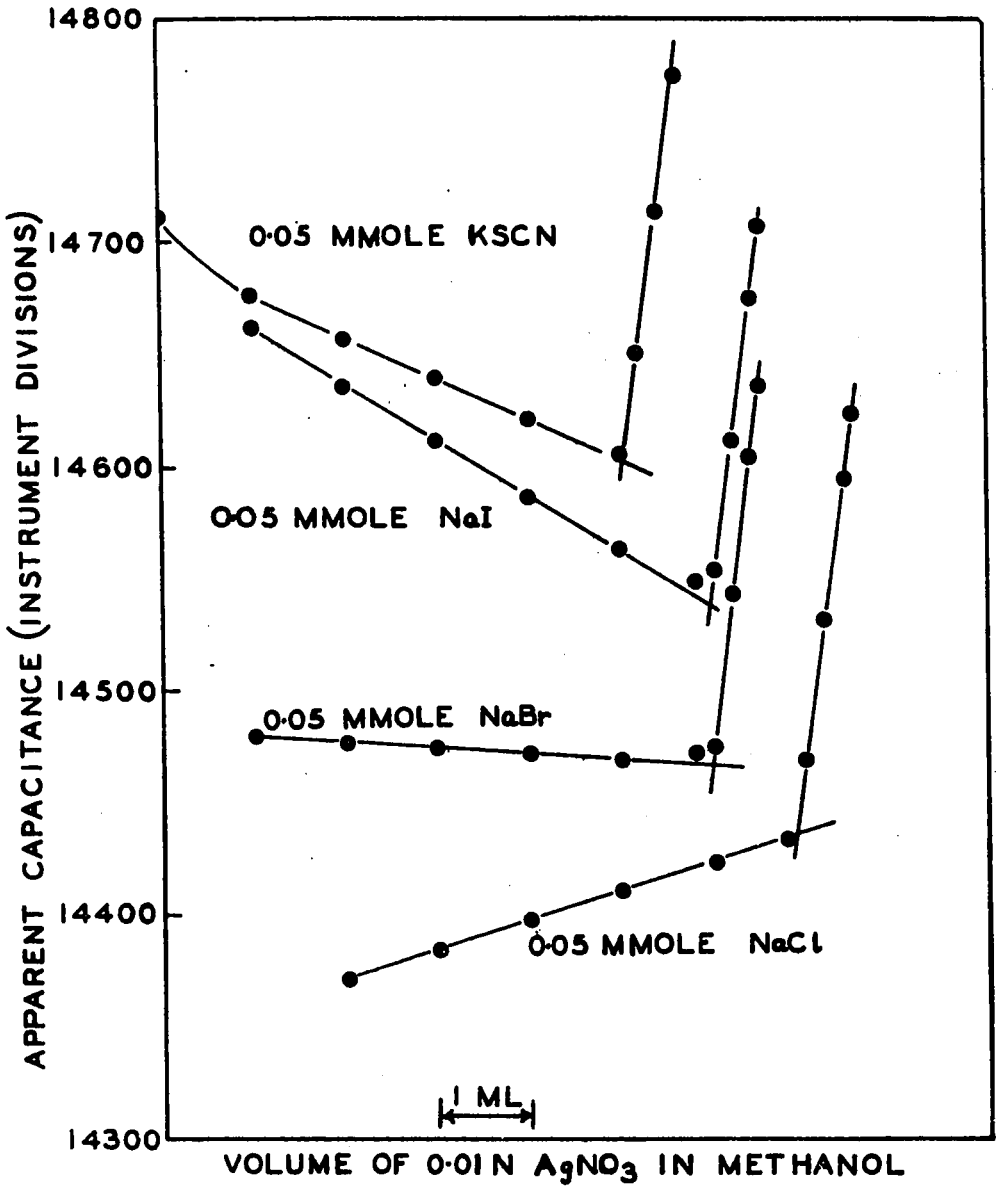
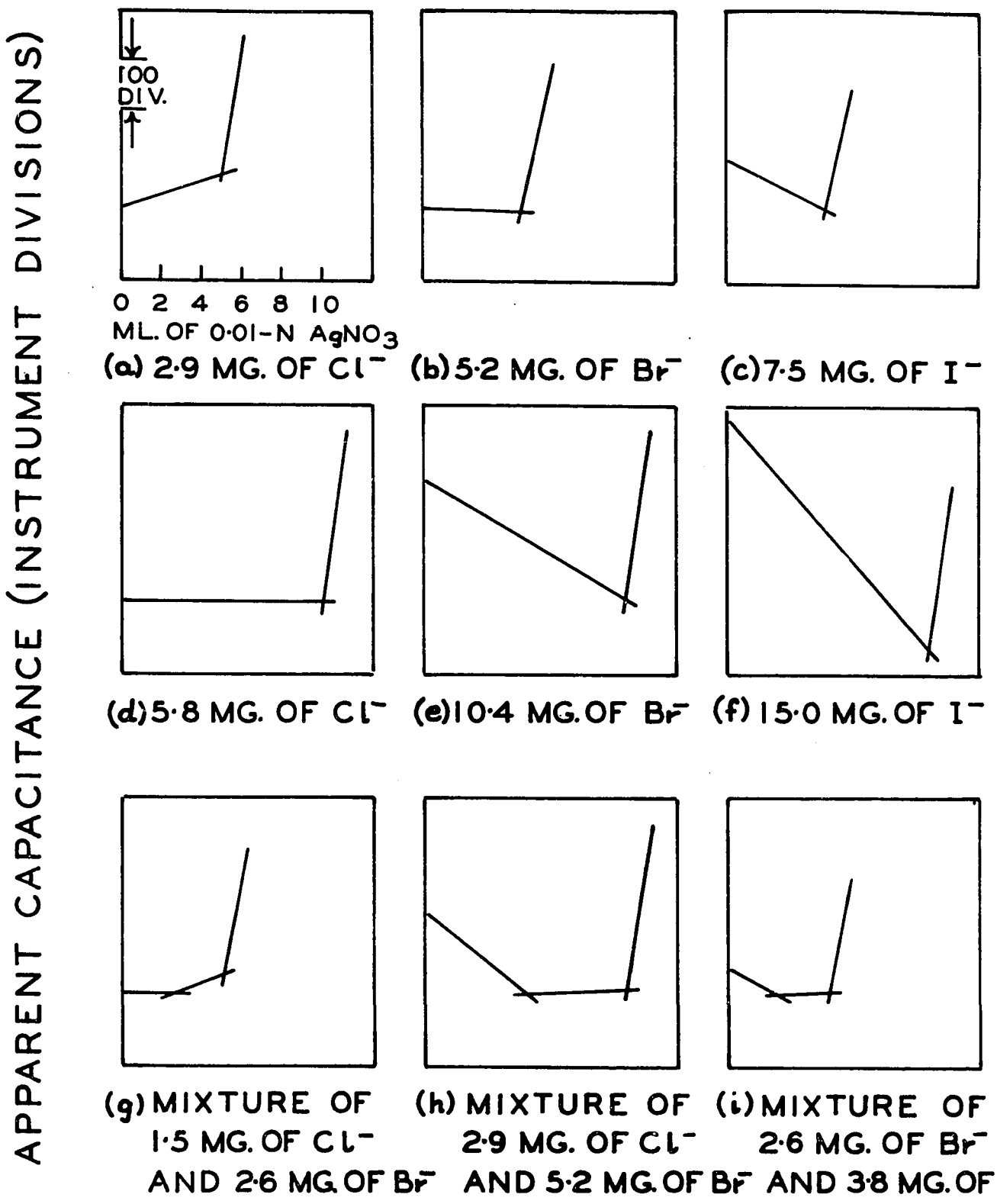

14800
14700
14600
14500
14400
14300
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
0·05 MMOLE KSCN
0·05 MMOLE NaI
0·05 MMOLE NaBr
0·05 MMOLE NaCl
1 ML
VOLUME OF 0·01 N AgNO3 IN METHANOL

FIGURE 6

DEPENDENCE OF THE SHAPE OF A TITRATION GRAPH
ON CONCENTRATION AND HALIDE SPECIES


APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
100 DIV.
0 2 4 6 8 10
ML. OF 0·01-N AgNO3
(a) 2·9 MG. OF Cl⁻
(b) 5·2 MG. OF Br⁻
(c) 7·5 MG. OF I⁻
(d) 5·8 MG. OF Cl⁻
(e) 10·4 MG. OF Br⁻
(f) 15·0 MG. OF I⁻
(g) MIXTURE OF 1·5 MG. OF Cl⁻ AND 2·6 MG. OF Br⁻
(h) MIXTURE OF 2·9 MG. OF Cl⁻ AND 5·2 MG. OF Br⁻
(i) MIXTURE OF 2·6 MG. OF Br⁻ AND 3·8 MG. OF I⁻

the solution, to depend on the total concentration of electrolyte present in the solution. The addition of sodium nitrate also served to increase the sharpness of the change of slope when a low concentration of halide was being analysed.

In high-frequency titrations it is not possible to correct the apparent capacitance by the simple factor $V/(v + V)$, because a linear relationship between apparent capacitance and concentration does not exist.

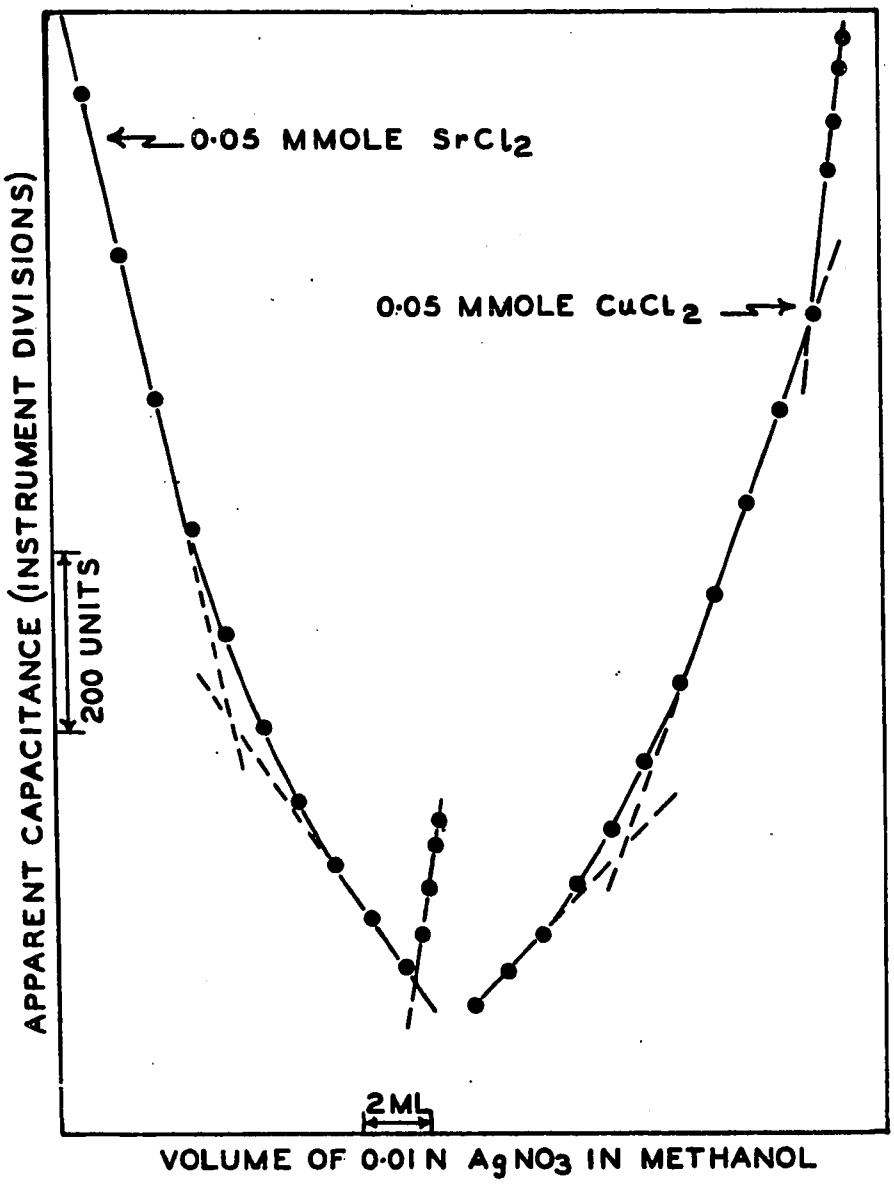
(ii) The titration of divalent and trivalent metal chlorides

Solutions in methanol, 5×10^{-3} N in strontium chloride, cupric chloride and ferric chloride were prepared from accurately weighed amounts of the dried salts. Ten-ml aliquots were titrated with 0.01-N silver nitrate in methanol. The titration graphs obtained with strontium chloride and cupric chloride are shown in Figure 7. Good changes of slope were obtained at the stoichiometric equivalence point; with curvature before the end point. Extrapolation of the straight line portions gave a point of intersection that corresponded closely to one half of an equivalent of silver nitrate.

The titration graph obtained for ferric chloride hexahydrate was poor; there was no change of slope for the final equivalence point.

FIGURE 7

TITRATION GRAPHS OF THE ARGENTIMETRIC TITRATION
OF STRONTIUM CHLORIDE AND OF CUPRIC CHLORIDE IN METHANOL


0·05 MMOLE $SrCl_2$
0·05 MMOLE $CuCl_2$
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
200 UNITS
2ML
VOLUME OF 0·01 N $AgNO_3$ IN METHANOL

(iii) The effect of the presence of acid in the titration of halides

The effect of acid in the titration solution is shown in Figure 8. Solutions of 5 x 10^{-3} N hydrochloric and nitric acids were prepared from the aqueous concentrated acids and diluted with methanol. Aliquots were added to 10 ml of 5 x 10^{-3} M sodium chloride. Curvature of the titration graph prior to the end point occurred.

Hydrochloric acid titrated alone also produced curvature. Sodium chloride, titrated in the presence of an equimolar amount of hydrochloric acid gave slight curvature.

Titrations of halides in methanol should therefore be performed in as nearly a neutral solution as possible.

(b) Titration of Binary Mixtures of Halides and Thiocyanate

(i) Titration of equimolar mixtures of halides and thiocyanate in methanol

Equimolar mixtures of the halides were titrated. Aliquots of 5 x 10^{-3} M halide solutions were pipetted into the titration vessel. After dilution to 120 ml with methanol, the solutions were titrated with standard 0.01-N silver nitrate in methanol. Representative titration graphs are shown in Figure 9. All combinations of the halides and thiocyanate were titrated and found to give sharp changes of slope both for the first component precipitated and for the total halide end point. The results are given in Table 3. In all cases the change of slope for the total

FIGURE 8

EFFECT OF ACID IN THE ARGENTIMETRIC TITRATION
OF HALIDE IN METHANOL

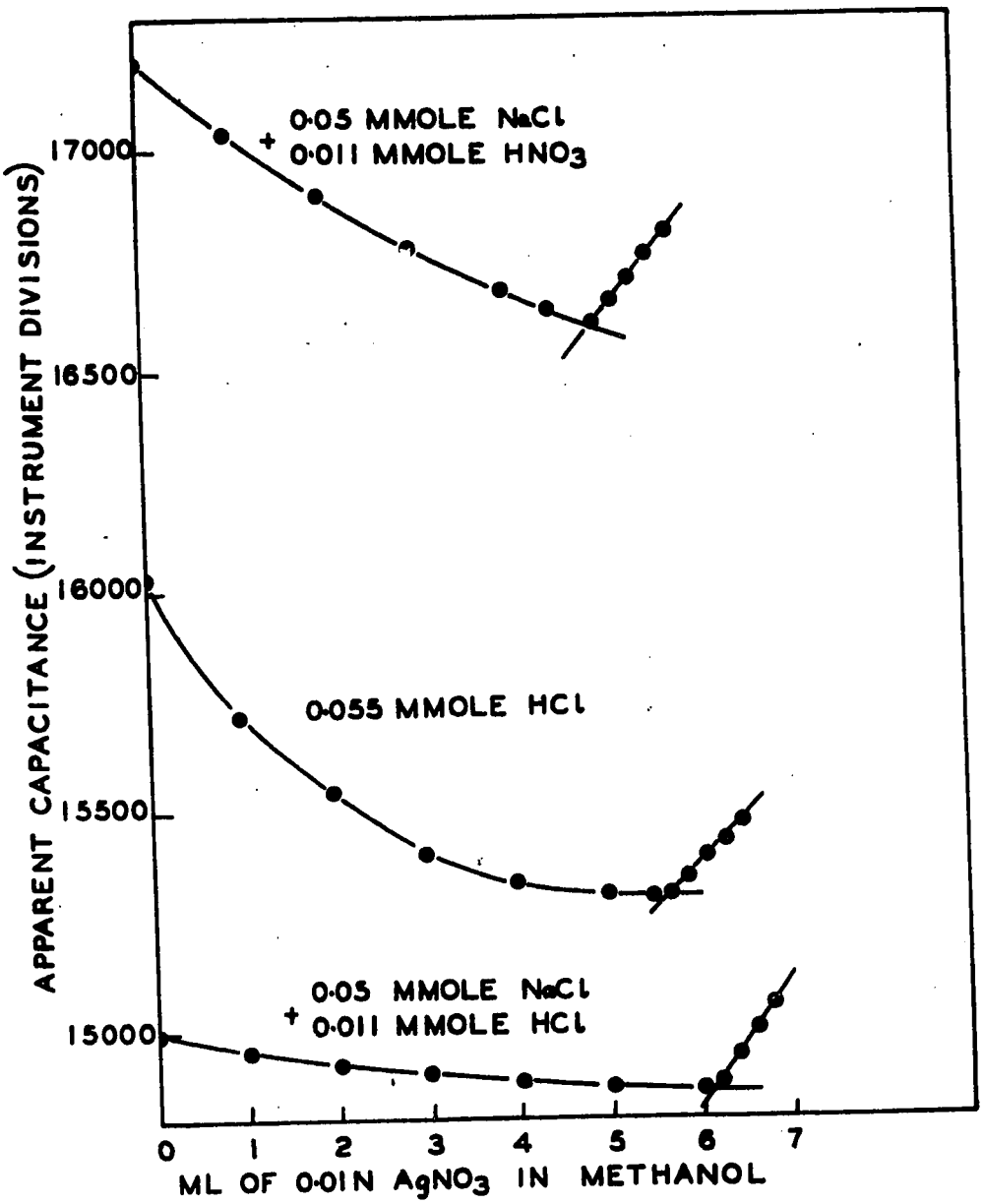

0·05 MMOLE NaCl
+ 0·011 MMOLE HNO3
0·055 MMOLE HCl
0·05 MMOLE NaCl
+ 0·011 MMOLE HCl
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
17000
16500
16000
15500
15000
0
1
2
3
4
5
6
7
ML OF 0·01N AgNO3 IN METHANOL

FIGURE 9

TYPICAL TITRATION GRAPHS OF ARGENTIMETRIC TITRATIONS OF PAIRS OF HALIDES IN METHANOL

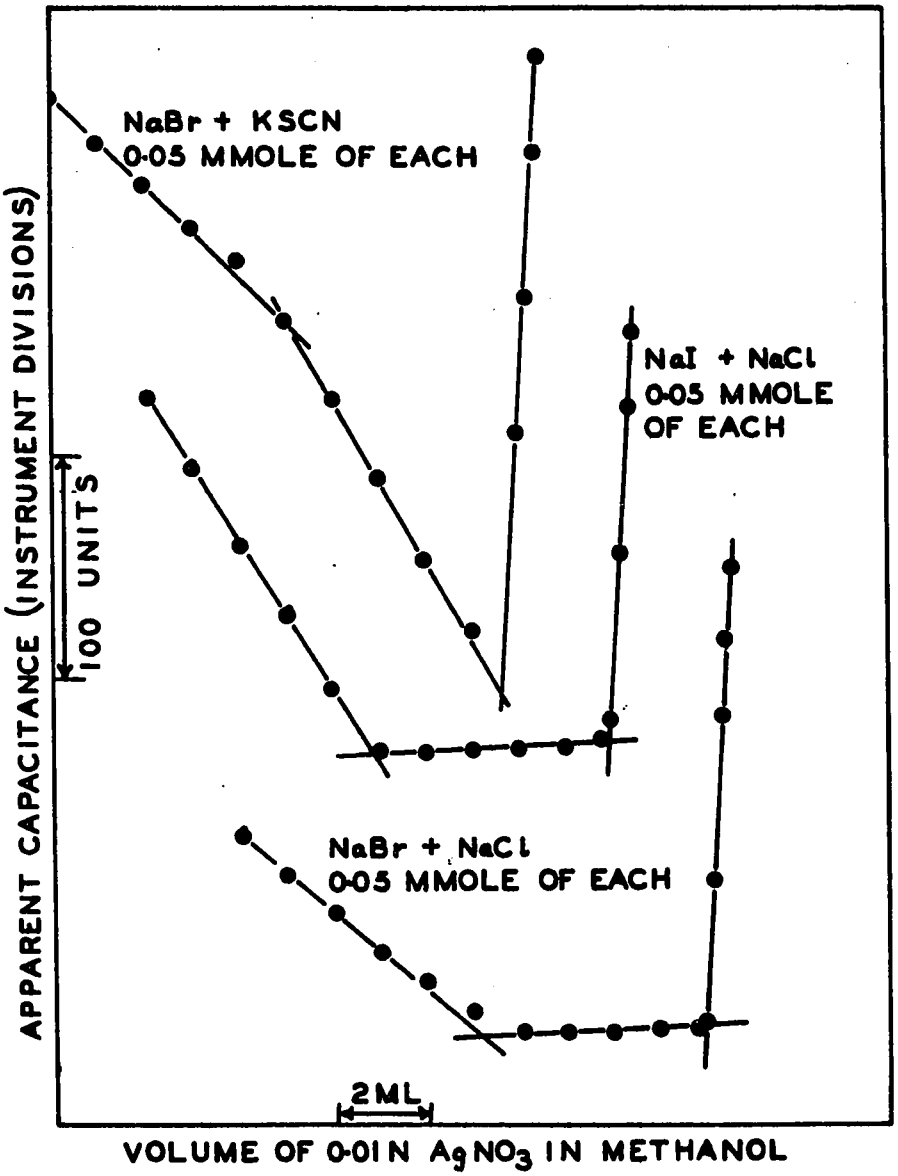

NaBr + KSCN
0·05 MMOLE OF EACH
NaI + NaCl
0·05 MMOLE
OF EACH
NaBr + NaCl
0·05 MMOLE OF EACH
100 UNITS
2 ML
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
VOLUME OF 0·01 N $AgNO_3$ IN METHANOL

TABLE 3

HIGH-FREQUENCY TITRATIONS OF SODIUM HALIDES AND THIOCYANATE MIXTURES IN METHANOL

Initial Volume of solution in titration cell: 120 ml
Normality of standard $AgNO_3$ in methanol : 0.01 N

Binary Mixtures	Taken µmole	Found* µmole	Ternary Mixtures	Taken µmole	Found* µmole	Quaternary Mixture	Taken µmole	Found* µmole
Br	50.6	54.6	I	50.6	59.6	I	25.3	22.5
Br + Cl	101.7	101.9	I + Br	102.0	111.0	I + Br	50.1	53.3
			I + Br + Cl	153.4	154.2	I + Br + SCN	75.6	73.6
Br	25.4	28.5				I + Br + SCN + Cl	100.5	100.6
Br + Cl	50.8	51.2	I	25.3	22.6			
			I + Br	51.0	52.4			
I	50.5	50.3	I + Br + Cl	76.7	77.1			
I + Cl	102.6	102.0						
			I	25.3	25.5			
I	25.3	25.6	I + Br	50.1	46.9			
I + Cl	51.3	51.4	I + Br + SCN	75.7	74.9			
I	50.5	49.8	I	25.3	24.9			
I + Br	102.0	102.8	I + SCN	50.9	48.1			
			I + SCN + Cl	75.7	75.6			
I	25.3	25.6						
I + Br	51.0	51.4	Br	24.8	27.8			
			Br + SCN	50.4	50.5			
Br	50.4	50.8	Br + SCN + Cl	75.3	75.4			
Br + SCN	101.0	100.7						
SCN	50.6	36.1						
SCN + Cl	100.8	101.1						
I	50.5	50.3						
I + SCN	101.1	100.9						

*Average of duplicate samples.

halide end point was sharp and the percentage error was very small. The most favourable combinations, according to the accuracy of the end point for the first component were:

1) iodide + chloride
2) iodide + thiocyanate
3) iodide + bromide
4) bromide + thiocyanate

In these cases the solubility products of the silver halides were sufficiently different to allow the first component to be almost completely precipitated before the second component began to precipitate. Of the four combinations listed only silver iodide and silver bromide form limited solid solutions in each other.

On the basis of the difference of the solubility products of silver chloride and silver bromide (see Appendix II) it should have been possible to titrate chloride-bromide mixtures accurately. However, silver chloride is known to form solid solutions with silver bromide; this has been shown to cause the error in the bromide end point (see Section IV subsection C).

As expected chloride-thiocyanate mixtures could not be satisfactorily titrated because the solubility products of silver chloride and silver thiocyanate in methanol only differ by a factor of 5 (see Appendix II).

The precision of the titration of equimolar chloride-bromide mixtures by the high-frequency method is given in

Table 4. These results show that chloride and bromide may be determined accurately in a mixture provided some correction is made for the error due to solid-solution formation in the bromide end point. R. C. Bowers et. al. (7) derived an empirical formula to correct for the error when the halides were titrated potentiometrically.

(ii) Effect of changing the chloride:bromide ratio in the titration of mixtures of these halides

Triplicate determinations on ratios of chloride:bromide from 1:20 to 20:1 were performed. The results are shown in Table 5. A more detailed discussion of the results is given in Section IV subsection C.

(iii) Effect of changing the chloride:thiocyanate ratio in the titration of mixtures of these halides

Duplicate titrations were performed on mixtures of chloride:thiocyanate from 10:1 to 1:10. The results are shown in Table 6. A more detailed discussion of the results is given in Section IV subsection D.

(iv) Titrations in acetone-water mixtures

Exploratory titrations were carried out on equimolar mixtures of chloride and bromide in acetone-water mixtures. As the water content was reduced the sharpness of the end point was increased. It was found that the addition of ethylenediamine as well as other nitrogen bases such as pyridine and hexamine dissolved in the acetone-water mixture reduced the sharpness of the end point. It was concluded

TABLE 4

PRECISION OF HIGH-FREQUENCY ARGENTIMETRIC TITRATIONS OF SODIUM CHLORIDE AND SODIUM BROMIDE IN EQUIMOLAR MIXTURES IN METHANOL

Initial Volume of solution in titration cell: 120 ml
Normality of standard $AgNO_3$ in methanol : 1.018×10^{-2} N

Halide Taken (μmole)		Mean Halide Found (μmole)			Standard Deviation	
Br + Cl	Br	Br + Cl	Br	No. of Samples	Br + Cl	Br
101.7	50.6	101.9	54.6	6	0.2	1.6
50.9	25.4	51.2	28.5	6	0.3	1.5

TABLE 5

THE EFFECT OF VARIATION IN THE MOLE RATIO OF CHLORIDE AND BROMIDE ON THE ACCURACY OF ARGENTIMETRIC TITRATIONS IN METHANOL

Initial Volume of solution in titration cell: 120 ml
Normality of standard $AgNO_3$ in methanol : 0.01 N

Mole Ratio Cl:Br	Chloride Taken µmole	Bromide Taken µmole	Bromide Found* µmole	Standard Deviation	% Difference	Chloride + Bromide Taken µmole	Chloride + Bromide Found* µmole	Standard Deviation	% Difference
1:20	4.8	101.5	98.1	0.49	- 3.4	106.3	106.3	0.10	0.0
1:10	9.7	101.5	98.8	0.64	- 2.6	111.2	111.1	0.25	- 0.1
1:3	24.3	76.2	78.3	0.58	2.8	100.5	101.0	0.16	0.5
1:1	51.1	50.6	54.6	1.70	7.9	101.7	101.9	0.17	0.2
3:1	72.8	25.4	27.9	0.41	9.9	98.2	99.3	0.29	1.1
10:1	97.0	10.2	12.1	1.25	19.4	107.2	107.5	0.15	0.3
20:1	97.0	5.1	8.7	0.41	71.2	102.1	102.8	0.23	0.7

*Average of three samples.

NOTE: "% Difference" is the percentage difference between the amount taken, and the average of triplicates of the amount found.

TABLE 6

THE EFFECT OF VARIATION IN THE MOLE RATIO OF CHLORIDE AND THIOCYANATE ON THE ACCURACY OF ARGENTIMETRIC TITRATIONS IN METHANOL

Initial Volume of solution in titration cell: 120 ml
Normality of standard $AgNO_3$ in methanol : 0.01 N

Mole Ratio SCN:Cl	Thiocyanate Taken µmole	Thiocyanate Found* µmole	Standard Deviation	% Difference	Thiocyanate + Chloride Taken µmole	Thiocyanate + Chloride Found* µmole	Standard Deviation	% Difference
10:1	100.5	84.8		- 15.6	111.2	109.6		- 1.4
5:1	50.6	45.6	2.20	- 9.2	60.6	60.9	0.42	0.6
3:1	75.8	65.7	0.24	- 13.3	101.0	101.1	0.20	0.1
1:1	50.6	36.0	0.53	- 28.7	100.8	101.1	0.10	0.3
1:2	25.3	23.4	3.20	- 7.4	75.5	75.1	0.42	- 0.6
1:3	25.3	41.0	1.80	+ 61.9	100.7	100.9	0.47	0.2
	Chloride Taken µmole	Chloride Found µmole	Standard Deviation	% Difference	Chloride + Thiocyanate Taken µmole	Chloride + Thiocyanate Found µmole	Standard Deviation	% Difference
1:5**	50.2	38.4	1.53	- 23.6	60.4	60.3	0.26	- 0.1
1:9	88.7	70.4		- 20.6	98.8	100.4		1.7
1:11	110.6	94.9		- 14.2	120.7	119.0		- 1.4

*Average of three samples.
**At these ratios chloride is presumed to precipitate first.

NOTE: See Table 5 for definition of "% Difference".

that amines interfere in the argentimetric determination of halides. The effect is illustrated in Figure 10.

(c) Titration of Ternary and Quaternary Mixtures of Halides and Thiocyanate in Methanol

Equimolar ternary mixtures were titrated with standard 0.01-N silver nitrate in methanol. All combinations of chloride, bromide, iodide and thiocyanate were titrated. Sharp changes of slope were obtained for each component in the mixture. A typical titration graph is shown in Figure 11. In general, the errors for each component were reproducible. Martin (20) found that in the potentiometric titration of chloride, bromide and iodide present together in a mixture in about equal concentrations, the percentage error in the amount of iodide found tended to be high. The error in the bromide end point was compensated for, and the most serious errors occurred in the iodide and chloride concentrations. The error for the total halide end point was less than one per cent. The results of the present work, given in Table 3 agree with his observations.

In Table 6 it was shown that when chloride and thiocyanate were titrated together in a mixture the error in the thiocyanate end point was -28.7%. From Table 3 it is seen that when these two ions were present together with a third ion the error in the thiocyanate end point was only -5.4% when iodide was present, and +0.2% when bromide was present.

FIGURE 10

ARGENTIMETRIC TITRATION OF CHLORIDE-BROMIDE MIXTURES
IN 88% ACETONE

(a) Free ethylenediamine absent.

(b) Solution contained 0.1 m mole of free ethylenediamine.

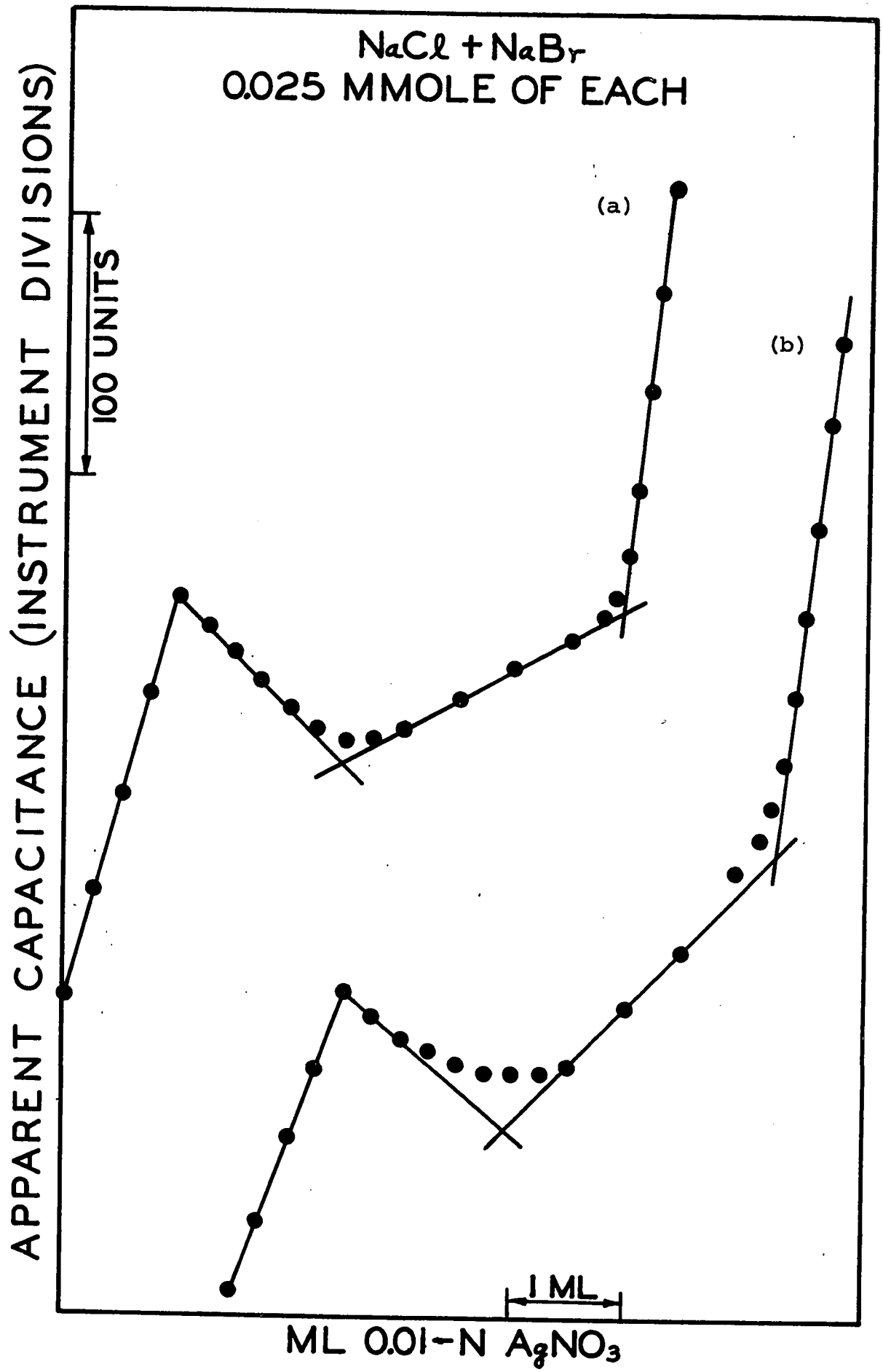
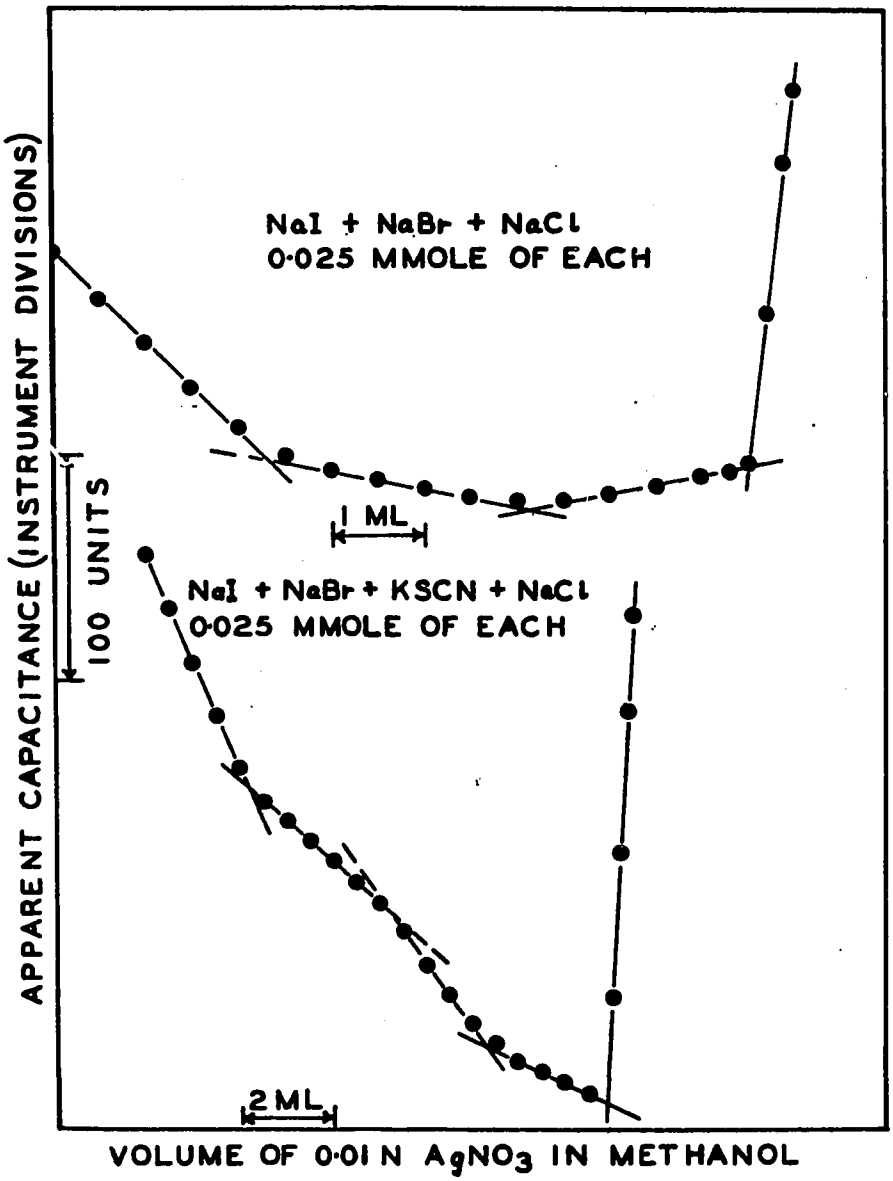

NaCl + NaBr
0.025 MMOLE OF EACH
(a)
(b)
100 UNITS
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
1 ML
ML 0.01-N AgNO3

FIGURE 11

TYPICAL TITRATION GRAPHS OF ARGENTIMETRIC TITRATIONS OF MIXTURES OF SEVERAL HALIDES IN METHANOL


NaI + NaBr + NaCl
0·025 MMOLE OF EACH
1 ML
NaI + NaBr + KSCN + NaCl
0·025 MMOLE OF EACH
100 UNITS
2 ML
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
VOLUME OF 0·01 N AgNO3 IN METHANOL

Duplicate titrations were performed on an equimolar mixture of the three halides plus thiocyanate using standard 0.01-N silver nitrate in methanol. The curve obtained is shown in Figure 11 and the results in Table 3. Good changes of slope were obtained for each component.

(d) Titration of Micro Amounts of Halides

Concentrations down to 43 microgram of chloride and 96 microgram of bromide were successfully determined in the large titration cell; 0.45 micromole of sodium nitrate had previously been added to the solutions. Precision and accuracy were poor at lower amounts of halide.

The small titration cell described in Section III A subsection 2 had an annulus of 5-ml capacity so that only 6 ml of solution were required for the titration. About two microgram (8.4×10^{-6} M) of chloride was titrated in the small cell. The solution had previously been made 10^{-5}-10^{-4} M in sodium nitrate. Reproducibility of the titrations was poor and in some cases no end point was observed. Much sharper and more reproducible end points were obtained on increasing the concentration of chloride to 3.6 microgram (1.67×10^{-5} M) and making the solution 2×10^{-5} M in sodium nitrate. Blank titrations were also run on the sodium nitrate alone. Halide was not found. The results for these analyses are given in Table 7 and a typical titration graph is shown in Figure 12. Similar results were obtained by titrating solutions that were 1.67×10^{-5} M in bromide or in iodide and 2×10^{-5} M in sodium nitrate.

TABLE 7

HIGH-FREQUENCY ARGENTIMETRIC TITRATIONS OF MICRO AMOUNTS OF HALIDE, ALONE AND IN THEIR MIXTURES, IN METHANOL

Initial Volume of solution in titration cell: 6 ml
Normality of standard $AgNO_3$ in methanol : 0.001 N

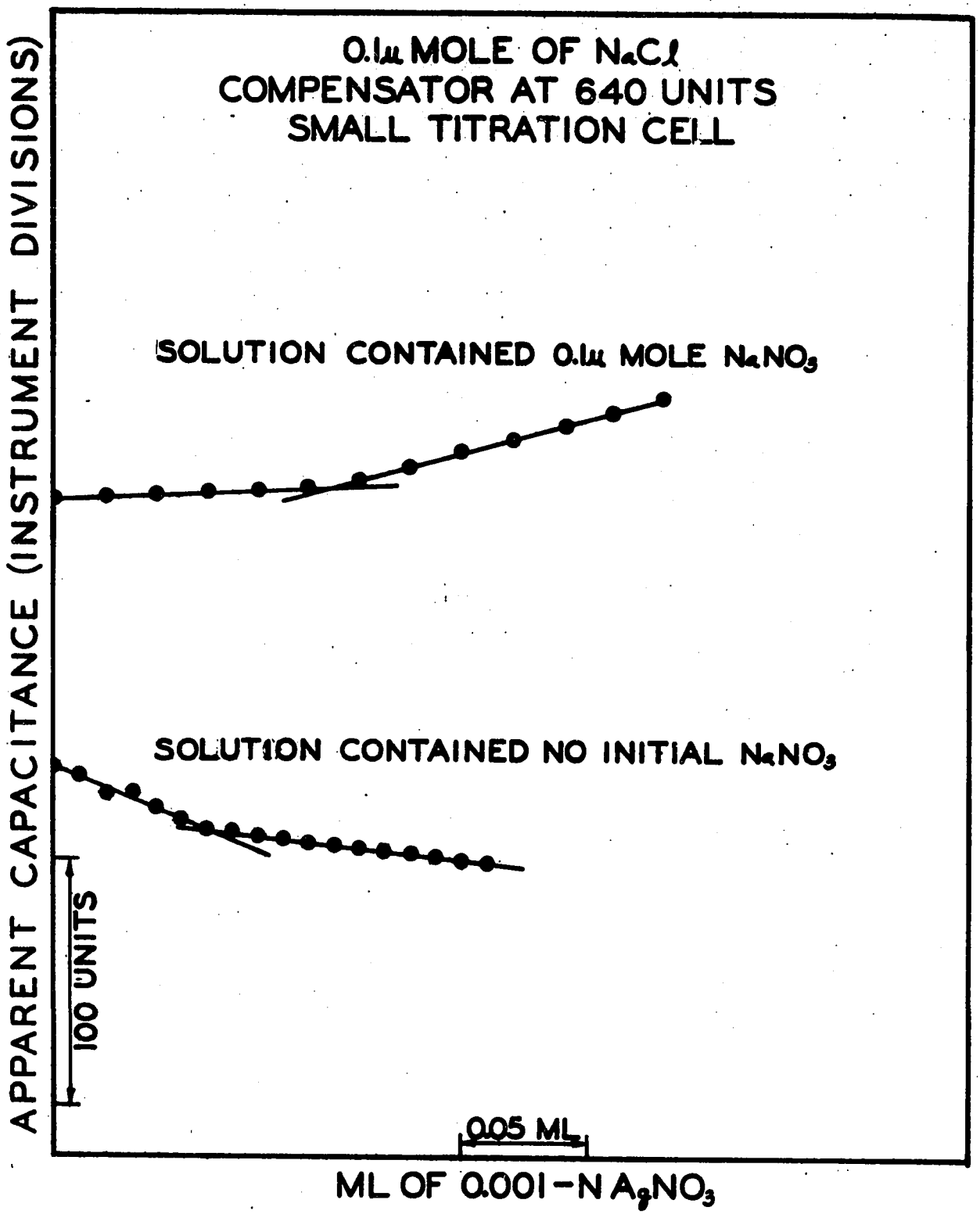
Mole Ratio Br:Cl	Bromide (μmole) Taken	Found*	Standard Deviation	N	Chloride (μmole) Taken	Found*	Standard Deviation	N	Bromide + Chloride (μmole) Taken	Found*	Standard Deviation	N
0	Nil				0.1005	0.101	0.0010	6				
1:1	0.1491	0.157	0.0070	7					0.3003	0.304	0.011	7
			% Difference								% Difference	
3:1	0.4485	0.443	-1.2	2					0.5996	0.578	-3.6	2
2:1	0.2988	0.297	-0.5	2					0.4498	0.432	-3.8	2
1:2	0.1491	0.160	7.4	2					0.4537	0.438	-3.3	2
1:3	0.1491	0.162	8.7	2					0.6051	0.600	-0.8	2

*Average of N samples.

NOTE: "% Difference" is the percentage difference between the amount taken and the average of N samples of the amount found. For the six samples of chloride alone, the methanol solutions were made 1.7×10^{-5} M in sodium nitrate; this salt was not added to the chloride-bromide mixtures.

FIGURE 12

TITRATION GRAPHS OF ARGENTIMETRIC TITRATIONS
OF MICRO AMOUNTS OF SODIUM CHLORIDE IN METHANOL,
CLOSE TO THE LOWER LIMIT OF CONCENTRATION


0.1μ MOLE OF NaCl
COMPENSATOR AT 640 UNITS
SMALL TITRATION CELL
SOLUTION CONTAINED 0.1μ MOLE NaNO3
SOLUTION CONTAINED NO INITIAL NaNO3
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
100 UNITS
0.05 ML
ML OF 0.001-N AgNO3

When binary mixtures of halide were titrated in the small cell a minimum concentration of 2.5×10^{-5} M of each halide was required for good precision and even then the sodium nitrate content had also to be 2.5×10^{-5} M. This lower limit was confirmed for chloride-iodide and chloride-bromide mixtures. Some typical results are given in Table 7 and illustrated in Figure 13.

Comparison of the standard deviations given in Table 7 with those given in Table 4 show that the determination of microgram amounts in the small titration cell can be carried out with almost as good accuracy and precision as titrations of macro amounts in the large cell.

In the titration of an equimolar mixture of chloride, bromide and iodide the lower limit of concentration for each component was found to be 3.3×10^{-5} M. In this case the total concentration of electrolyte was high enough that the addition of sodium nitrate was unnecessary. A typical titration graph is shown in Figure 13.

3. The Response Curves

Response curves for sodium chloride, sodium bromide, sodium iodide, sodium nitrate, silver nitrate and cupric chloride were obtained in methanol; for sodium chloride, sodium bromide, sodium iodide and silver nitrate in ethanol. The curves for methanol are shown in Figures 14 and 15. The curve for silver nitrate in ethanol is also shown in Figure 14 for comparison.

FIGURE 13

TYPICAL TITRATION GRAPHS OF ARGENTIMETRIC TITRATIONS OF MIXTURES OF MICRO AMOUNTS OF HALIDES IN METHANOL

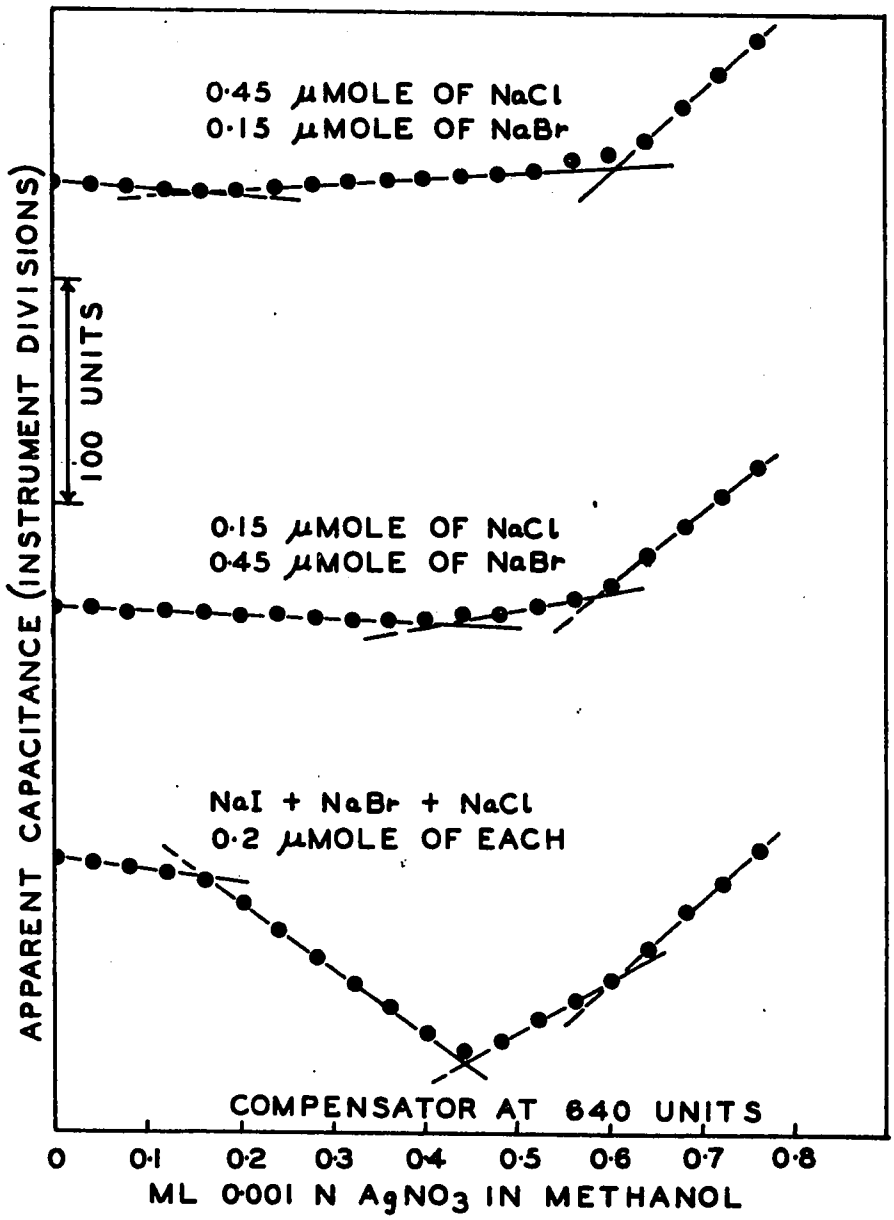

0·45 μMOLE OF NaCl
0·15 μMOLE OF NaBr
100 UNITS
0·15 μMOLE OF NaCl
0·45 μMOLE OF NaBr
NaI + NaBr + NaCl
0·2 μMOLE OF EACH
COMPENSATOR AT 640 UNITS
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
ML 0·001 N AgNO3 IN METHANOL

FIGURE 14

RESPONSE CURVES OF ELECTROLYTES IN METHANOL,
AND OF SILVER NITRATE IN ETHANOL

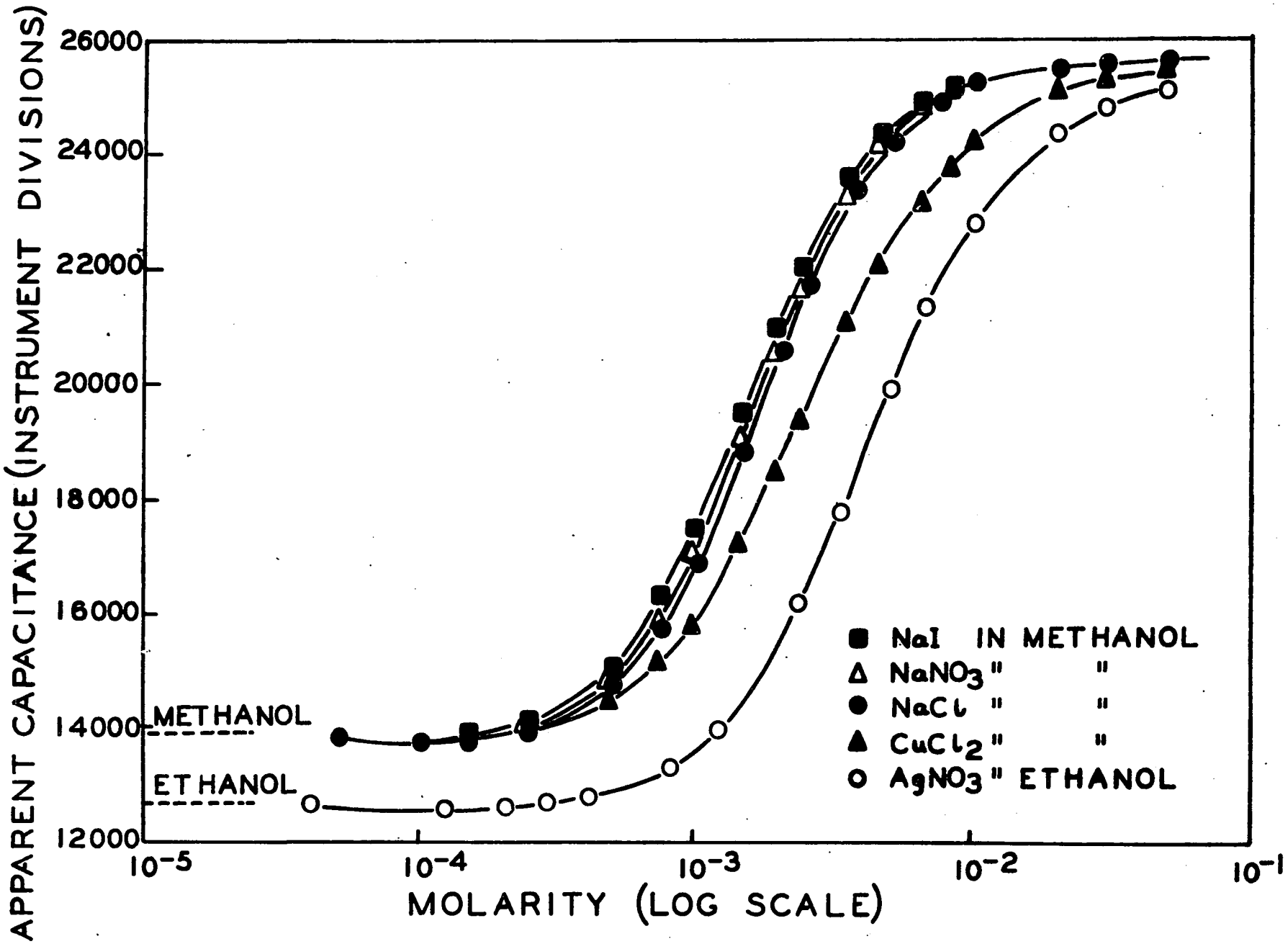
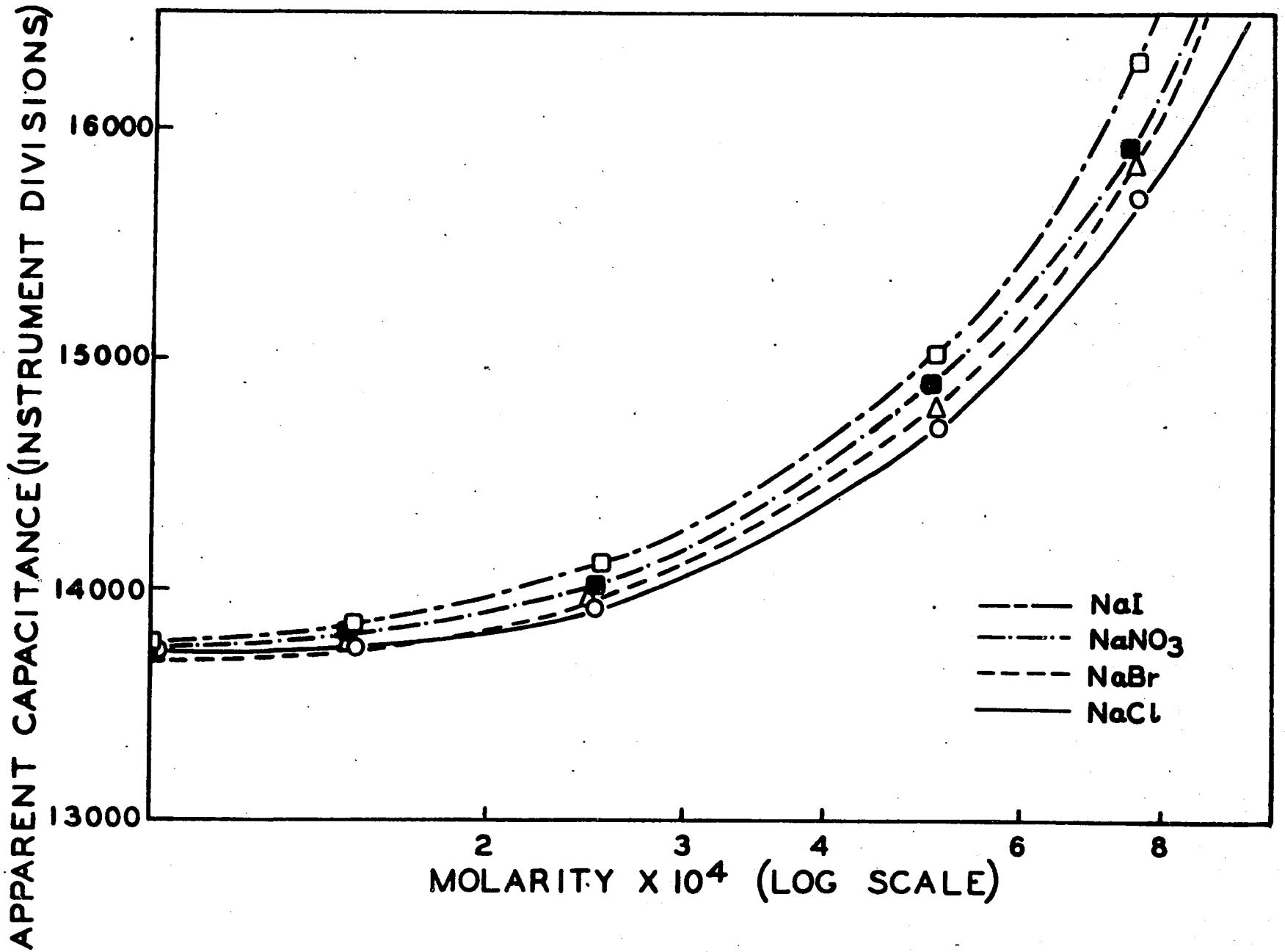

APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
26000
24000
22000
20000
18000
16000
14000
12000
METHANOL
ETHANOL
10⁻⁵
10⁻⁴
10⁻³
10⁻²
10⁻¹
MOLARITY (LOG SCALE)
■ NaI IN METHANOL
△ NaNO3 " "
● NaCl " "
▲ CuCl2 " "
○ AgNO3 " ETHANOL

FIGURE 15

SECTIONS OF THE RESPONSE CURVES OF SEVERAL ELECTROLYTES IN METHANOL, IN THE LOW CONCENTRATION RANGE


APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
16000
15000
14000
13000
2
3
4
6
8
MOLARITY X 10⁴ (LOG SCALE)
NaI
NaNO3
NaBr
NaCl

It was found that the response curves for an individual salt did not coincide, except at low ($<10^{-4}$ M) and high (>0.01 M) concentrations. The order of increasing apparent capacitance, at any given concentration of electrolyte in methanol or ethanol, in the range 10^{-4} to 0.01 M, was

$$CuCl_2 < NaCl < NaBr < NaNO_3 \approx AgNO_3 < NaI.$$

A feature of all response curves in methanol was that a minimum occurred at about 10^{-4} M, when the large titration cell was used. A minimum also occurred in the curves for ethanol, but it was shifted to about 8×10^{-4} M. At higher concentrations of electrolyte, >0.01 M, the curves for methanol became horizontal and merged. The curves for ethanol did not merge until about 0.08 M.

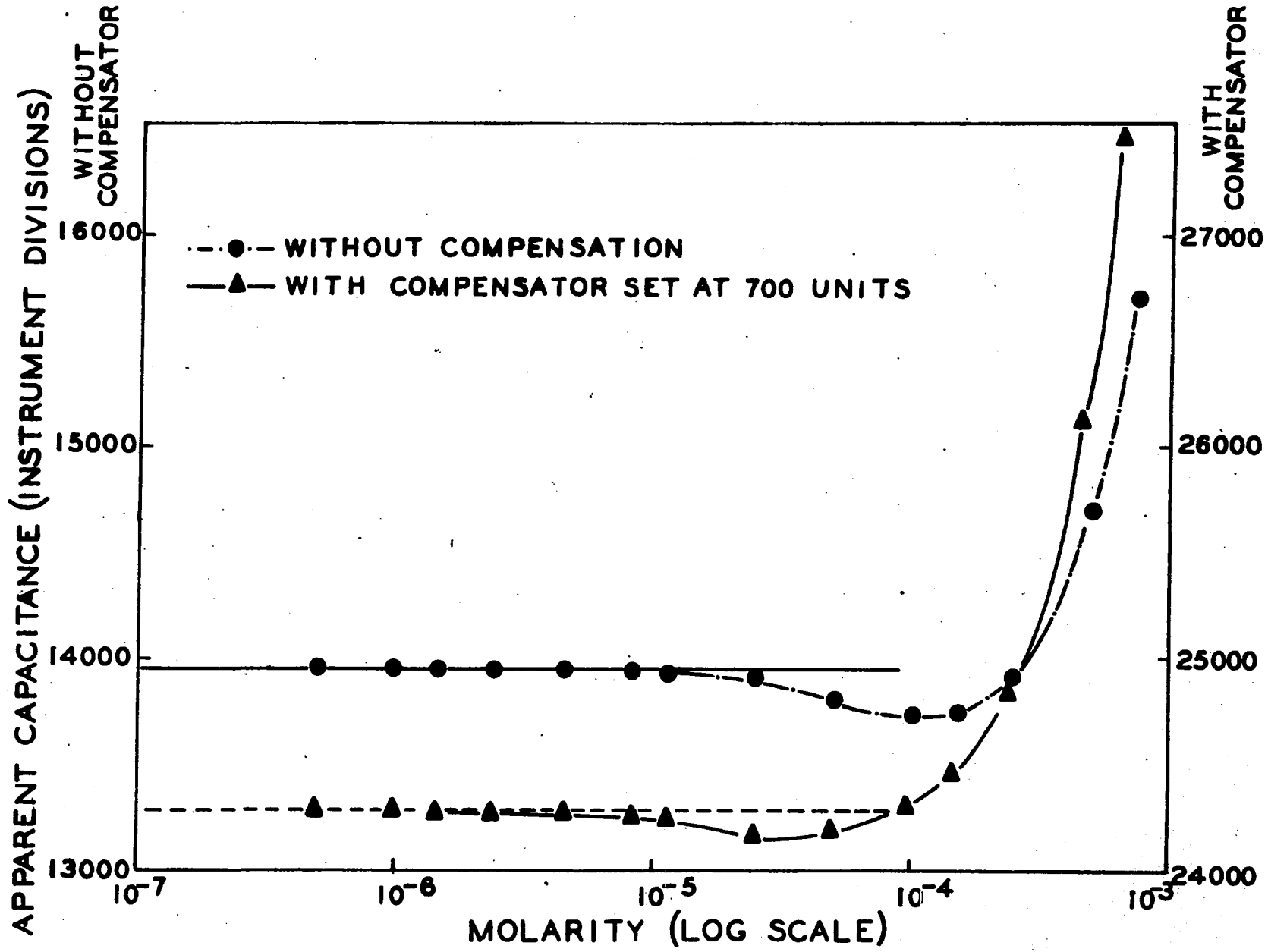
The left-hand portion of the response curve of sodium chloride in methanol is shown in greater detail in Figure 16. Curve (b) was obtained with the Sargent Cell Compensator coupled between the instrument and the cell assembly; it was set at 700 units. The minimum in the curve was found to shift to a lower concentration (2×10^{-5} M).

Curve (b) of Figure 16 was typical of all the electrolytes studied. It was also found that the curves of the individual electrolytes did not coincide until 2×10^{-5} M; without the cell compensator they coincided at 10^{-4} M. Due to this property of the response curves lower concentrations of halides could be titrated.

Response curves were also obtained with the use of the small titration cell. In Section III D subsection 1 the

FIGURE 16

LOW CONCENTRATION REGION OF THE RESPONSE CURVE OF SODIUM CHLORIDE IN METHANOL, WITH AND WITHOUT THE USE OF THE SARGENT CELL COMPENSATOR


APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
WITHOUT COMPENSATOR
WITH COMPENSATOR
16000
15000
14000
13000
27000
26000
25000
24000
WITHOUT COMPENSATION
WITH COMPENSATOR SET AT 700 UNITS
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
MOLARITY (LOG SCALE)

sensitivity of the small cell to changes in ambient temperature was discussed. Since the cell was not thermostated during the determination of the response curves their reliability was doubtful. However, the same order of increasing apparent capacitance as that given above was observed. A minimum was also obtained which was at a lower concentration than the minimum observed with the large cell. The minimum was also shifted when the cell compensator was coupled between the instrument and the cell assembly.

IV. DISCUSSION OF RESULTS

A. INTRODUCTION

The argentimetric determination of halides is well known. The Mohr, Fajans and Volhard volumetric methods use visual end-point detection in the analysis of single halides. Single halides and their mixtures in aqueous solutions have been determined potentiometrically (3,5,18-25), conductometrically (3,25) and amperometrically (26). Only single halides in aqueous solution have been determined by high-frequency titrations (5,27).

A few workers have described analyses of halides in nonaqueous solvents. The high-frequency determination of chloride in 90% acetone has been reported (5). The potentiometric titration of mixtures of bromide and thiocyanate in aqueous acetone and in 95% ethanol was reported by Léon (21). Micro amounts of chloride and halides in nonaqueous solvents (28), in ethylene glycol (29) and in 90-99% acetone (30,31) have also been determined potentiometrically.

In the present work, an excellent high-frequency titrimetric method has been developed. It readily allows the titration of the components in mixtures of halides, present either in macro or micro amounts in certain nonaqueous solvents.

B. TITRATION OF SINGLE HALIDES

The titration graphs shown in Figure 5 exhibit curvature at the end point. The amount of this curvature in-

creases in order

$$Cl^- < SCN^- < Br^- < I^-$$

Shiner and Smith (32) and W. Clark (33) observed during the argentimetric potentiometric titration of halides in water, that distortions of the titration graphs decreased in magnitude from iodide to chloride (they do not report on thiocyanate). This, they state, corresponds to "decreased adsorption of the lattice ions on the precipitate". It is reasonable to assume that a similar phenomenon is taking place in methanol solution.

In the titration of strontium and cupric chlorides, Figure 7 indicates a break in the titration graph after one half of an equivalent of silver nitrate had been added. This suggests the possible existence of $SrCl^+$ and $CuCl^+$ but without additional evidence this must be considered a speculation. However, the existence of $CuCl^+$ in water and 90% ethanol has been reported (34,35); and the existence of $SrCl^+$ in 90% and in 40% ethanol has also been reported (36).

The sodium halides were used for the titrations reported in the present work. They were convenient because they were readily soluble in methanol. Titrations of divalent metal halides were not as satisfactory; and the titration of trivalent metal halides appears to be quite unsatisfactory. Therefore if halides are to be determined by the present method the prior conversion of di- and tri-

valent metal halides to alkali metal halides is indicated. Such conversion may require the prior solution of the multivalent metal halide in a minimum of water before its conversion to an alkali halide and dilution by methanol.

C. SOLID-SOLUTION FORMATION IN THE TITRATION OF BINARY MIXTURES OF CHLORIDE AND BROMIDE

The solubility products of silver chloride and silver bromide differ by a factor of 150 in methanol (see Appendix II), which is sufficient to permit the bromide to be quantitatively precipitated before that of chloride begins. However, it was observed (see Section III D subsection 2(b)) in the titration of equimolar mixtures, that a reproducible positive error occurred at the bromide end point.

Flood and coworkers (37-39), and Thiel (40) concluded that such an error was due, in aqueous solutions, to solid-solution formation between silver chloride and silver bromide. They derived theoretical expressions for the relative percentage error in the less soluble component as the ratio of the components was changed. They also found that the effect of solid-solution formation was less pronounced in silver iodide and silver bromide mixtures. Silver iodide and silver chloride did not form solid solutions. A summary of Flood's treatment (37-39) follows.

If pure silver bromide is equilibrated with a solution containing chloride ions, a solid solution is formed,

$$\underset{\text{Solid}}{Ag(Br,Cl)} \rightleftarrows Ag^+ + Cl^- + Br^- \qquad \text{IVC-1}$$

This may be regarded as a distribution equilibrium of the two halide ions between solid and solution, namely

$$\underset{\text{Solid}}{AgBr[\text{in } Ag(Br,Cl)]} + Cl^- \rightleftarrows \underset{\text{Solid}}{AgCl[\text{in } Ag(Br,Cl)]} + Br^- \qquad \text{IVC-2}$$

This equilibrium is described by a distribution coefficient D, where

$$D = \frac{(Br^-)_{SOLN.}}{(Cl^-)_{SOLN.}} \cdot \frac{N_{AgCl}}{N_{AgBr}} \qquad \text{IVC-3}$$

and the composition of the solid is in mole fractions, N.

There are two extreme cases for solid-solution formation, when silver nitrate is added to a solution containing chloride and bromide ions. In one case, the precipitate recrystallizes so rapidly that, as the solution composition changes when silver nitrate is added, the precipitate is at all times homogeneous and in equilibrium with the particular composition of the solution at that instant. In the other case, the fresh solid is only in equilibrium with the solution composition at the instant of its formation, and does not undergo recrystallization. The solid-solution phase would then be heterogeneous.

The theoretical expression for homogeneous solid-solution formation, assuming ideal solid solutions, is given by equation IVC-3. The relationship for heterogeneous solid-solution formation was derived by Doerner and Hoskins (41)

and is given by the following equation

$$\log \frac{(Br^-)_f}{(Br^-)_i} = \lambda \log \frac{(Cl^-)_f}{(Cl^-)_i} \qquad \text{IVC-4}$$

The subscripts f and i refer to final and initial concentrations in solution. The coefficient λ is identical with D and is used only to distinguish between the two types of equilibria.

For homogeneous solid-solution formation Flood (37) used equation IVC-4 to obtain the following expression:

$$\varepsilon_A = 100 \left(\frac{C_B}{C_A} - 1\right) \frac{K_{MA}\ \gamma_{MA}}{K_{MA}\ \gamma_{MA} + K_{MB}\ \gamma_{MB}} \qquad \text{IVC-5}$$

where

ε_A = relative percentage error in determining the less soluble component A by precipitation from a binary aqueous solution

C_A, C_B = initial molar concentrations of A and B

K_{MA}, K_{MB} = activity products of MA and MB

γ_{MA}, γ_{MB} = activity coefficients of MA and MB in the solid

If $K_{MB} >> K_{MA}$, equation IVC-5 becomes approximately

$$\varepsilon_A \approx 100 \left(\frac{C_B}{C_A} - 1\right) \frac{K_{MA}\ \gamma_{MA}}{K_{MB}\ \gamma_{MB}} = 100 \left(\frac{C_B}{C_A} - 1\right) D \qquad \text{IVC-6}$$

For heterogeneous solid-solution formation, Flood gave the following approximate expression for the relative percentage error in the less soluble component:

$$\varepsilon_A \approx 100 \frac{C_B}{C_A} \left[1 - \left(\frac{C_B}{\lambda C_A}\right)^{\lambda} - \lambda\right] \qquad \text{IVC-7}$$

where all symbols are as given above, and λ is identical with D.

The results given in Table 5 can be interpreted in terms of solid-solution formation. The question now to be answered is whether such solutions are homogeneous or heterogeneous. The amount of bromide left in solution at the end point divided by the total amount of bromide taken will give the error in the bromide end point. From formulae given by Kolthoff and Stenger (15) it is readily shown that for homogeneous solutions

$$\frac{a - x}{x} = \frac{(b - m + x)}{(m - x)} \quad D \qquad \text{IVC-8}$$

where

a = initial equivalents of bromide taken

b = initial equivalents of chloride taken

m = equivalents of $AgNO_3$ added to the bromide end point

x = equivalents of bromide precipitated

D = the distribution coefficient as defined above

m - x = equivalents of chloride precipitated

a - x = equivalents of bromide left in solution

b - m + x = equivalents of chloride left in solution

It can be shown from equation IVC-3 that

$$D = \frac{K_{AgBr}}{K_{AgCl}} \qquad \text{IVC-9}$$

if it is assumed that ideal solid solutions are formed. For methanol

$$K_{AgBr} = 5.8 \times 10^{-16} \text{ at } 25°C$$

$$K_{AgCl} = 8.9 \times 10^{-14} \text{ at } 25°C$$

$$D = 6.51 \times 10^{-3}$$

An analogous equation to equation IVC-8 can be derived for heterogeneous solid solutions:

$$\log \frac{a - x}{a} = \lambda \log \frac{(b - m + x)}{b} \qquad \text{IVC-10}$$

where the symbols are the same as those defined above and λ is numerically equal to D.

By using these two formulae the calculated percentage error in the bromide end point for a homogeneous solid solution and separately for a heterogeneous solid solution were calculated for the data in Table 5. The results are shown in columns 5 and 7 in Table 8; in column 8 the percentage errors found experimentally and recorded in Table 5 are repeated.

The experimental errors agree more closely with those calculated for homogeneous solid-solution formation. Exceptions are the 20:1, 10:1 and 1:20 NaCl:NaBr ratios. An explanation of them is given in the next paragraph. During a titration the precipitates did not coagulate but remained colloidally dispersed. Kolthoff and Eggertson (42) in studies on the precipitation of equimolar mixtures of chloride and bromide found that when the precipitate remained in colloidal solution, homogeneous solid-solution formation took place. Heterogeneous solid-solutions were approached when a coagulant such as aluminum nitrate was present in the solution.

TABLE 8

COMPARISON OF CALCULATED ERRORS IN THE BROMIDE END POINT FOR HOMOGENEOUS AND HETEROGENEOUS SOLID-SOLUTION FORMATION WITH EXPERIMENTAL ERRORS IN THE ARGENTIMETRIC TITRATION OF CHLORIDE-BROMIDE MIXTURES IN METHANOL

Mole Ratio Cl:Br	Chloride Taken µmole	Bromide Taken µmole	Homogeneous Solid-Solution Formation		Heterogeneous Solid-Solution Formation		Experimental % Difference
			Bromide in solution µmole	Calculated % Difference	Bromide in solution µmole	Calculated % Difference	
1:20	4.8	101.5	2.0	2.0			- 3.4
1:10	9.7	101.5	2.5	2.2	0.4	0.4	- 2.7
1:3	24.3	76.2	3.6	4.7	1.3	1.6	2.8
1:1	50.6	50.6	3.8	7.5	1.0	2.0	7.9
3:1	72.8	25.4	3.2	12.6	1.1	4.3	9.9
10:1	97.0	10.2	2.2	21.8	1.2	11.8	19.4
20:1	97.0	5.1	1.5	29.6			71.2

NOTE: "Calculated % Difference" is the percentage ratio of µmole of Bromide in solution and µmole bromide taken. "Experimental % Difference" is the percentage difference between the amount of bromide taken and the amount of bromide found.

Bowers et. al. (7) found that the experimental potentiometric titration graph approached that for homogeneous precipitation when calcium nitrate was present in the aqueous solution. These authors also found that when coagulant was absent, the experimental titration graph did not coincide with the calculated graph for homogeneous solid-solution formation nor with that for heterogeneous solid-solution formation. Their results are not in agreement with those found in the present work. It is possible that in the absence of coagulant, both homogeneous and heterogeneous solid-solution formation occurs. Precipitations carried out in methanol as a solvent may favour homogeneous solid-solution formation.

According to equations IVC-5 to IVC-10 the percentage error in the bromide end point should never be negative. However the ratios of 1:20 and 1:10 NaCl:NaBr did give negative experimental errors for the bromide end point. The explanation appears to be that for these ratios estimation of the bromide end point was difficult and uncertain; this is graphically shown in Figure 17. It is therefore concluded that these two negative errors are statistical rather than real.

D. THE TITRATION OF BINARY MIXTURES OF THIOCYANATE AND CHLORIDE

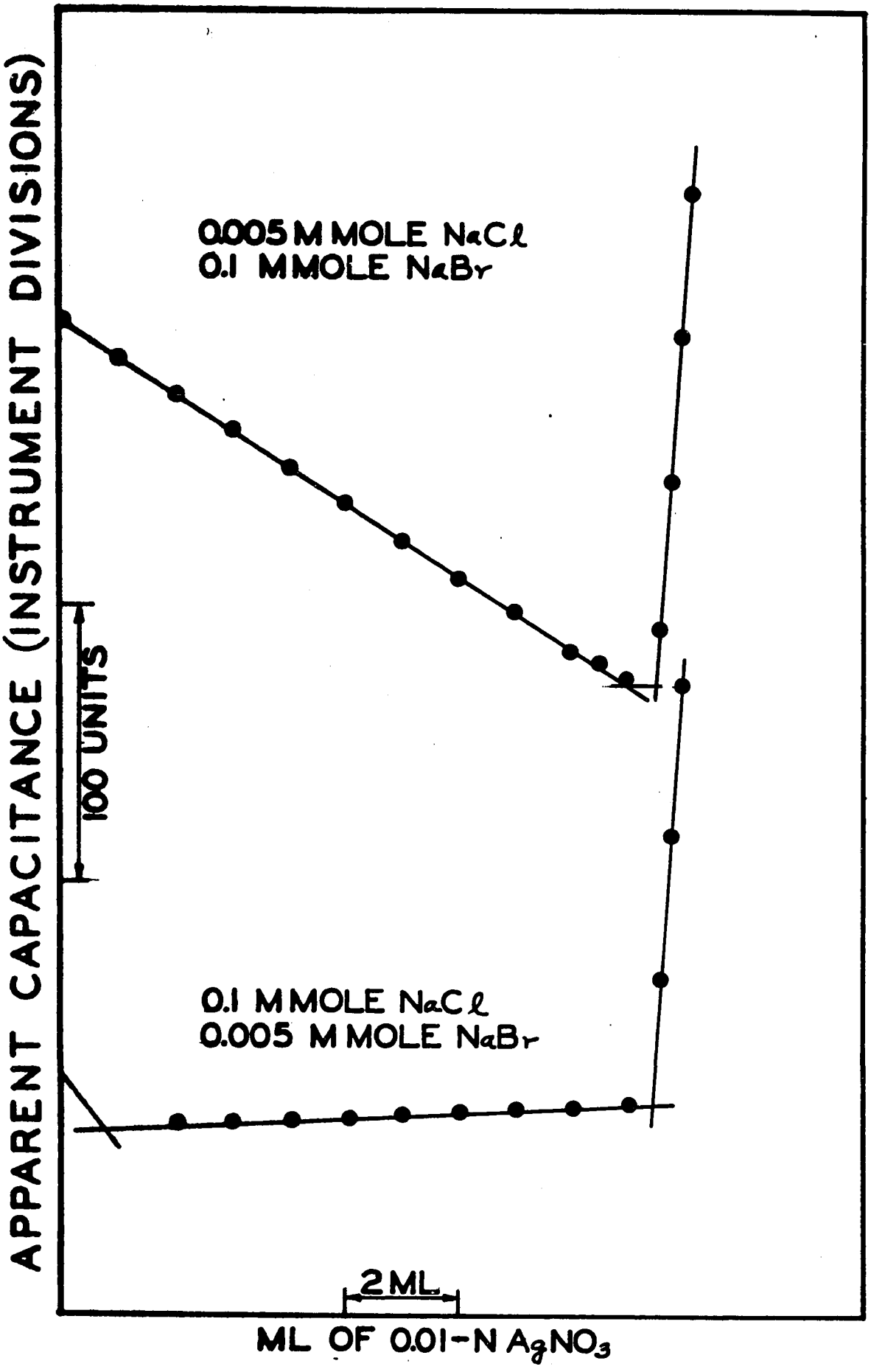
Whether chloride or thiocyanate precipitates first should depend on the ratio of their initial concentrations as well as upon their solubility products. The ratio of

FIGURE 17

TITRATION GRAPHS OF THE ARGENTIMETRIC TITRATION OF MIXTURES OF CHLORIDE AND BROMIDE IN METHANOL

(a) The Mole Ratio of Cl:Br was 1:20

(b) The Mole Ratio of Cl:Br was 20:1


APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
0.005 M MOLE NaCl
0.1 M MOLE NaBr
100 UNITS
0.1 M MOLE NaCl
0.005 M MOLE NaBr
2 ML
ML OF 0.01-N AgNO3

the solubility products of silver thiocyanate to that of silver chloride in methanol is 4.95 (see Appendix II). Therefore for a solution in which the concentration of thiocyanate:chloride is 1:5 both ions should be precipitated from the beginning of the titration in a ratio of 1:5 and no change in the slope of the titration graph should be observed. A change of slope was found to occur. A possible explanation is that solid-solution formation took place between silver thiocyanate and silver chloride during the first part of the titration.

Quite apart from solid-solution formation, anomalies were found to exist between the observed and calculated positions of the first end point. These anomalies can also be explained on the basis of solid-solution formation. Such formation appears not be have been previously reported.

E. INTERPRETATION OF THE TITRATION GRAPHS

1. Introduction

In the argentimetric titrations reported in Section III D-2, the titration graphs consisted of intersecting straight lines. It is the purpose of the present section to consider the factors that determine the slopes of these lines. It will then be shown possible to predict these slopes. Such predictions enable the best conditions to be selected for the titration of the particular halide in order to ensure a sharp end point.

When a halide in methanol is precipitated with a methanol solution of silver nitrate, an equivalent amount of nitrate

replaces the halide in the solution. The left-hand branch of the high-frequency titration graph will represent the exchange of nitrate for halide and the right-hand branch will represent the increasing concentration of excess silver nitrate. The following factors will determine the slopes of these branches:

(1) The extent of dilution by the titrant during titration.

(2) Solid-solution formation.

(3) Adsorption.

(4) The presence of a precipitate.

(5) The particular halide being precipitated.

(6) The ionic strength of the solution.

(7) The nature of the solvent.

The effect of factors (5) and (6) was clearly indicated in Figure 6.

Several authors (10,43,44) including Blaedel and Malmstadt (4) and Reilley (11) have resolved high-frequency titration graphs into two components (a) a capacitance graph and (b) a conductance graph. They measured these two factors separately during a titration. Reilley, in particular, used transfer plots to construct a high-frequency titration graph for acid-base titrations in aqueous solution, from the slope of the corresponding low-frequency conductometric titration graph. His method of transfer plots is illustrated in Figures 18A and 18B.

The specific conductance of the sodium halides and nitrate in methanol is shown as a function of their molar

FIGURE 18A

TRANSFER PLOTS FOR PARALLEL CAPACITANCE CHANGES

(Reproduced by permission of "Analytical Chemistry"
from C. N. Reilley and W. H. McCurdy, Anal. Chem., 25, 86(1953))

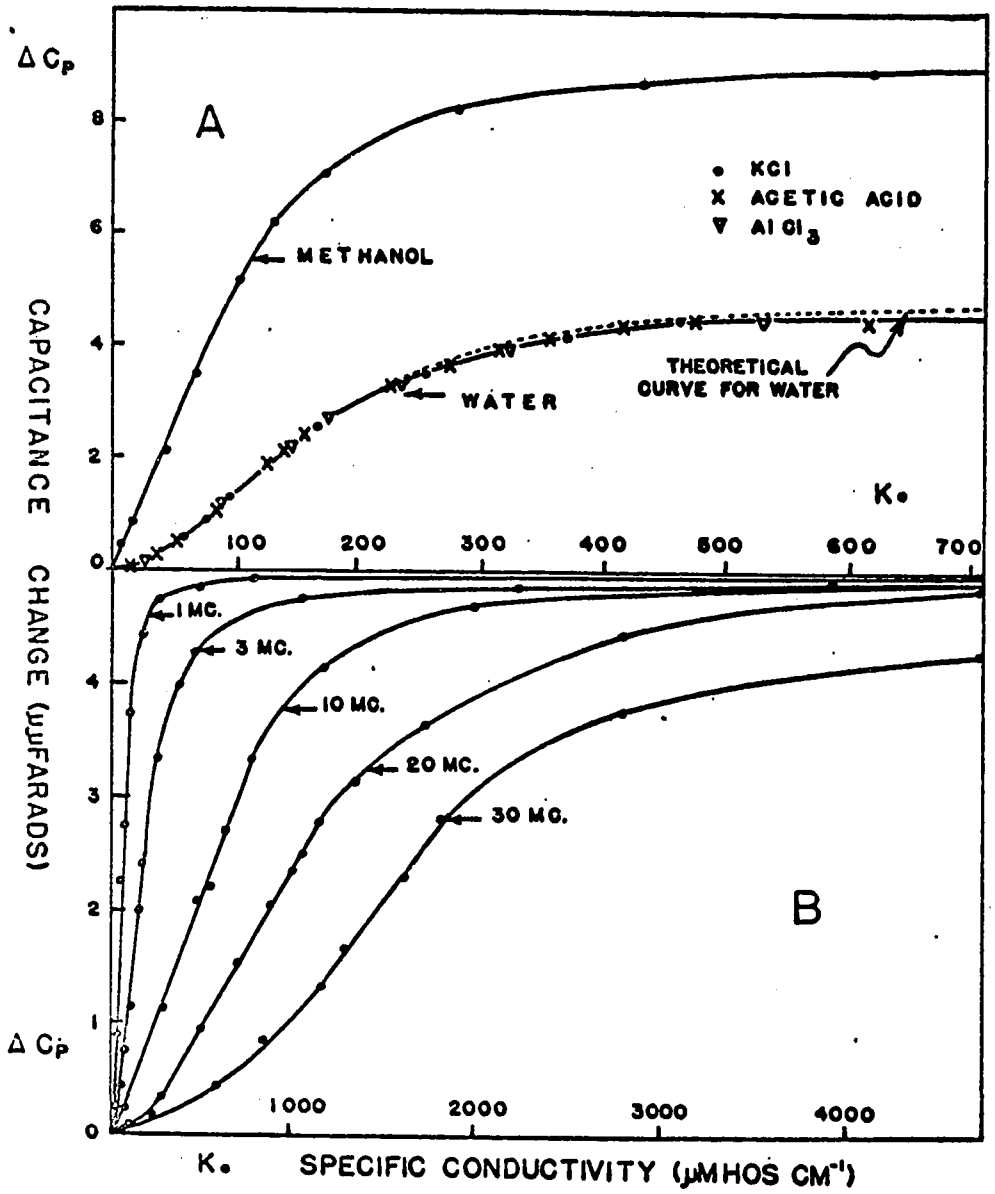

ΔCp
A
• KCl
X ACETIC ACID
▼ AlCl3
METHANOL
WATER
THEORETICAL CURVE FOR WATER
K•
100
200
300
400
500
600
700
1 MC.
3 MC.
10 MC.
20 MC.
30 MC.
B
ΔCp
1000
2000
3000
4000
K• SPECIFIC CONDUCTIVITY (μMHOS CM⁻¹)
CAPACITANCE CHANGE (μμFARADS)

FIGURE 18B

CORRELATION OF CAPACITANCE-CHANGE TITRATIONS
TO LOW-FREQUENCY CONDUCTIVITY TITRATIONS IN AQUEOUS SOLUTION

A. Capacitance titration curves at 10 Mc.

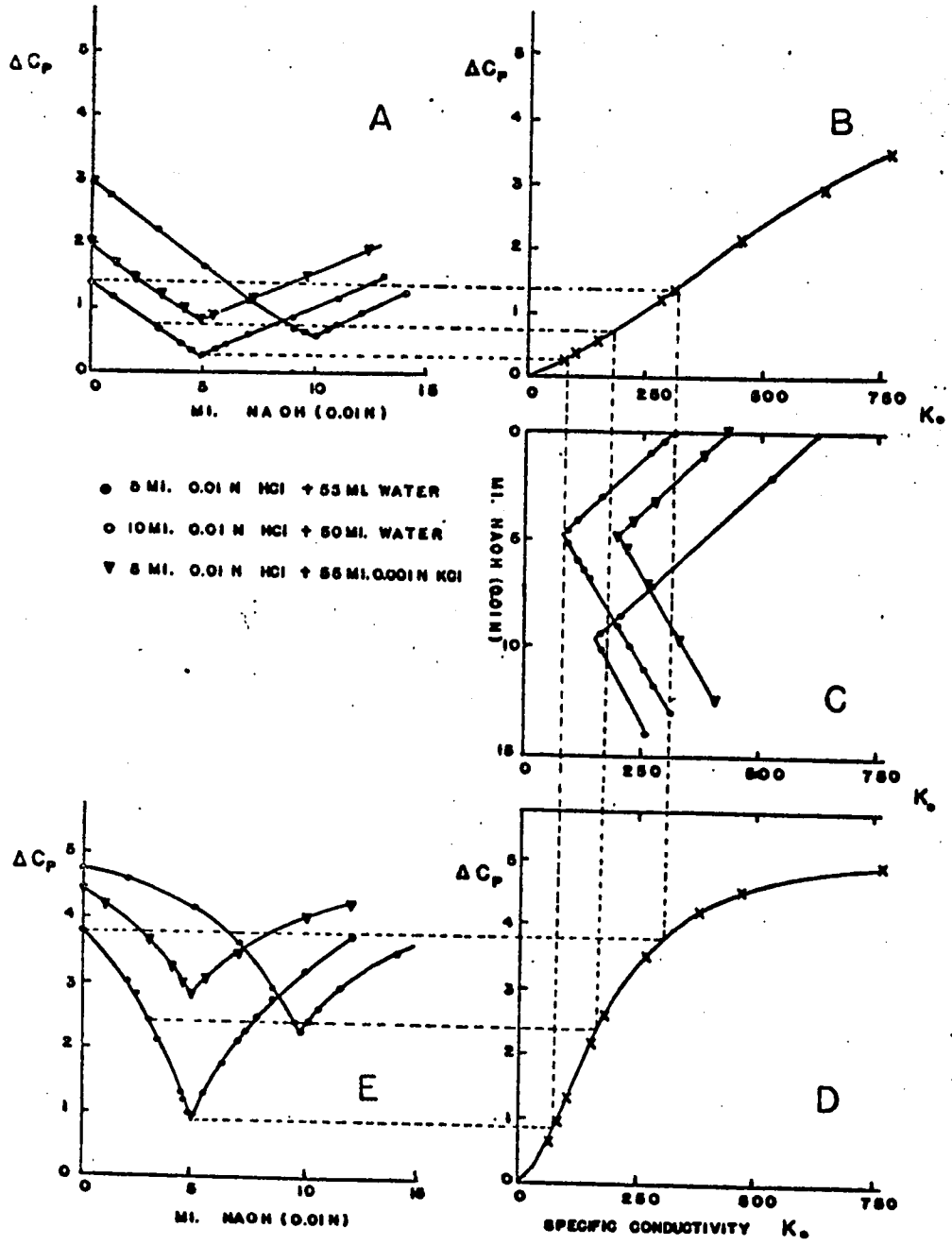
B. Transfer plot for 10 Mc.

C. Low-frequency conductivity titration curves.

D. Transfer plot for 3 Mc.

E. Capacitance titration curves at 3 Mc.

(Reproduced by permission of "Analytical Chemistry"
from C. N. Reilley and W. H. McCurdy, Anal. Chem., 25, 86(1953))


ΔCp
A
B
C
D
E
MI. NAOH (0.01N)
● 5 MI. 0.01 N HCl + 55 ML WATER
○ 10MI. 0.01 N HCl + 50MI. WATER
▼ 5 MI. 0.01 N HCl + 55 MI. 0.001N KCl
MI. NAOH (0.01N)
SPECIFIC CONDUCTIVITY Ko

concentration in Figure 19, and as a function of the apparent capacitance in Figure 20. The values of the specific conductance in methanol at 25°C were calculated from the corresponding equivalent conductance data of Schiff and Gordon (45) for NaCl, Gordon et. al. for NaBr (46), Blokker for NaI (47) and Hartley and Frazer for $NaNO_3$ (48). For this purpose, the Debye-Hückel-Onsager equation for methanol at 25°C (49) was employed:

$$\Lambda_c = \Lambda_o - (0.957\Lambda_o + 158.1)\sqrt{C}$$

where

Λ_c is the equivalent conductance in mhos cm^2 of the solution of normality C

Λ_o is the equivalent conductance in mhos cm^2 at infinite dilution

$\Lambda_c = \frac{1000\ \kappa}{C}$

κ is the specific conductance in mhos cm^{-1}

	Λ_o in methanol at 25°C (mhos cm^2)
NaCl	97.61
NaBr	101.76
NaI	106.7
$NaNO_3$	106.45

The above authors quote a precision of 1% of the value for their measurements of specific conductance. In Figure 20, a 1% change of conductance from 5.0×10^{-5} to 5.05×10^{-5} mhos cm^{-1} produces an apparent capacitance change of about

FIGURE 19

THE SPECIFIC CONDUCTANCE OF SODIUM HALIDES
AND SODIUM NITRATE SOLUTIONS IN METHANOL AS A FUNCTION
OF MOLAR CONCENTRATION AT 25°C

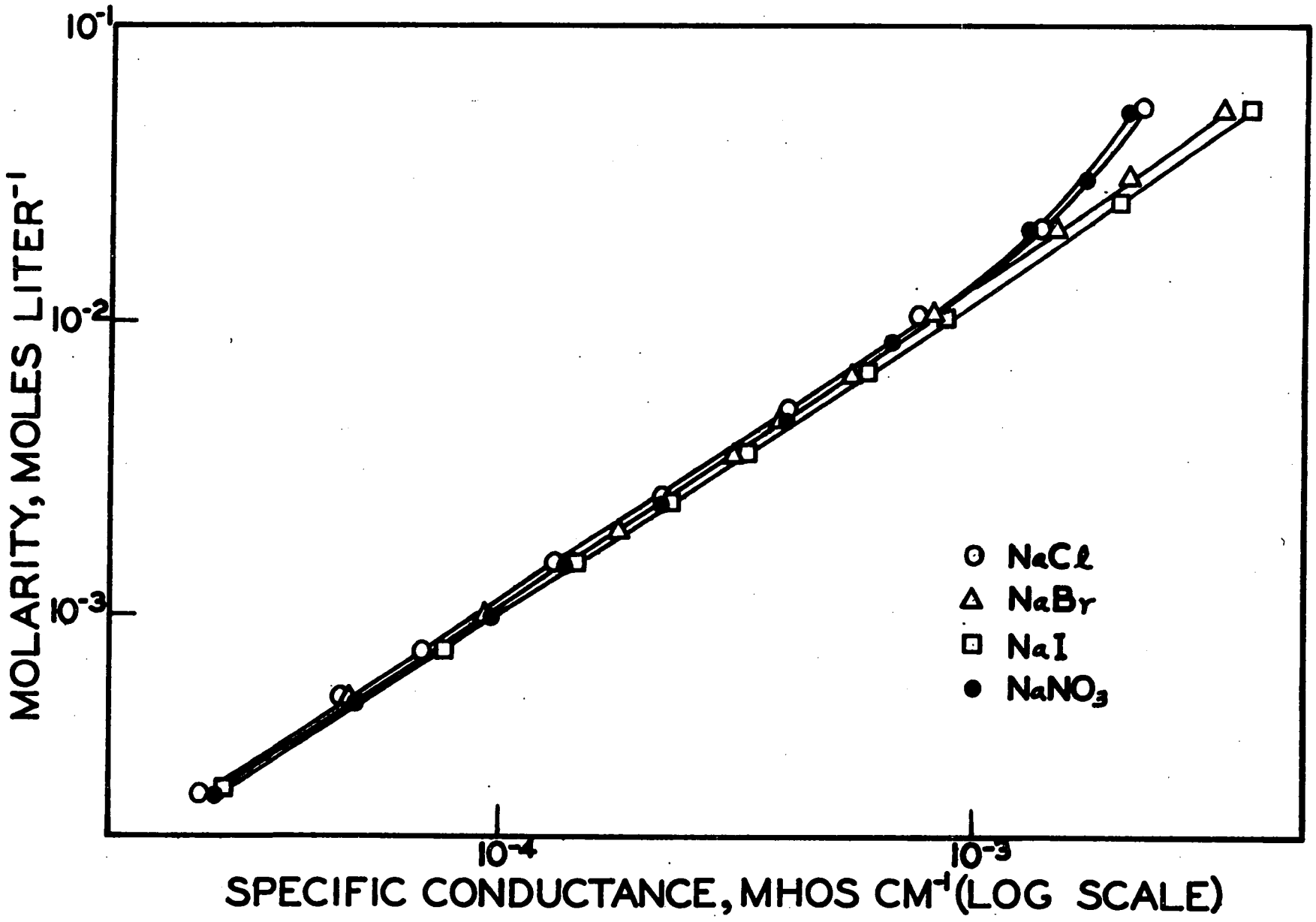
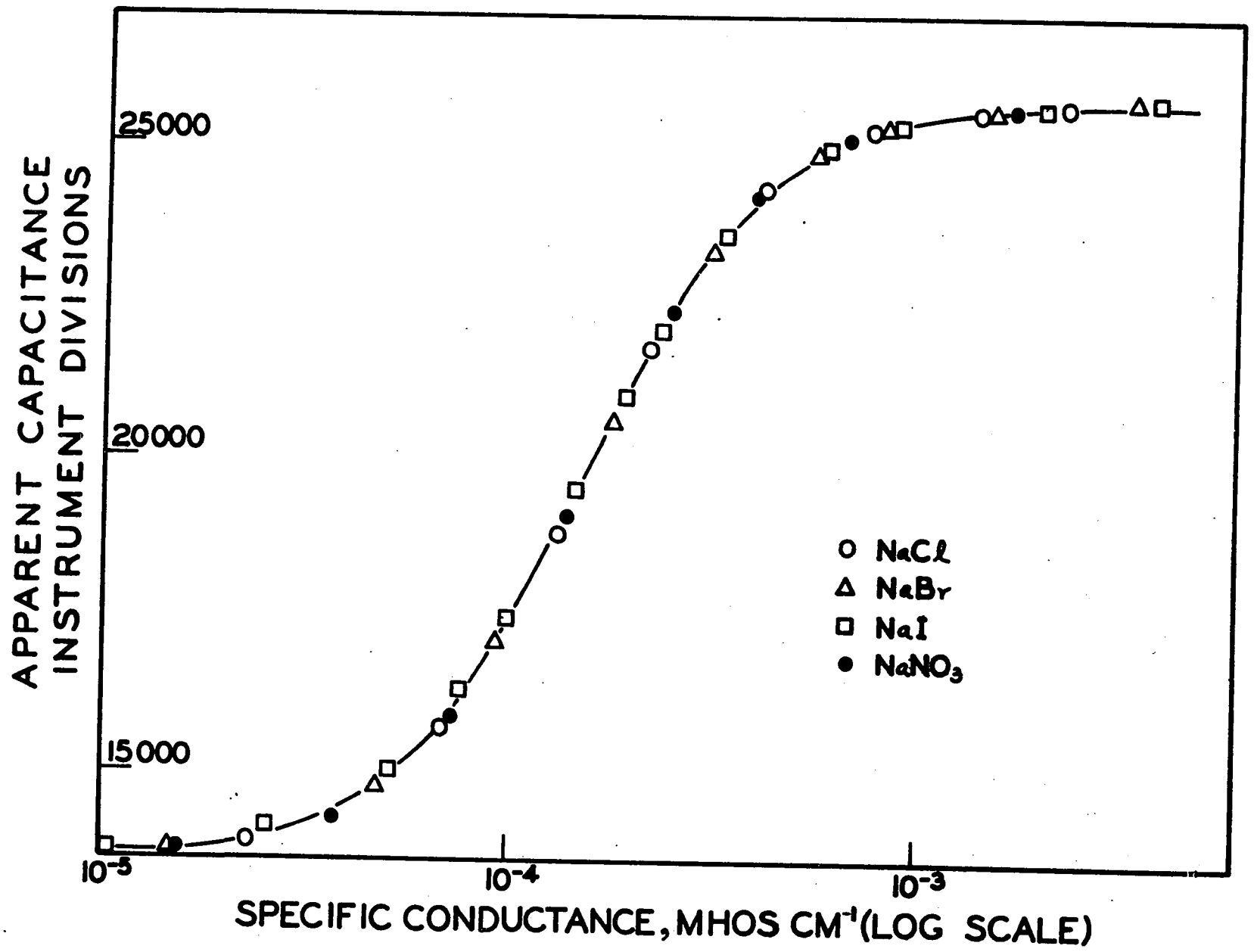

10^{-1}
10^{-2}
10^{-3}
MOLARITY, MOLES LITER^{-1}
10^{-4}
10^{-3}
SPECIFIC CONDUCTANCE, MHOS CM^{-1} (LOG SCALE)
NaCl
NaBr
NaI
$NaNO_3$

FIGURE 20

APPARENT CAPACITANCE OF METHANOL SOLUTIONS OF SODIUM HALIDE AND SODIUM NITRATE, AS A FUNCTION OF THE SPECIFIC CONDUCTANCE AT 25°C


APPARENT CAPACITANCE
INSTRUMENT DIVISIONS
25000
20000
15000
10⁻⁵
10⁻⁴
10⁻³
SPECIFIC CONDUCTANCE, MHOS CM⁻¹ (LOG SCALE)
NaCl
NaBr
NaI
NaNO₃

50 instrument divisions. A similar change of conductance from 1.0×10^{-4} to 1.01×10^{-4} mhos cm^{-1} produces an apparent capacitance change of about 100 instrument divisions. These quantities are readily measured by the oscillometer which has a precision of ± 5 instrument divisions.

Thus high-frequency conductance measurements are more precise than high-precision low-frequency conductance measurements.

In the present section a simple method of constructing theoretical high-frequency titration graphs is presented. It requires only the response curves for the substances participating in the titration. Therefore it has the advantage of requiring only data which are readily obtained from the instrument used for the high-frequency titrations themselves; without the need of other expensive equipment.

2. Interpretation of the Titration Graph of a Single Halide

The high-frequency argentimetric titration of sodium chloride and sodium iodide in methanol will be considered, and for clarity the following specific examples are used. A 10-ml aliquot of a 0.005-M sodium chloride or iodide solution is diluted to 120 ml with methanol. The initial concentration of sodium halide is 4.17×10^{-4} M. When silver nitrate is added sodium halide is exchanged for sodium nitrate. The silver halide precipitates.

The response curves for NaCl, NaI, $NaNO_3$ and $AgNO_3$ were shown in Figure 14. In Figure 21 (a) and (b) the relevant

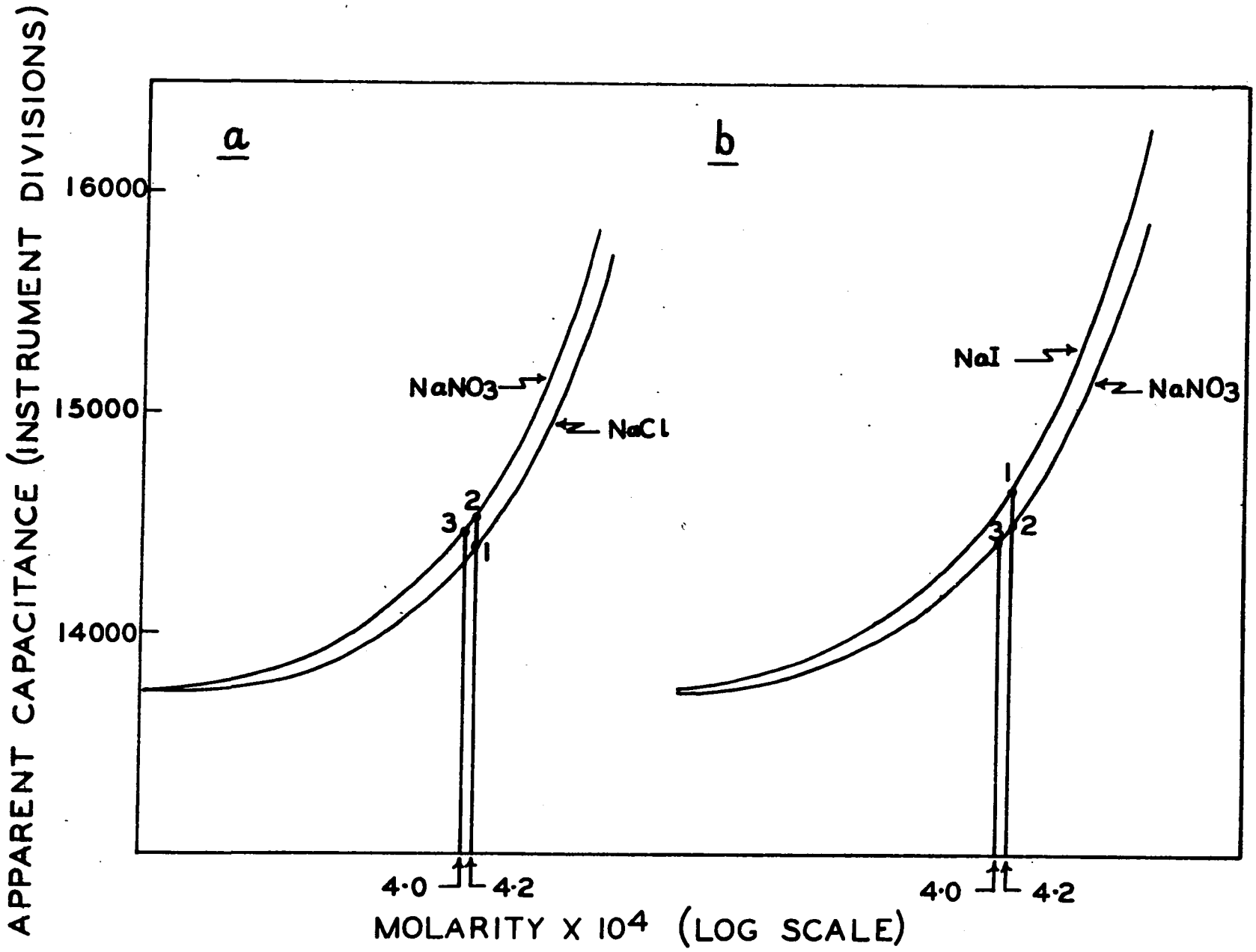
FIGURE 21 (a)

EXPANDED RESPONSE CURVES FOR SODIUM CHLORIDE AND SODIUM NITRATE SOLUTIONS IN METHANOL

FIGURE 21 (b)

EXPANDED RESPONSE CURVES FOR SODIUM IODIDE AND SODIUM NITRATE SOLUTIONS IN METHANOL

NOTE: The curves are not drawn to scale but their positions relative to each other are correct.


a
b
16000
15000
14000
NaNO3
NaCl
NaI
NaNO3
1
2
3
1
2
3
4·0
4·2
4·0
4·2
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
MOLARITY X 10⁴ (LOG SCALE)

portions of the response curves of NaCl, NaI and $NaNO_3$ are presented. They have been expanded for clarity; they are not drawn to scale but their positions with respect to each other are correct.

The initial concentration of sodium chloride, 4.17×10^{-4} M, is shown as point 1 in Figure 21 (a) on the NaCl response curve. This point gives an initial apparent capacitance of 14485 instrument divisions. At the end point of the titration, the resultant solution is 4.17×10^{-4} M in sodium nitrate. This concentration is indicated by point 2 on the $NaNO_3$ response curve. The apparent capacitance is 14555 instrument divisions. In the absence of dilution by titrant, the apparent capacitance would change from 14485 to 14555 instrument divisions in the titration graph. If 5 ml of 0.01-N $AgNO_3$ is required for the end point, the molar concentration of $NaNO_3$ will be 4.00×10^{-4} M. At this concentration, point 3 on the response curve represents an apparent capacitance of 14498 instrument divisions. Thus, in an actual titration the apparent capacitance should change from 14485 to 14498 instrument divisions. A positive slope is predicted and is observed experimentally (Figure 5). The positions of 1 and 3 will depend on the initial concentration of halide, the initial volume of solution and the extent of dilution.

By a similar procedure it may be shown that in the titration of sodium iodide the apparent capacitance should change from point 1 (14700 instrument divisions) in Figure 21 (b)

to point 2 (14500 instrument divisions), in the absence of dilution, and to point 3 (14560) with dilution. A sharp, negative slope is predicted and is observed experimentally (Figure 5).

The right-hand portion of the titration graph will be given by the response curve for silver nitrate, starting at an ionic strength of 4.00×10^{-4} M. As the concentration of silver nitrate increases, the apparent capacitance increases. The increase will be sharp because at 4.00×10^{-4} M initial ionic strength, the response curve of silver nitrate rises sharply.

A simulated graph for the titration of sodium chloride was constructed by preparing solutions of sodium chloride and sodium nitrate in which the ratio was changed from 0:1 to 1:0 $NaCl:NaNO_3$. The initial concentration of sodium chloride was 4.17×10^{-4} M. It was found that the simulated graphs, with and without dilution, coincided with the titration graphs predicted from the response curves. The apparent capacitances as instrument divisions of the predicted, simulated and experimental titration graphs are given in Table 9. The results are shown graphically in Figure 22.

In the predicted and simulated titration graphs, precipitate was absent. In the experimental graph it was present. It seems reasonable to conclude that the colloidally dispersed precipitate contributed to the apparent capacitance and caused the slope of the experimental graph to be somewhat different from that of the predicted and the simulated graphs.

TABLE 9

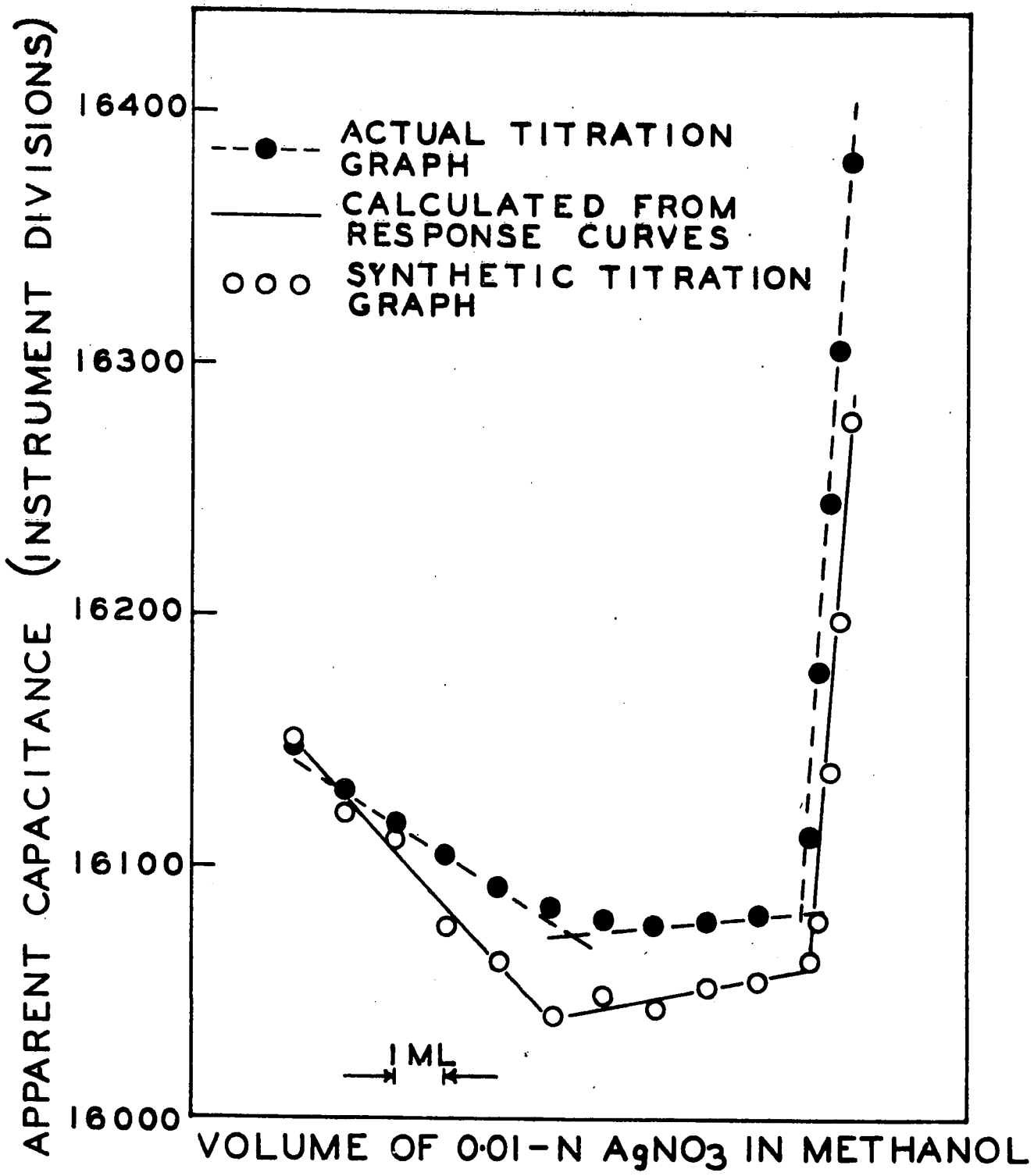
COMPARISON OF PREDICTED, SIMULATED AND EXPERIMENTAL TITRATION GRAPHS FOR THE HIGH-FREQUENCY ARGENTIMETRIC TITRATION OF SODIUM CHLORIDE IN METHANOL

Initial ionic strength of NaCl : 4.17×10^{-4} M
Initial volume of solution in cell: 120 ml
Apparent capacitance is given in instrument divisions
Predicted graph: obtained from the response curves for NaCl, $NaNO_3$ and $AgNO_3$
Simulated graph: obtained from solutions of NaCl and $NaNO_3$ in the appropriate ratio

	Without Dilution			With Dilution			
Ml 0.01-N Silver Nitrate	Ionic Strength, Molar $x10^4$	Apparent Capacitance, Predicted Graph	Apparent Capacitance, Simulated Graph	Ionic Strength, Molar $x10^4$	Apparent Capacitance, Predicted Graph	Apparent Capacitance, Simulated Graph	Apparent Capacitance, Experimental Graph
0.0	4.17	14485	14480	4.17	14485	14480	14478
1.0	4.17		14494	4.14		14478	14487
2.0	4.17		14504	4.10		14478	14494
3.0	4.17		14530	4.07		14488	14504
4.0	4.17		14550	4.04		14495	14515
5.0	4.17	14555	14557	4.00	14498	14495	14535
5.2	4.34		14612	4.16		14520	14590
5.4	4.51		14670	4.32		14596	14626
5.6	4.68		14718	4.47		14653	14703
5.8	4.85	14780	14773	4.63	14715	14710	14757

FIGURE 22

EXPERIMENTAL, CALCULATED AND SIMULATED TITRATION GRAPHS
FOR THE HIGH-FREQUENCY ARGENTIMETRIC TITRATION
OF SODIUM CHLORIDE IN METHANOL


APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
16400
16300
16200
16100
16000
ACTUAL TITRATION GRAPH
CALCULATED FROM RESPONSE CURVES
SYNTHETIC TITRATION GRAPH
1 ML
VOLUME OF 0·01-N AgNO3 IN METHANOL

It was found possible by using the above described method to predict correctly the slopes of the titration graphs of all single alkali-metal halides used in the present work.

3. Interpretation of the Titration Graph for a Binary Mixture of Sodium Chloride and Sodium Bromide

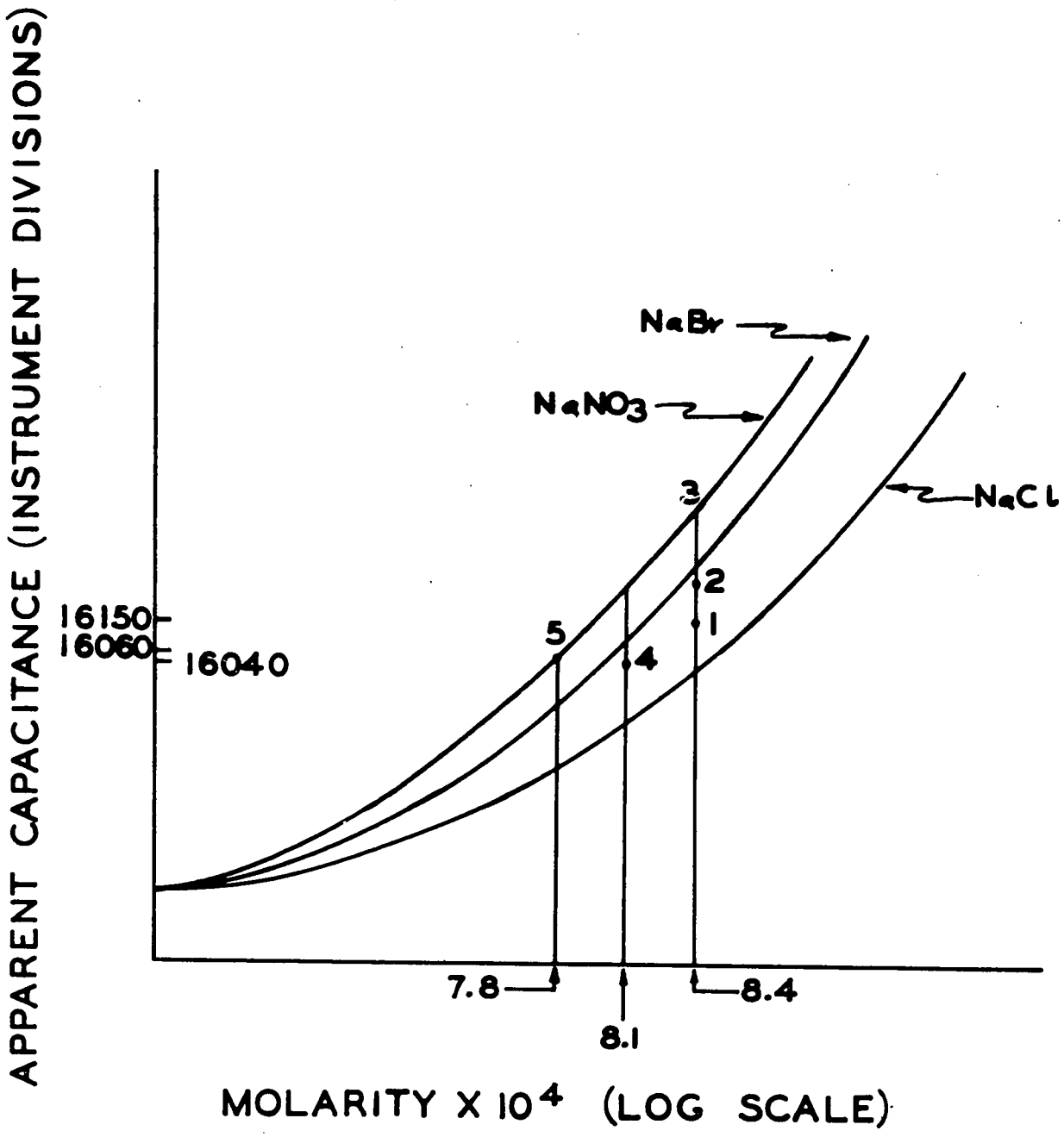
The titration of an equimolar mixture of sodium chloride and sodium bromide will be considered. From the solubility products of their silver salts it can be shown that 99.9% of the bromide will be precipitated before the precipitation of chloride starts, in the absence of extraneous factors. A typical experimental titration graphs was shown in Figure 9. In the first branch bromide is exchanged for nitrate. In the second branch chloride is exchanged for nitrate. In the third branch silver nitrate is added to the resultant solution of sodium nitrate.

For clarity a specific example is taken: 10-ml aliquots of 0.005-M solutions of NaCl and NaBr are mixed and diluted to 120 ml with methanol in the titration cell. The concentrations of NaCl and NaBr will each be 4.17×10^{-4} M giving an ionic strength of 8.4×10^{-4} M. Figure 14 shows the complete response curves of NaCl, NaBr, $NaNO_3$ and $AgNO_3$; Figure 23 is a sketch, not to scale, of the relevant portions expanded for clarity. At an ionic strength of 8.4×10^{-4} M, NaCl produces an apparent capacitance of 16050 instrument

FIGURE 23

EXPANDED RESPONSE CURVES FOR SOLUTIONS OF SODIUM CHLORIDE, SODIUM BROMIDE AND SODIUM NITRATE IN METHANOL

NOTE: The curves are not drawn to scale but their positions relative to each other are correct.


APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
NaBr
NaNO3
NaCl
3
2
1
5
4
16150
16060
16040
7.8
8.1
8.4
MOLARITY X 10^4 (LOG SCALE)

divisions and that of NaBr 16250 instrument divisions. Now it had been found by measuring the apparent capacitance of several ratios of sodium chloride to sodium bromide that a linear interpolation between the apparent capacitances of the sodium chloride and of the sodium bromide gave the correct apparent capacitance of the mixture. Consequently on the above described solution the apparent capacitance would be the average of 16050 and 16250; this is shown as point 1 in Figure 23.

At the bromide end point, the net apparent capacitance in the absence of dilution would be the average of the response of sodium chloride (16050 instrument divisions) and of sodium nitrate (16220 instrument divisions), namely 16185 instrument divisions (point 2). However, dilution due to the addition of 5 ml of 0.01-N silver nitrate will produce a net apparent capacitance of 16040 instrument divisions (point 4), namely the average of the response of sodium chloride 15880 instrument divisions and of sodium nitrate 16200 instrument divisions.

At the total halide end point the net apparent capacitance in the absence of dilution would be at point 3. Dilution due to the addition of 10 ml of 0.01-N $AgNO_3$ solution will result in an apparent capacitance of 16060 instrument divisions at point 5. The branch of the curve after the total halide end point is due to the increasing concentration of silver nitrate.

In summary the response curves predict, for the titration of an equimolar mixture of chloride and bromide, that during the precipitation of bromide the titration graph would have a positive slope, in the absence of dilution; the apparent capacitance would change from 16150 to 16185 instrument divisions. With dilution, as in an actual titration, the prediction is for a negative slope; the apparent capacitance would change from 16150 to 16040 instrument divisions. During the precipitation of chloride, the response curves predict that in the absence of dilution, there would be a sharp positive slope; the apparent capacitance would change from 16185 to 16345 instrument divisions. With dilution there would be a less steep positive slope, and the apparent capacitance will change from 16040 to 16060 instrument divisions. The positions of 1, 4 and 5 depend on the ionic strength, the initial volume of solution and the extent of dilution. These factors can be adjusted to produce the sharpest changes of slope for the individual end points.

Simulated titration graphs, with and without dilution, were prepared in which the ratios of NaCl:NaBr:$NaNO_3$ in the solutions were varied. The apparent capacitances of these solutions coincided with those predicted from the response curves for an ionic strength of 8.4×10^{-4} M. The apparent capacitances of the predicted, simulated and experimental titration graphs are given in Table 10, and are shown graphically in Figure 24.

TABLE 10

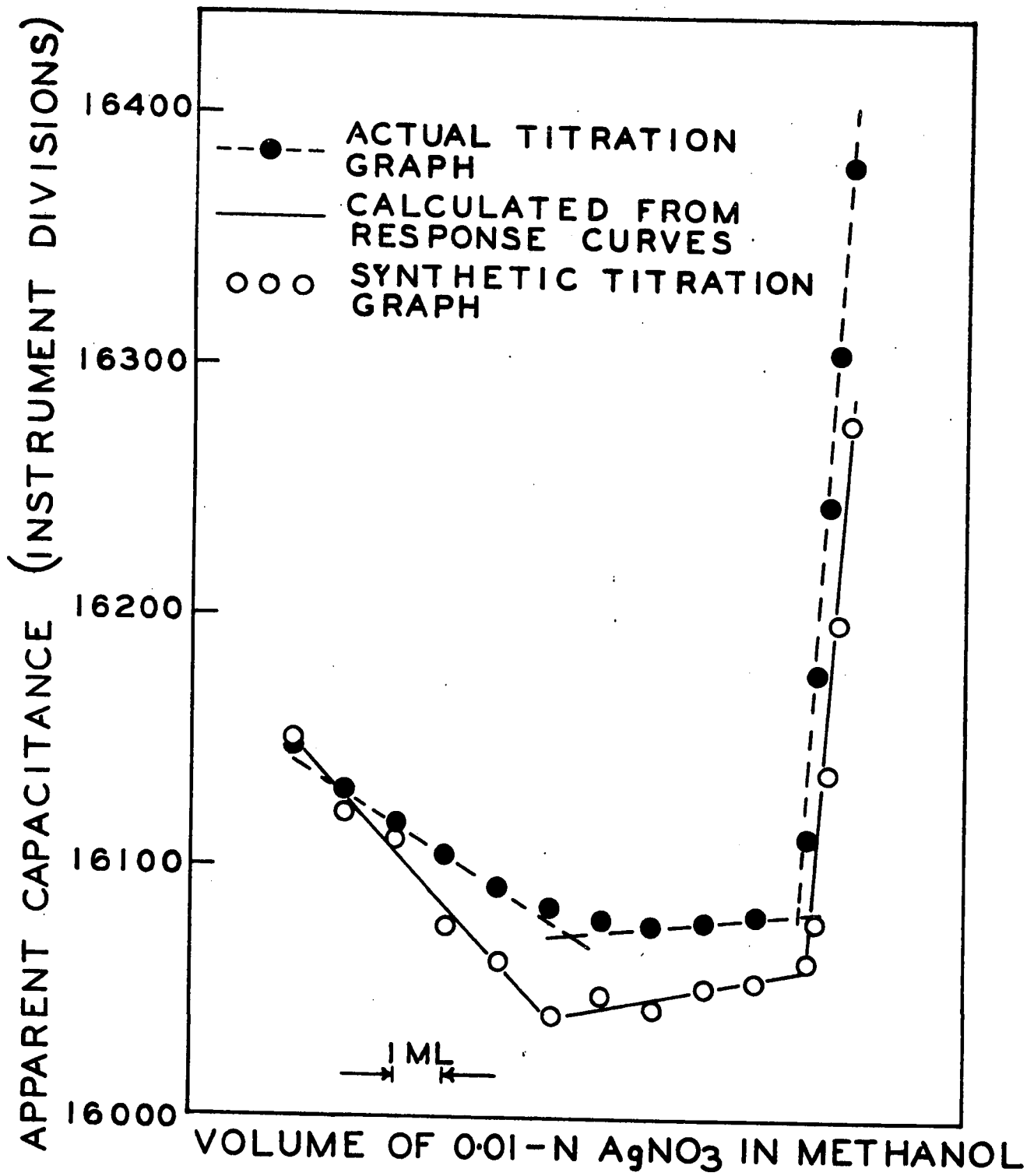
COMPARISON OF PREDICTED, SIMULATED AND EXPERIMENTAL TITRATION GRAPHS FOR THE HIGH-FREQUENCY ARGENTIMETRIC TITRATION OF AN EQUIMOLAR MIXTURE OF SODIUM CHLORIDE AND SODIUM BROMIDE IN METHANOL

Initial ionic strength : 4.17×10^{-4} M NaCl + 4.17×10^{-4} M NaBr = 8.34×10^{-4} M
Initial volume of solution in cell: 120 ml
Apparent capacitance is given in instrument divisions
Predicted graph: obtained from the response curves for NaCl, NaBr, $NaNO_3$ and $AgNO_3$
Simulated graph: obtained from solutions of NaCl, NaBr and $NaNO_3$ in the appropriate ratios

	Without Dilution			With Dilution			
Ml 0.01-N Silver Nitrate	Ionic Strength, Molar $x10^4$	Apparent Capacitance, Predicted Graph	Apparent Capacitance, Simulated Graph	Ionic Strength, Molar $x10^4$	Apparent Capacitance, Predicted Graph	Apparent Capacitance, Simulated Graph	Apparent Capacitance, Experimental Graph
0.0	8.34	16150	16143	8.34	16150	16143	16147
1.0	8.34		16156	8.27		16118	16130
2.0	8.34		16168	8.20		16103	16115
3.0	8.34		16163	8.13		16076	16104
4.0	8.34		16169	8.06		16055	16094
5.0	8.34	16185	16181	8.00	16040	16039	16082
6.0	8.34		16225	7.94		16048	16076
7.0	8.34		16252	7.86		16043	16077
8.0	8.34		16282	7.81		16051	16078
9.0	8.34		16308	7.75		16050	16081
10.0	8.34	16345	16343	7.69	16060	16056	16112
10.2	8.51			7.84		16078	16177
10.4	8.68			7.99		16155	16245
10.6	8.85			8.14		16234	16306
10.8	9.02			8.29	16310	16305	16381

FIGURE 24

EXPERIMENTAL, CALCULATED AND SIMULATED TITRATION GRAPHS FOR THE HIGH-FREQUENCY ARGENTIMETRIC TITRATION OF AN EQUIMOLAR MIXTURE OF SODIUM CHLORIDE AND SODIUM BROMIDE IN METHANOL


APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
16400
16300
16200
16100
16000
ACTUAL TITRATION GRAPH
CALCULATED FROM RESPONSE CURVES
SYNTHETIC TITRATION GRAPH
1 ML
VOLUME OF 0·01-N AgNO3 IN METHANOL

The experimental titration graph does not coincide exactly with the simulated graph. It has curvature at the first end point; the simulated graph has none. Moreover, the slopes of its two straight-line portions are less than those of the simulated graph.

The experimental graph and the simulated graph differ only in that precipitate was present for the former, and was absent for the latter. It was demonstrated in Section IV C that solid-solution formation occurred for silver chloride-silver bromide mixtures. The above-mentioned curvature in the experimental graph at the bromide end point is attributed to this solid-solution formation.

The difference noted in the slopes of the straight-line portions of the experimental and the simulated graphs can be quantitatively explained as being due to the contribution of the precipitate to the apparent capacitance reading. The calculations to confirm this conclusion are given in Appendix I. When the corrections due to the presence of precipitate are applied to the simulated graph, the resulting graph coincides with the experimental graph.

After the bromide end point solid-solution formation will result in the presence of less chloride and more bromide than would otherwise be expected in the supernatant solution. Now the difference in response between sodium nitrate and sodium bromide is smaller than that between sodium chloride and sodium nitrate. Therefore the experimental graph should be, and is, less steep than the simulated one.

The explanations provided for the titration of the sodium chloride-sodium bromide mixture can with equal validity be applied to the other binary mixtures considered in the present work.

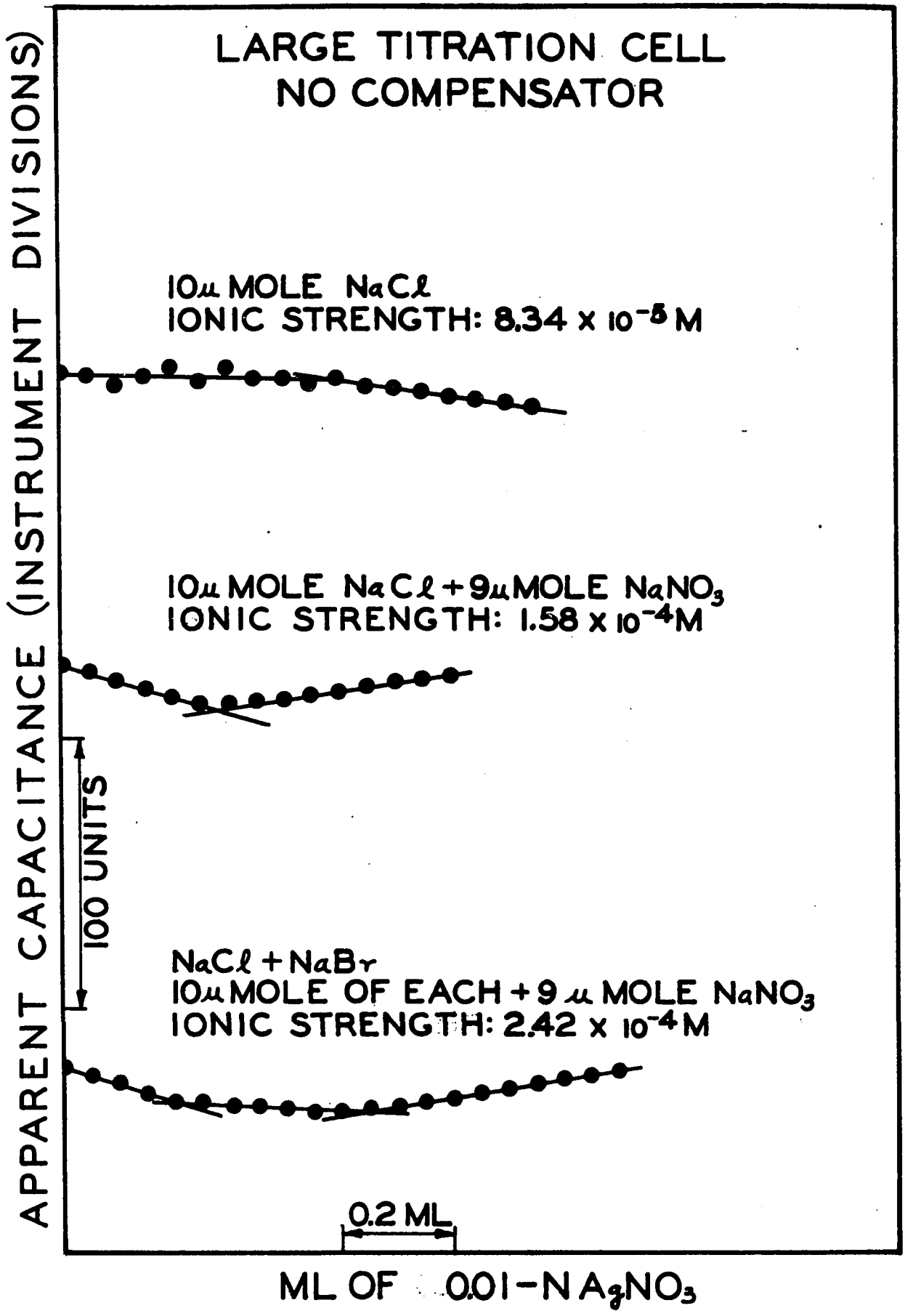
F. MICRO-TITRATIONS

1. The Effect of the Addition of Sodium Nitrate

Inspection of Figure 15 in Section III D subsection 3 shows that at ionic strengths below 10^{-4} M the response curves of the electrolytes merge. There is also a minimum in the response curves of all electrolytes (Figure 14, 16). Titrations carried out at ionic strengths less than 10^{-4} M will not produce any changes of slope during the precipitation of a halide. However, if the ionic strength can be raised by the addition of an indifferent electrolyte, such as sodium nitrate, then changes of slope would be expected. For example, if the concentration of halide in the large titration cell is 10^{-4} M, the solution can be made 2×10^{-4} M in sodium nitrate. Inspection of Figure 15 shows that at an ionic strength of 3×10^{-4} M the response curves are separated. This ionic strength, therefore, would be expected to produce good changes of slope in the titration graph. Figure 25 illustrates the experimental observations. Curve (a) is a titration of a 8.4×10^{-5} M sodium chloride solution in methanol containing no sodium nitrate. A poor change of slope was obtained. For curve (b) the solution was 7.5×10^{-5} M in sodium nitrate in addition to the above concentration of

FIGURE 25

EFFECT OF ADDITION OF SODIUM NITRATE TO THE TITRATION SOLUTION IN THE ARGENTIMETRIC TITRATION OF MICRO AMOUNTS OF CHLORIDE AND CHLORIDE + BROMIDE IN METHANOL


LARGE TITRATION CELL
NO COMPENSATOR
10μ MOLE NaCl
IONIC STRENGTH: 8.34 x 10⁻⁵ M
10μ MOLE NaCl + 9μ MOLE NaNO₃
IONIC STRENGTH: 1.58 x 10⁻⁴ M
NaCl + NaBr
10μ MOLE OF EACH + 9 μ MOLE NaNO₃
IONIC STRENGTH: 2.42 x 10⁻⁴ M
100 UNITS
0.2 ML
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
ML OF 0.01-N AgNO₃

sodium chloride. The ionic strength of the solution was 1.58×10^{-4} M. A measurable change of slope was obtained. The titration graph for the titration of an equimolar mixture of sodium chloride and sodium bromide with added sodium nitrate is shown in curve (c). The ionic strength was 2.42×10^{-4} M. At this concentration a measurable change of slope at the bromide end point as well as at the total halide end point would be expected. This was confirmed experimentally as shown in the Figure.

The concentration of sodium nitrate added to the solution of halide should not be excessive. It was found that the molarity of the sodium nitrate in the solution should not exceed five times the initial molar concentration of halide. With higher concentrations of sodium nitrate, the response due to the sodium nitrate would be large compared to that of the halide. Any change in apparent capacitance resulting from the precipitation of halide would not be measurable.

2. The Effect of the Cell Compensator

The use of the Sargent Cell Compensator was discussed in Section III A subsection 3. The effect on a response curve when the Cell Compensator was coupled into the circuit, with the use of the large titration cell, is illustrated in Figure 16. In this Figure the low concentration range of the sodium chloride response curve is shown in detail. Curve (a) is the response curve without the use of the Cell Compensator, curve (b) with the Cell Compensator set at 700 units.

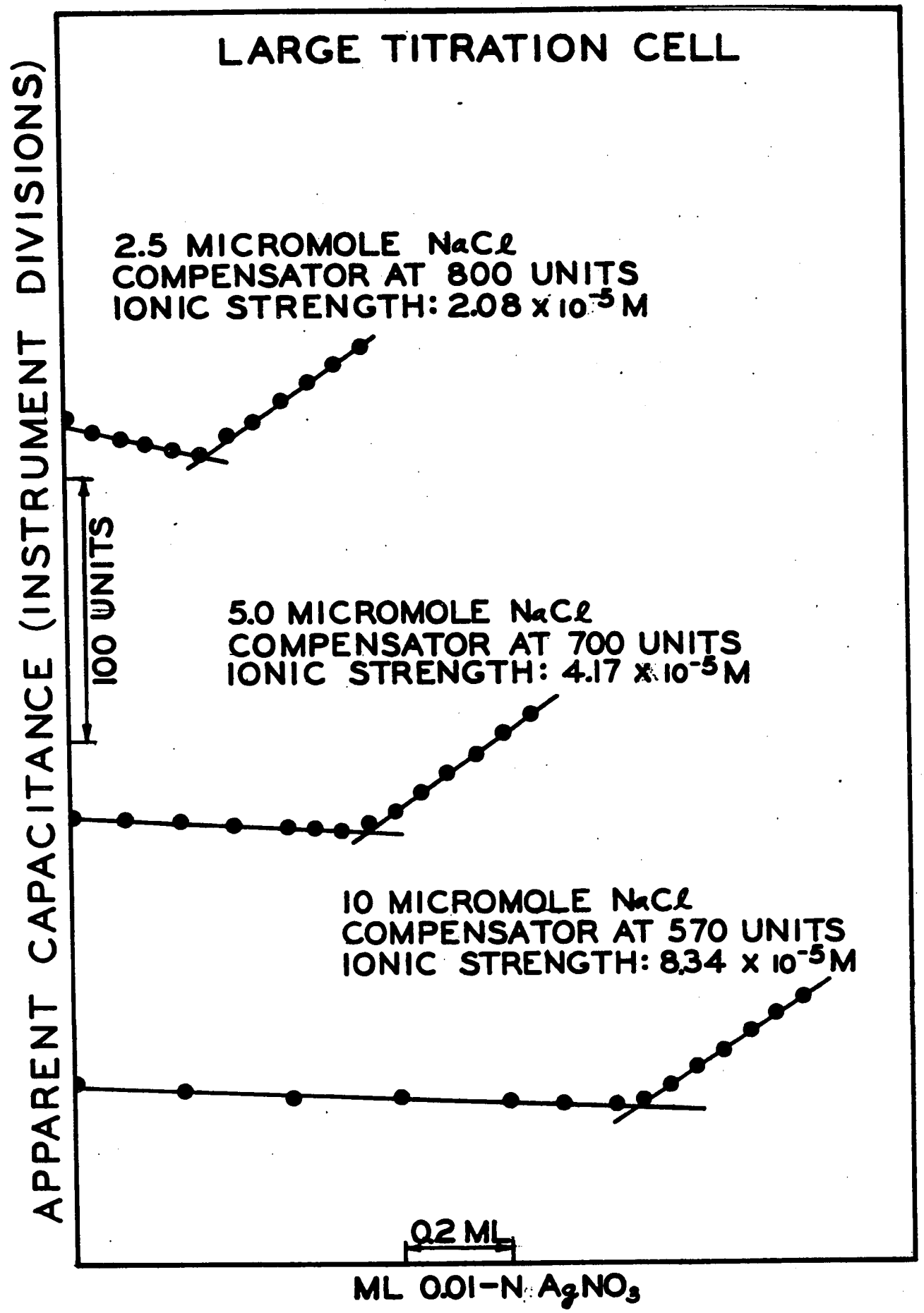
With the use of the Cell Compensator the minimum in the response curve was shifted to a lower concentration (2×10^{-5} M). Therefore, for the titration of a single halide a measurable change of slope will be expected when the ionic strength of the solution in the cell is 2×10^{-5} M. This was confirmed experimentally. Typical titration graphs for the titration of sodium chloride which illustrate the effect of the Cell Compensator are shown in Figure 26. With the use of sodium nitrate to increase the ionic strength, and the Cell Compensator, a measurable change of slope would still be obtained when only 10^{-5} M sodium chloride was titrated.

At an ionic strength of 2×10^{-5} M no reliable change of slope would be expected for the bromide end point in the titration of binary mixtures of chloride and bromide. The response curves are not sufficiently separated at this ionic strength. With the Cell Compensator in the circuit the response curves are separated enough to produce measurable changes of slope at an ionic strength of about 10^{-4} M.

In order to lower the dilution factor and therefore make it possible to titrate smaller weights of halide, the 10-ml titration cell was used. With the Cell Compensator set at 640 units and with the addition of an equimolar concentration of sodium nitrate (to give an ionic strength of 4×10^{-5} M) the response curves showed that it would be possible to titrate a solution that was 2×10^{-5} M in

FIGURE 26

EFFECT OF THE SARGENT CELL COMPENSATOR
IN THE ARGENTIMETRIC TITRATION OF MICRO AMOUNTS
OF CHLORIDE IN METHANOL


LARGE TITRATION CELL
2.5 MICROMOLE NaCl
COMPENSATOR AT 800 UNITS
IONIC STRENGTH: 2.08 x 10⁻⁵ M
100 UNITS
5.0 MICROMOLE NaCl
COMPENSATOR AT 700 UNITS
IONIC STRENGTH: 4.17 x 10⁻⁵ M
10 MICROMOLE NaCl
COMPENSATOR AT 570 UNITS
IONIC STRENGTH: 8.34 x 10⁻⁵ M
APPARENT CAPACITANCE (INSTRUMENT DIVISIONS)
0.2 ML
ML 0.01-N AgNO3

sodium halide (equivalent to 4 microgram of chloride). This was confirmed experimentally as shown in Table 7. The reproducibility and accuracy were excellent.

With the use of the small titration cell the lower limits for the titration of mixtures of halides had to be raised somewhat compared to those for the titration of single halides. This was because the separation of the response curves at an ionic strength of 4×10^{-5} M was not sufficient.

V. RANGE OF TITRATABLE CONCENTRATIONS

A. CONCENTRATION RANGES FOR THE HALIDES AND THIOCYANATE

The response of the high-frequency titrimeter to changes in ionic strength of a solution has been shown to produce a sigmoid-shaped curve (Figure 14). The curve, for any given electrolyte and solvent, becomes horizontal at low and high ionic strengths. The curves for different electrolytes in a given solvent also merge at high and low ionic strengths. There are, therefore, limits to the concentrations of halide and thiocyanate that can be titrated by the high-frequency method. The response curves enable the range of titratable concentrations to be predicted and these concentrations, for methanol, are given in Table 11. They were confirmed experimentally.

With methanol as solvent and in the upper range of concentration, the ionic strength of the solution in the large titration cell can be 0.01 M. At this ionic strength, slight though measurable changes of slope would be obtained for the titration of single halides. Mixtures of halides could only be titrated if the ionic strength were lowered to 8×10^{-3} M.

In the low concentration range, with methanol as solvent and with the use of the large titration cell, the ionic strength of the solution should be 10^{-4} M for the titration of single halides and about 2.5×10^{-4} M for the titration of mixtures of halides. These lower limits can be reduced with the use of the Cell Compensator.

TABLE 11

UPPER AND LOWER CONCENTRATION LIMITS IN THE HIGH-FREQUENCY ARGENTIMETRIC TITRATION OF HALIDES AND THIOCYANATE IN METHANOL

Ion Precipitated by Silver Nitrate	UPPER LIMIT in milligram	LOWER LIMIT in microgram		
	Large Titration Cell	Large Titration Cell	Large Titration Cell + Compensator @ 700 units + equimolar $NaNO_3$	Small Titration Cell + Compensator @ 640 units + equimolar $NaNO_3$
CHLORIDE				
Alone	43	430	43	3.5
Binary Mixture	17	430	43	5.8
Ternary Mixture	9	430	43	8.7
BROMIDE				
Alone	96	960	96	8.5
Binary Mixture	45	960	96	12.8
Ternary Mixture	25	960	96	19.0
IODIDE				
Alone	152	1520	152	15.0
Binary Mixture	61	1520	152	22.0
Ternary Mixture	34	1520	152	33.0
THIOCYANATE				
Alone	70	700	70	6.5
Binary Mixture	28	700	70	9.8
Ternary Mixture	16	700	70	14.7

The same lower limits, with and without the Cell Compensator, for the ionic strength of the solution for titration apply to the 10-ml titration cell. The advantage of the smaller cell is that smaller weights of halide can be titrated because, with the lower dilution factor, the ionic strength is the same as that in the large titration cell.

B. USE OF OTHER SOLVENTS TO VARY THE RANGE OF TITRATABLE CONCENTRATIONS

The limits given in Table 11 are for methanol as solvent. Inspection of the response curve of silver nitrate in ethanol in Figure 14 shows that it is shifted to a higher ionic strength with respect to those in methanol. The response curves of the sodium halides and silver nitrate would not become horizontal and would not merge until about 0.08 M. This means that more concentrated halide solutions can be titrated. However, the low solubility of the sodium halides and, particularly, sodium nitrate in ethanol must be considered (see Table 1 of Appendix III). By using a mixed solvent of, for example, 50% methanol and 50% ethanol, the solubility could be raised sufficiently to allow higher concentrations of halides to be titrated. Ethanol is not a good solvent when very low concentrations of halides must be titrated. This is because the response curves in ethanol merge at about 10^{-3} M.

It would be possible to use other solvents and combinations of solvents to vary the range of titratable concentrations. For example, the sodium halides are quite soluble in ethylene glycol. However, ethylene glycol is difficult to use because of its high viscosity. Mixtures with methanol or ethanol could be used to overcome this problem. An example of the use of mixed solvents was the titration of iodide in orthodichlorobenzene-methanol mixtures (50). Excellent results were obtained. Acetonitrile would be a useful solvent for transition metal halides because of their high solubility in this solvent (see Table 3 of Appendix III).

VI. SUMMARY AND CONCLUSIONS

The results obtained with the high-frequency method developed for the argentimetric titration of halides and thiocyanate in methanol have shown that:

(a) Chloride, bromide, iodide and thiocyanate can be titrated accurately and precisely in some nonaqueous solvents,

and an improvement over existing methods in these respects:

(b) It was possible to titrate mixtures of halides and thiocyanate, and to obtain measurable and reproducible end points for the individual halides providing the ratio of the halides and pseudohalide is not too unfavourable. Sharp, reproducible end points were obtained even when the concentration of one halide was greater than the other, provided the solubility products of the relevant silver halides were sufficiently different.

(c) Precision of the titration of mixtures was such that, even though the end point was in error due to solid-solution formation, corrections could be made to compensate for the error.

(d) The method could be used for titrations in nonaqueous solutions without the need for special precautions or manipulations.

(e) Very low concentrations of halides, singly and in mixtures, were titrated precisely and accurately.

The method proposed for the interpretation of titration graphs by means of response curves predicted correctly the shapes of titration graphs, without the need for expensive auxiliary equipment. Agreement between experimental and predicted titration graphs was in fact excellent.

VII. SUGGESTIONS FOR FURTHER WORK

Several anions, other than halides and thiocyanate, are precipitated by silver nitrate. For example:

$SO_4^{=}$, CN^{-}, $PO_4^{\equiv}$, $S_2O_3^{=}$, $VO_4^{\equiv}$ and $ASO_4^{\equiv}$.

Titrations of these ions alone and in mixtures should prove fruitful. The direct titration of metals in nonaqueous solvents with the use of organic precipitants as titrants should also be considered.

The high-frequency technique may prove useful in the identification of ions such as $CuCl^{+}$ in methanol and other nonaqueous solvents.

VIII. CLAIMS OF ORIGINAL WORK

The contributions to knowledge claimed in Part I of the present work are:

(a) The accurate titration of macro and micro amounts of halide and thiocyanate in mixtures (all combinations up to chloride + bromide + iodide + thiocyanate) in methanol by the high-frequency method.

(b) The interpretation and prediction of the titration graphs by a simple method based on the response curves of the individual sodium halide and nitrate salts in methanol.

PART II

CHELATE-EXCHANGE TITRATIONS IN NONAQUEOUS SOLVENTS BY SPECTROPHOTOMETRIC TITRIMETRY

I. INTRODUCTION

Liquid-liquid extraction of a metal from an aqueous solution into an immiscible organic solvent is a conventional procedure in analytical chemistry. It is widely used for the selective extraction of trace amounts of sought-for metals, from unwanted substances.

Solvent extraction systems have been reviewed and classified by Marcus (52). One of those classes comprises metal chelates, extracted into low dielectric-constant solvents such as benzene, carbon tetrachloride, and chloroform. Thus, the metal forms with a chelating agent a neutral metal chelate. Most of these chelates are much more soluble in a nonaqueous solvent than in water. Three widely used organic chelating agents are 8-quinolinol, diphenylthiocarbazone and diethyldithiocarbamic acid. They are used in the present investigation.

After a metal has been selectively extracted as a chelate into a nonaqueous solvent, it is then necessary to determine its concentration. Heretofore, this final step has usually been carried out by one of the following methods: (a) a direct colorimetric determination on the nonaqueous solution; (b) separation of the nonaqueous phase, evaporation of the solvent, decomposition of the metal chelate residue, and finally determination of the metal by some conventional method; (c) a radiometric technique.

Each of these methods is useful in some cases; but all have drawbacks. Thus, in the first method the metal chelate must have a high absorptivity when a trace amount is to be measured. The second method is time-consuming. Moreover, in trace analysis serious losses can accompany the evaporation and decomposition steps. The third method requires that the metal be radioactive. Therefore it is useful in solvent-extraction studies only when a radioactive tracer can be added initially to the aqueous phase.

The direct titration of the extracted metal chelate in the separated nonaqueous phase would obviously be an attractive method of determining the metal content. In the present investigation a practicable method was developed based on this idea. The titrant was another chelating agent in a nonaqueous solvent of low dielectric constant. This approach has not previously been reported in the literature. The investigation was further concerned with elucidation of the chemistry of the titrations. Indeed, it is to be emphasized that the primary consideration was elucidation of chemistry, molecular structure, and spectroscopic properties of the metal chelates that participated in the titration reactions.

Little attention has previously been given to the use in titrimetry of organic chelating agents in nonaqueous solvents. Brummet and Hollweg (53) quantitatively formed a chelate with a given metal, in 4:1 benzene-methanol solution.

They then determined the liberated hydrogen ions by potentiometric titration with a standard alkali solution. Underwood and Underwood (54) determined metal oxinates by conductometric titration with potassium methoxide in ethylenediamine.

Chelating agents have been used as titrants in spectrophotometric titrations of metals, mostly in aqueous solutions. For example, aminocarboxylic acids such as EDTA have been widely used as titrants in aqueous systems (55,56).

Several authors (57-61) have titrated metal ions directly with organic chelating agents as titrants, in nonaqueous solvents. They used ionizing solvents or ionizing solvent mixtures, which dissolved and dissociated the initial metal salt prior to the titration. Accordingly, their technique differs in a fundamental way from the presently proposed method.

II. STATEMENT OF THE PROBLEM AND PLAN OF RESEARCH

A purpose of the present work was the development of a quantitative analytical procedure for metals present as chelates in solvents of low dielectric constant. The procedure was required to be rapid, precise, and accurate. The general method chosen for study was a spectrophotometric titration of the metal chelate in the original solvent, with another chelating agent as titrant, also in a nonaqueous solvent.

The titration can properly be termed a chelate-exchange reaction, for the overall reaction was

$$MX_n + nHY = MY_n + nHX \qquad \text{II-1}$$

where HX and HY were organic chelating agents, and MX_n and MY_n were the corresponding chelates of the metal M of valency n.

Two systems were chosen for study:

(A) The sample solution was a metal diphenylthiocarbazonate dissolved in chloroform, and the titrant was sodium diethyldithiocarbamate dissolved in absolute ethanol.

(B) The sample solution was a metal 8-quinolinate in benzene, and the titrant was diphenylthiocarbazone in benzene.

These systems were chosen for several reasons:

(a) The chelating agents themselves are readily available and widely used.

(b) The solid metal chelates were well-defined, easily-prepared compounds; and with due precautions their non-aqueous solutions were stable.

(c) Metal diphenylthiocarbazonates in solvents such as benzene and chloroform are highly coloured. Therefore the proposed chelate-exchange reaction could be followed by a conventional spectrophotometric titration. The appearance or disappearance in reaction II-1 of either the diphenylthiocarbazone or its metal chelate could be followed.

(d) The high molar absorptivity of metal diphenylthiocarbazonates in nonaqueous solvents permitted trace amounts of metals to be determined by titration.

Chloroform was the solvent chosen for system (A) because of its availability and ease of purification. It is also somewhat less toxic than carbon tetrachloride, the usual solvent in diethyldithiocarbamate systems. Benzene was the solvent for system (B). It could readily be obtained in pure form. Moreover, the solubilities of the relevant metal chelates are greater in benzene than in carbon tetrachloride, so that a wider range of concentrations could be studied. This higher solubility, together with the high purity of benzene, made it possible to carry out a theoretical treatment of the data for system (B). For system (A), a theoretical treatment would have been uncertain, due to the presence of ethanol both in the titrant solution and as a stabilizer in the chloroform.

The effect of an initial excess of free chelating agent (HX) in the sample solution (MX_n) on the accuracy and pre-

cision of the chelate-exchange titration was studied (the titrant being HY). Such an excess would in many cases be present after a metal has been extracted as a metal chelate from an aqueous phase.

The following additional factors were studied, for their effect on the precision and accuracy of the chelate-exchange titrations:

(a) The wavelength at which a titration was performed.

(b) The method of locating the end point, namely by visual inspection, or by a least-squares method.

(c) The temperature of the solution for titration, where applicable.

(d) Whether titrations should be carried out in subdued light.

Following a study of the titration of single metal chelates, the titrations of binary and ternary mixtures were investigated.

A second purpose of the present investigation was the theoretical interpretation or prediction of the chelate-exchange titration graphs, in terms of the relevant equilibrium constants, and the molar absorptivities of the participating species. For the reason stated above, theoretical studies were carried out only on the metal oxinate-diphenylthiocarbazone systems. This fundamental approach has an advantage over a purely empirical study; with basic information (equilibrium constants and molar absorptivities), pre-

dictions can be made as to the feasibility of titrating mixtures of metal oxinates. Moreover new and interesting mixed chelates and adducts were thereby detected, in the present work.

For this theoretical study, the basic needs were: (a) to identify the participating species; and (b) to determine their equilibrium concentrations. Therefrom, the equilibrium constants could be found. Spectrophotometric techniques were used exclusively. For identification, Job's Method of Continuous Variations (62) and Vosburgh and Cooper's extension of that method (63) were available. Ratio solutions in which the concentration of one component was held constant while the other was varied were also used. This permitted a wide range of concentrations to be used. For measurement of the equilibrium concentrations of species, several techniques have been described (64,65,66).

In the present work, the mass-balance equations were formulated wherein the total, measured concentrations of metal chelate or organic chelating agent were equated with the sum of the relevant, unknown equilibrium concentrations of all species present in the solution. Absorbance equations were also formulated wherein the total absorbance of a solution, at a given wavelength, was equated with the sum of the product of molar absorptivity and equilibrium concentration of all species present in the solution. Thus a set of M linear equations was obtained in N unknowns. These

equations were normalized by least squares, to give N equations which were then solved for the unknown equilibrium concentrations. The relevant equilibrium constants were then calculated from these concentrations.

Where the absorptivities of certain species were unknown and could not be measured directly an alternate procedure was used. Equations were generated which incorporated the data for a series of the nonaqueous solutions. The left-hand side of each equation was a polynomial in the sought-for absorptivity. The right-hand side of each equation was the reciprocal of the equilibrium constant. Experiments were designed so that for a given system only one unknown absorptivity had to be evaluated. The constants in the polynomials contained the known quantities, namely total concentrations of reactants and known absorptivities. The resulting equations were normalized by least squares and solved for the equilibrium constant and the sought-for absorptivity by using a conventional iteration.

III. PRELIMINARY SURVEY

Several chelate-exchange reactions in chloroform were investigated by means of spectrophotometric titrations. These were:

1. Reaction of zinc, cadmium, lead, copper (II), cobalt (II), nickel (II) and ferric (III) acetylacetonates with 8-quinolinol or diphenylthiocarbazone as the titrant.
2. Reaction of the pyridine complexes of copper (II), cobalt (II) and nickel (II thiocyanates with 8-quinolinol or diphenylthiocarbazone as the titrant.
3. Reaction of nickel (II) dimethylglyoximate with 8-quinolinol or diphenylthiocarbazone as the titrant.
4. Reaction of zinc, cadmium, lead, mercury, indium, silver, copper (II), cobalt (III) and nickel (II) diphenylthiocarbazonates with sodium diethyldithiocarbamate in ethanol as the titrant.
5. Reaction of zinc, cadmium, lead, indium, silver, copper (II), cobalt (II) and nickel (II) 8-quinolinates with diphenylthiocarbazone as the titrant.

Typical titration graphs obtained for the first three reactions are in Figure 27. Sharp breaks at the stoichiometric end points were observed in the titration with 8-quinolinol, of the metal acetylacetonates and of the pyridine complexes of the metal thiocyanates, when the formation of metal 8-quinolinate was followed spectrophoto-

FIGURE 27

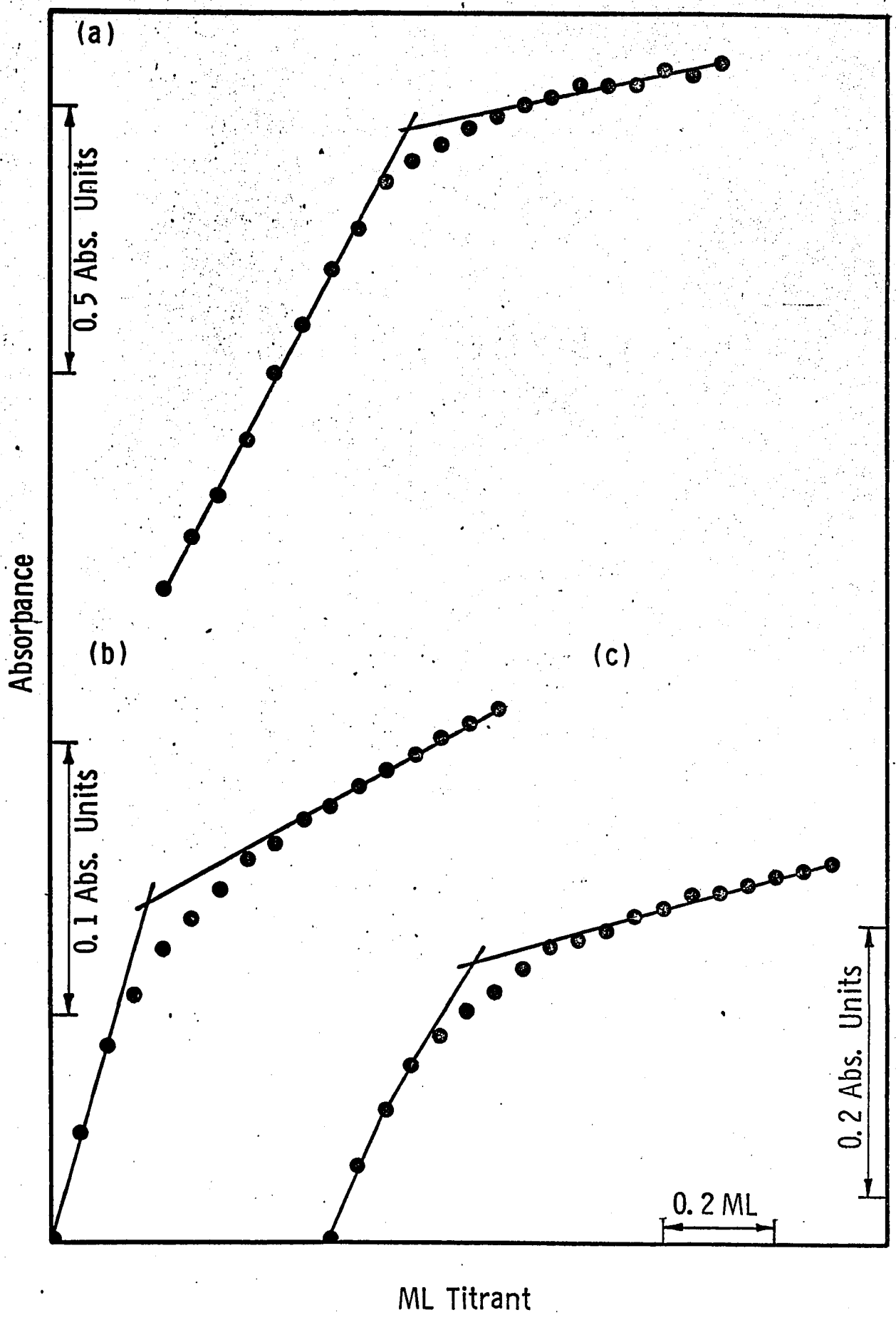
TYPICAL TITRATION GRAPHS FOR THE TITRATION OF METAL CHELATES WITH 8-QUINOLINOL OR DIPHENYLTHIOCARBAZONE IN CHLOROFORM

(a) Titration of 1.0 μeq. Ferric (III) Acetylacetonate with 8-Quinolinol at 470 mμ.

(b) Titration of 1.0 μeq. $CoPy_4(NCS)_2$ with 8-Quinolinol at 420 mμ.

(c) Titration of 1.0 μeq. Nickel (II) Dimethylglyoximate with Diphenylthiocarbazone at 460 mμ.

Initial volume of solution: 50 ml
Molarity 8-quinolinol in chloroform: 2.003×10^{-3} M


(a)
0.5 Abs. Units
Absorbance
(b)
(c)
0.1 Abs. Units
0.2 Abs. Units
0.2 ML
ML Titrant

metrically. Unfortunately, for the quantitative solvent extraction of these metal complexes a large excess of acetylacetone or pyridine must be present in the chloroform phase. It was found in titrations of metal acetylacetonates with 8-quinolinol that as the initial concentration of free acetylacetone was increased, curvature at the end point became more pronounced. In fact, at a sufficiently high concentration of free acetylacetone, there was no break in the titration graph. This increase in curvature is illustrated in Figure 28 for the titration of copper (II) acetylacetonate. The same effect occurred in the titration with 8-quinolinol of the pyridine complexes of the metal thiocyanates.

When metal acetylacetonates were titrated with diphenylthiocarbazone, there was pronounced curvature in the first branch of the titration graph even in the absence of excess acetylacetone. This made it impossible to locate the end point with certainty.

When nickel (II) dimethylglyoximate was titrated with either diphenylthiocarbazone or 8-quinolinol, the first branch of the titration graph was curved and there was also pronounced curvature in the region of the end point. This is illustrated in Figure 27 where the formation of nickel (II) diphenylthiocarbazonate was being followed.

These findings indicated that titration procedures based on reactions 1-3 would be of limited use. Further study of them was abandoned.

FIGURE 28

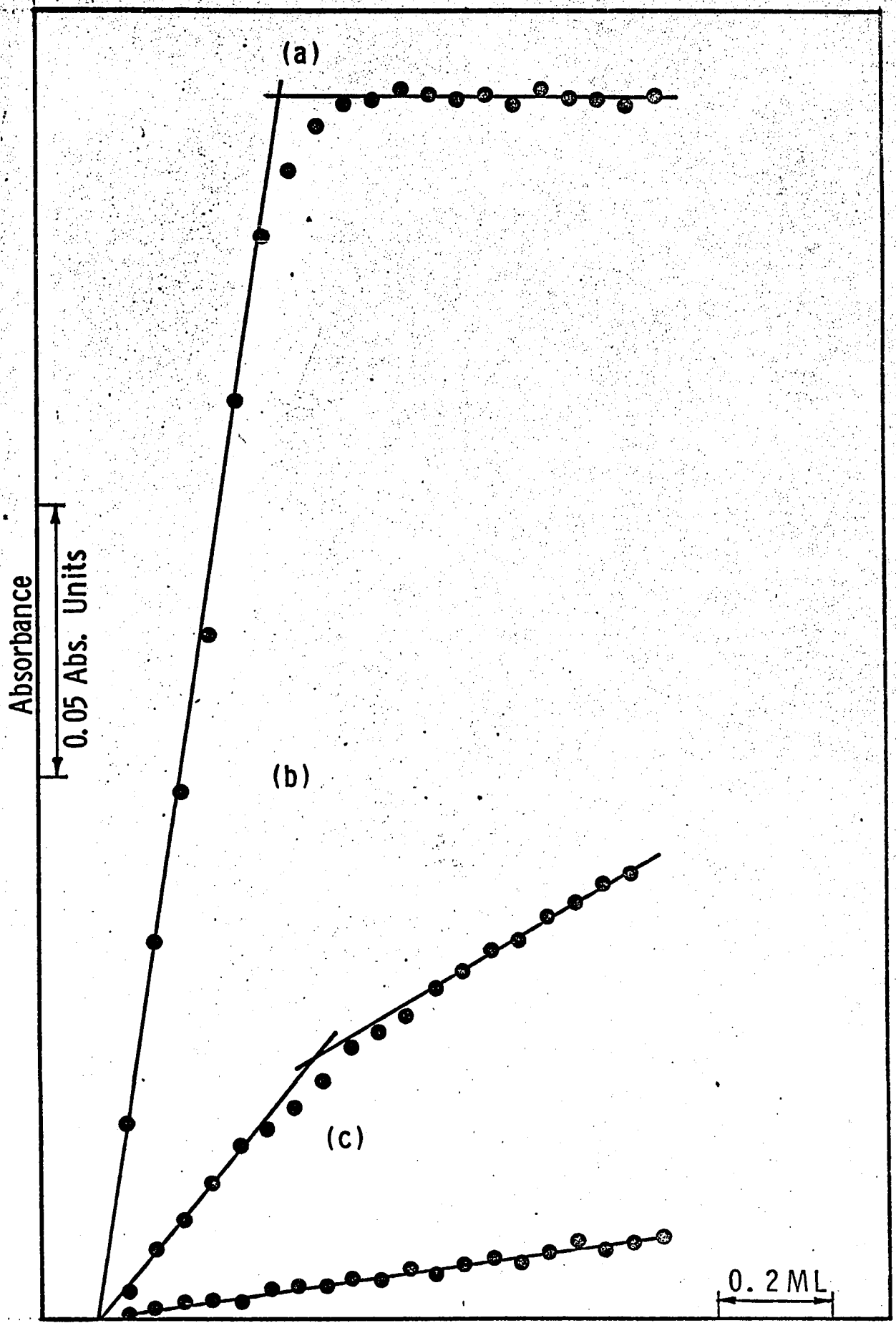
EFFECT OF INITIAL CONCENTRATIONS OF FREE ACETYLACETONE IN THE TITRATION OF COPPER (11) ACETYLACETONE WITH 8-QUINOLINOL IN CHLOROFORM AT 410 mμ

Initial volume of solution	:	50 ml
μeq. $Cu(AcAc)_2$ taken	:	0.7 μeq.
Molarity 8-quinolinol in chloroform:		2.003×10^{-3} M

(a) No initial free acetylacetone.

(b) Solution contained initially, 5.0 m mole free acetylacetone.

(c) Solution contained initially, 25.0 m mole free acetylacetone.


(a)
(b)
(c)
Absorbance
0.05 Abs. Units
0.2 ML
ML Titrant

Good titration graphs were obtained even in the presence of excess diphenylthiocarbazone for those reactions listed in 4, except for mercury, cobalt (III)* and nickel (II) dithizonates. The titration graphs of these latter three dithizonates had pronounced curvature, which made the titrations impractical.

Titrations of the metal 8-quinolinates listed in 5 with diphenylthiocarbazone as the titrant were acceptable except for the cases of silver, nickel (II) and cobalt (II) oxinates. The reactions of silver and nickel (II) oxinates with dithizone were very slow, and hence impractical for titrations. Cobalt (II) oxinate did not react at all with diphenylthiocarbazone under the conditions used for a titration. Therefore its study was abandoned.

---

*See Reference 191.

IV. EXPERIMENTAL

A. APPARATUS

1. Apparatus for Spectrophotometric Titrations

A Beckmann Model DU manual spectrophotometer with a conventional tungsten lamp was used. The wavelength scale was calibrated with a didymium filter and the corrections obtained are given in Appendix IV.

A special non-magnetic cell compartment was built for this spectrophotometer in order to accomodate a 65-ml rectangular titration cell as well as the tip of a micro-buret (See Plate II-A). This compartment occupied the position of the conventional Beckmann cell compartment. Details of the compartment are given in Appendix V A. A view of the cell in the cell compartment is given in Plate II-B. The platinum-rhodium needle which served as the buret tip was pushed through a Silicone-rubber septum which was countersunk into the lid of this special compartment. The photo-tube housing of the compartment was protected from organic solvent vapours by a fused-silica plate which was sealed over the shutter opening.

In order to maintain constant temperature inside this compartment two hollow copper tanks were installed in the compartment on either side of the rectangular cuvette. Water from a constant temperature bath was circulated at approximately 0.5 litre per minute through these tanks by means of a circulating pump.

PLATE II

SPECTROPHOTOMETRIC TITRATION APPARATUS

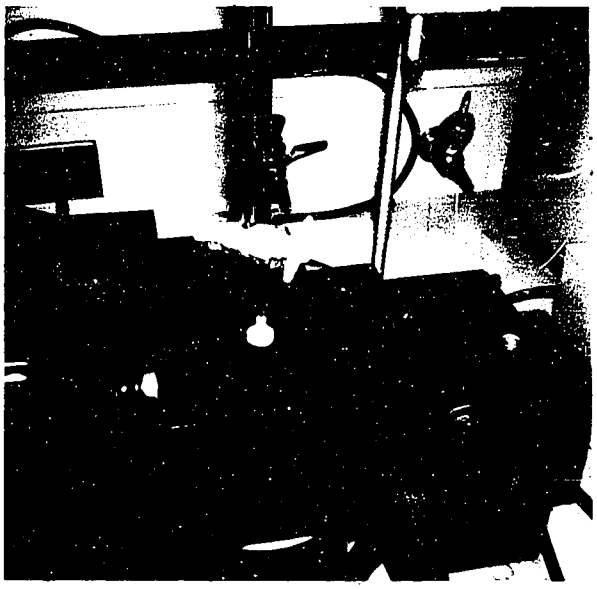
A. Cell Compartment used for Spectrophotometric Titrations.

B. Titration Cell in Cell Compartment.

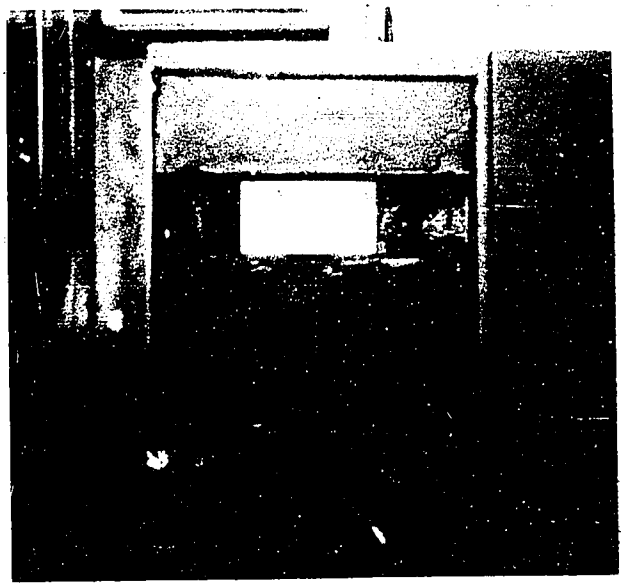
C. 3-ml Cell Holder.

D. Titration Cell with Cell Cover.

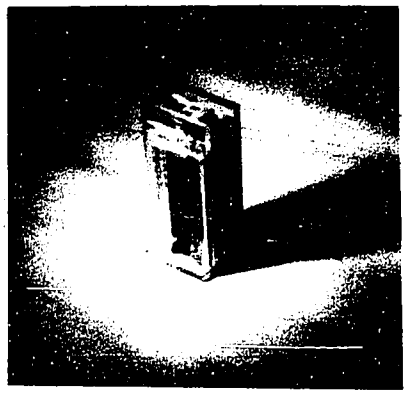
E. Platinum-rhodium hyperdermic needle attached to Buret tip.



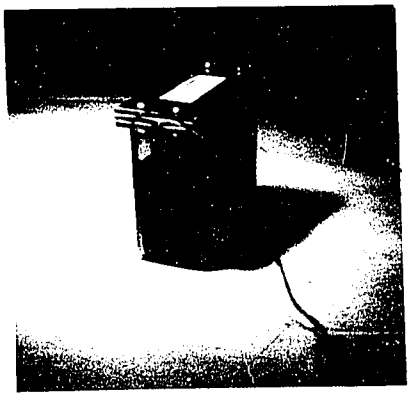
A



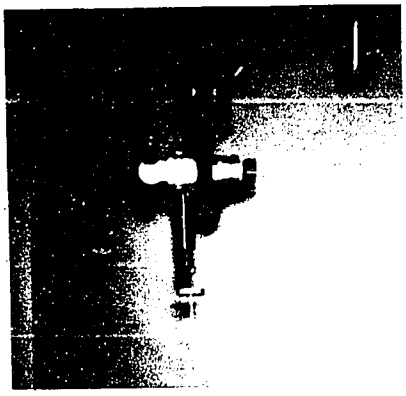
B



C



D



E

Care was taken in the design of the compartment to ensure that it was light tight.

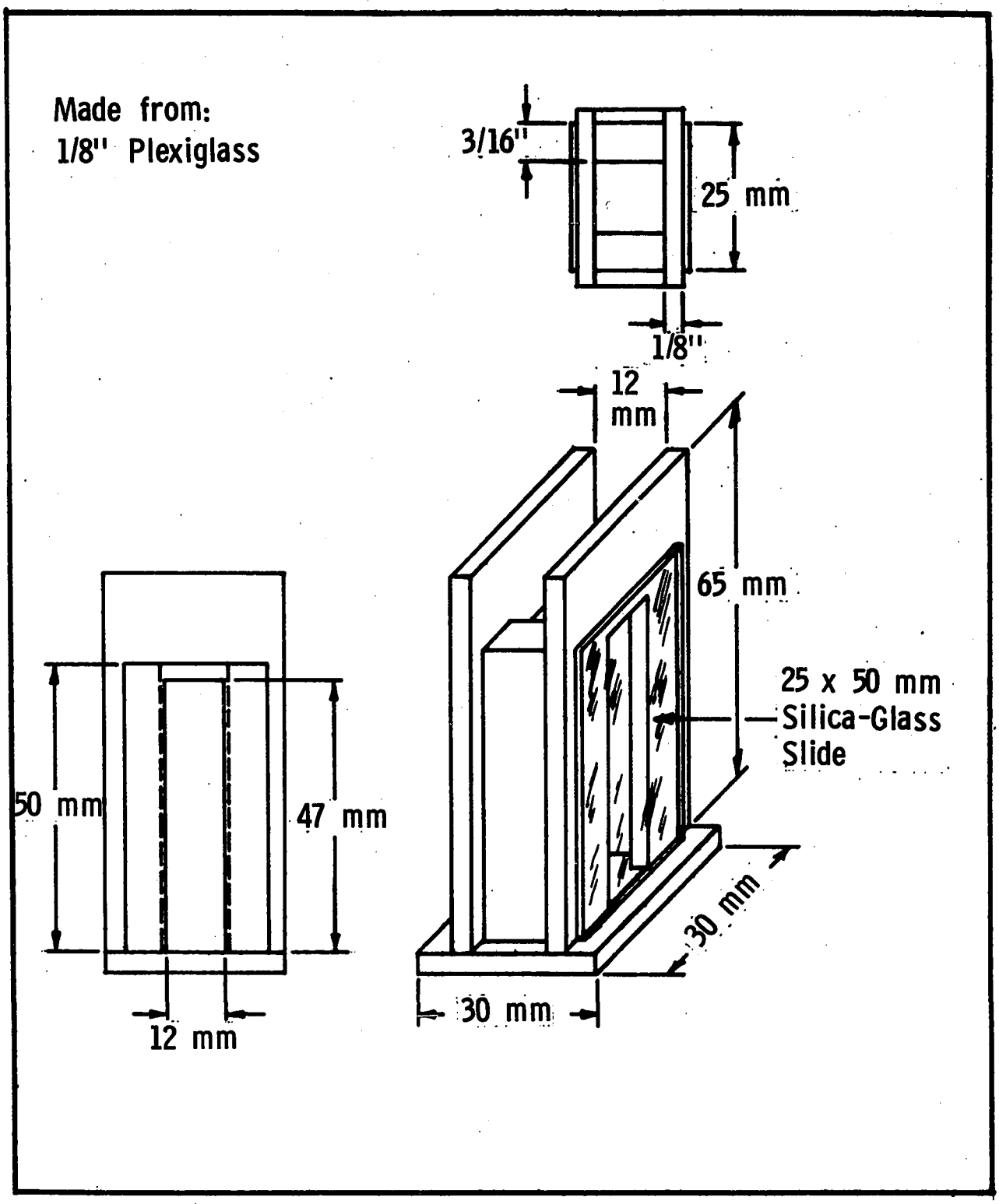
The temperature of the solution for titration in the titration cell was measured by means of a copper-constantan thermocouple (Appendix V B).

Cells of two capacities were used. One was a glass cell of 65-ml capacity with outside dimensions of 54 mm long by 30 mm wide by 55 mm deep. The path length of one of these cells was measured by a cathetometer and found to be 5.005 cm and for the other cell, 5.008 cm. The other cells were conventional 1-cm path length, rectangular, matched, silica cells of capacity 3 ml (see Appendix V C). A plexiglass holder was constructed in order to hold the 3-ml cells in place in the cell compartment. This holder is illustrated in Figure 29 and Plate II-C.

To prevent evaporation of solvent from all of these cells covers were constructed (see Appendix V D). For the 65-ml cell the cover consisted of a sandwich of $\frac{1}{8}$" Silicone rubber between two $\frac{1}{8}$" aluminum plates bolted together. Coincident holes had previously been bored through the centers of the aluminum plates to provide access for the needle of the micro-buret through the Silicone rubber septum. The thermocouple wires were also passed through this Silicone-rubber septum. A thin smear of Silicone grease along the top edge of the cell provided an effective seal between the cell and this cover. The assembly is shown in Plate II-D. A similar type of cover was constructed for the 3-ml cells.

FIGURE 29

THE 3-ML CELL HOLDER


Made from:
1/8" Plexiglass
3/16"
25 mm
1/8"
12 mm
65 mm
25 x 50 mm
Silica-Glass
Slide
30 mm
30 mm
50 mm
47 mm
12 mm

Calibrated Koch 1-ml and 5-ml micro-burets with detachable tips and Luer joints at the tips were used to deliver titrant. The burets had two-way, Teflon stopcocks and a 60-ml reservoir. The glass capillary buret tips normally provided with the burets were replaced by platinum-rhodium hyperdermic needles, 2" long and 28 standard gauge bore. They were connected to the buret by means of an integral, tight-fitting, Kel-F Luer joint*. The needle connected to the buret is shown in Plate II-E. To deliver the titrant, the needle was inserted through the Silicone-rubber septum which had been fitted to the lid of the cell compartment.

When diphenylthiocarbazone was used as a titrant all operations, including titrations, were carried out in subdued light. This was provided by a lamp equipped with a 40-watt red bulb. Tests showed that this light source produced no change in the titre of the diphenylthiocarbazone solutions over a period of eight hours.

2. Perkin Elmer Model 350 Ultraviolet, Visible and Near Infrared Spectrophotometer

For a spectrophotometric study of the reaction of metal 8-quinolinates with diphenylthiocarbazone, a Perkin Elmer Model 350 spectrophotometer was used. It is a double beam, double monochromator, recording instrument. The sources of

*The needles, with attached Kel-F Luer joint, were commercially available from the Hamilton Company, Whittier, California, U. S. A.

radiation were a tungsten incandescent lamp and a deuterium arc. With this instrument, the base-line could be compensated for any difference in path length of the blank and sample cells.

The wavelength was calibrated with a holmium oxide filter each time the instrument was used. The high absorbance range was calibrated with the "Chance" filter supplied with the instrument; it had a certified peak absorbance of 1.971. The high range was checked every hour during a series of measurements.

For all measurements and calibrations, the scan speed was 2½ on the instrument dial, corresponding to 1 min. 15 sec. scanning time from 750 to 350 mμ. The resolution was set at 1, and the pen response at 3.

A Perkin Elmer constant-temperature cell housing was used, except when measurements were made with 0.1-cm and 10-cm cells. Water from a constant temperature bath was circulated through the cell housing at a rate of 200 ml per min. The temperature of the solution in the cell was measured with a calibrated, copper-constantan thermocouple; the reference junction was in an ice-water mixture.

3. Cambridge General Purpose Polarograph

For the standardizations of several metal 8-quinolinate and metal diphenylthiocarbazonate solutions, the metals were analyzed polarographically. A Cambridge General Purpose Polarograph was used.

A conventional dropping mercury electrode and H-cell assembly (see Figure 30) was used; one side of the cell was a saturated calomel electrode. This electrode made contact with the solution under analysis through a glass frit and agar plug. The polarographic current was measured with a conventional strip-chart recorder having an input impedance of 10,000 ohms and one millivolt full scale deflection. The value of $m^{2/3}\ t^{1/6}$ at the potential of the saturated calomel electrode was 3.56. Nitrogen saturated with water vapour was used to remove oxygen from the solution for analysis.

To obtain a polarogram on a small volume of solution, a 5-ml cell was constructed from 13-mm diameter Pyrex glass tubing containing a fritted-glass disc sealed into it (see Figure 30).

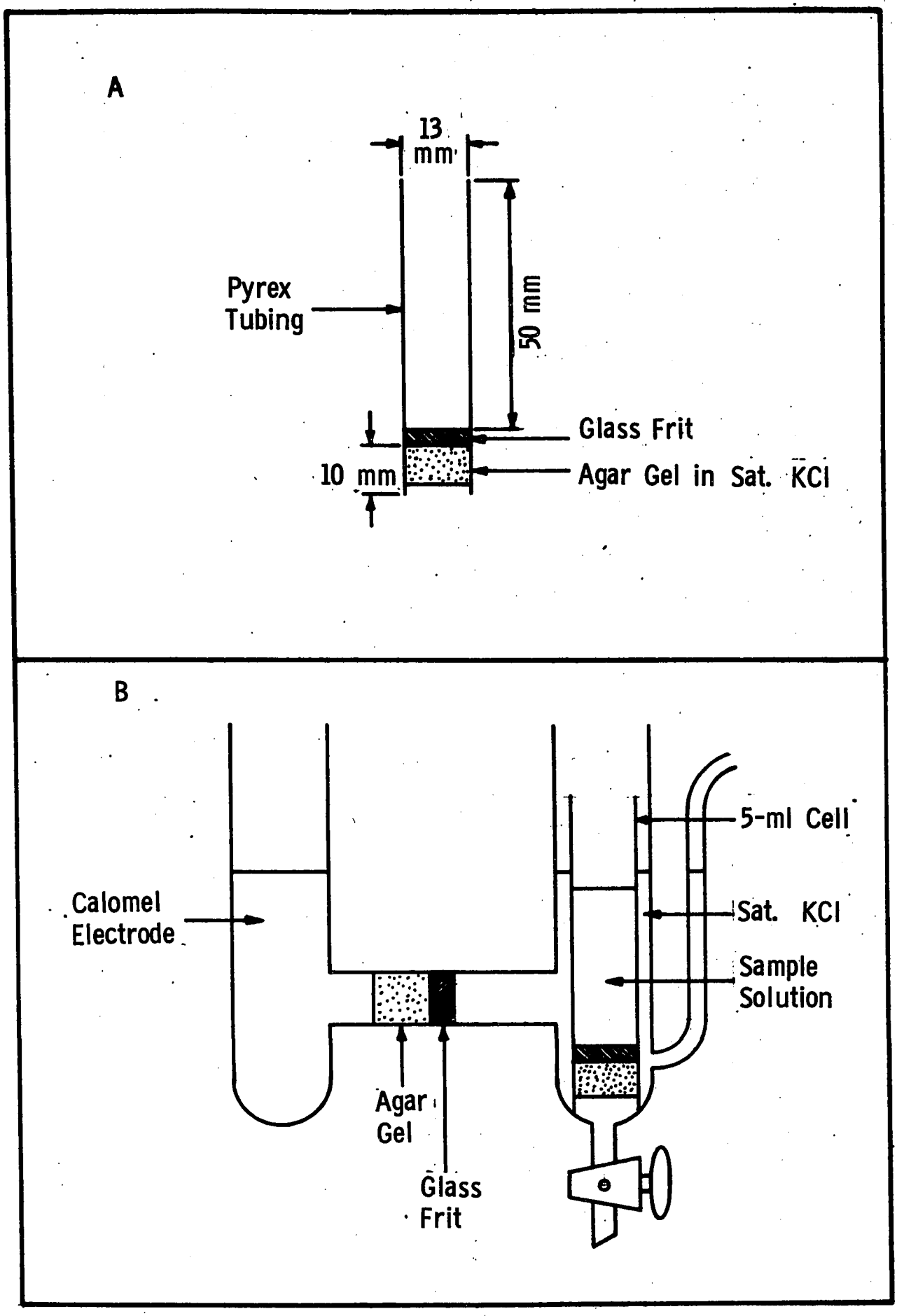
For calibration purposes, ten standard solutions covering the concentration range 10^{-3} M to 10^{-5} M were prepared. The polarograms of each of the unknown metal solutions and the standards were run in triplicate. The average step height was found. The calibration curve was found to be a straight line; its equation was calculated by least squares, whence the concentration of the metal solutions was found.

4. Eberbach Electro-Analysis Apparatus

For the electrolysis of copper, cadmium and cobalt, an Eberbach Electro-Analysis Apparatus was employed. It is a conventional two-position electro-analyzer.

FIGURE 30

THE 5-ML POLAROGRAPHIC CELL AND H-CELL ASSEMBLY


A
13 mm
Pyrex Tubing
50 mm
Glass Frit
10 mm
Agar Gel in Sat. KCl
B
5-ml Cell
Calomel Electrode
Sat. KCl
Sample Solution
Agar Gel
Glass Frit

Platinum gauze electrodes were used for cathodes and platinum spirals for anodes. Before electrolyzing cadmium, the platinum cathode was first plated with copper. Solutions were stirred during electrolysis.

5. Manual, Controlled-Potential Electrolysis Apparatus

The controlled-potential electrolysis technique was used to prepare pure metal solutions, and to determine the purity of standard metals.

The apparatus was constructed from available laboratory apparatus. The circuitry was obtained from (67). A diagram of the components is given in Figure 31. Details of the components are in Appendix VI.

6. Vacuum Sublimation Apparatus

A conventional all-glass sublimation apparatus was used for the purification of oxine. Details of its construction and operation are in Appendix VII.

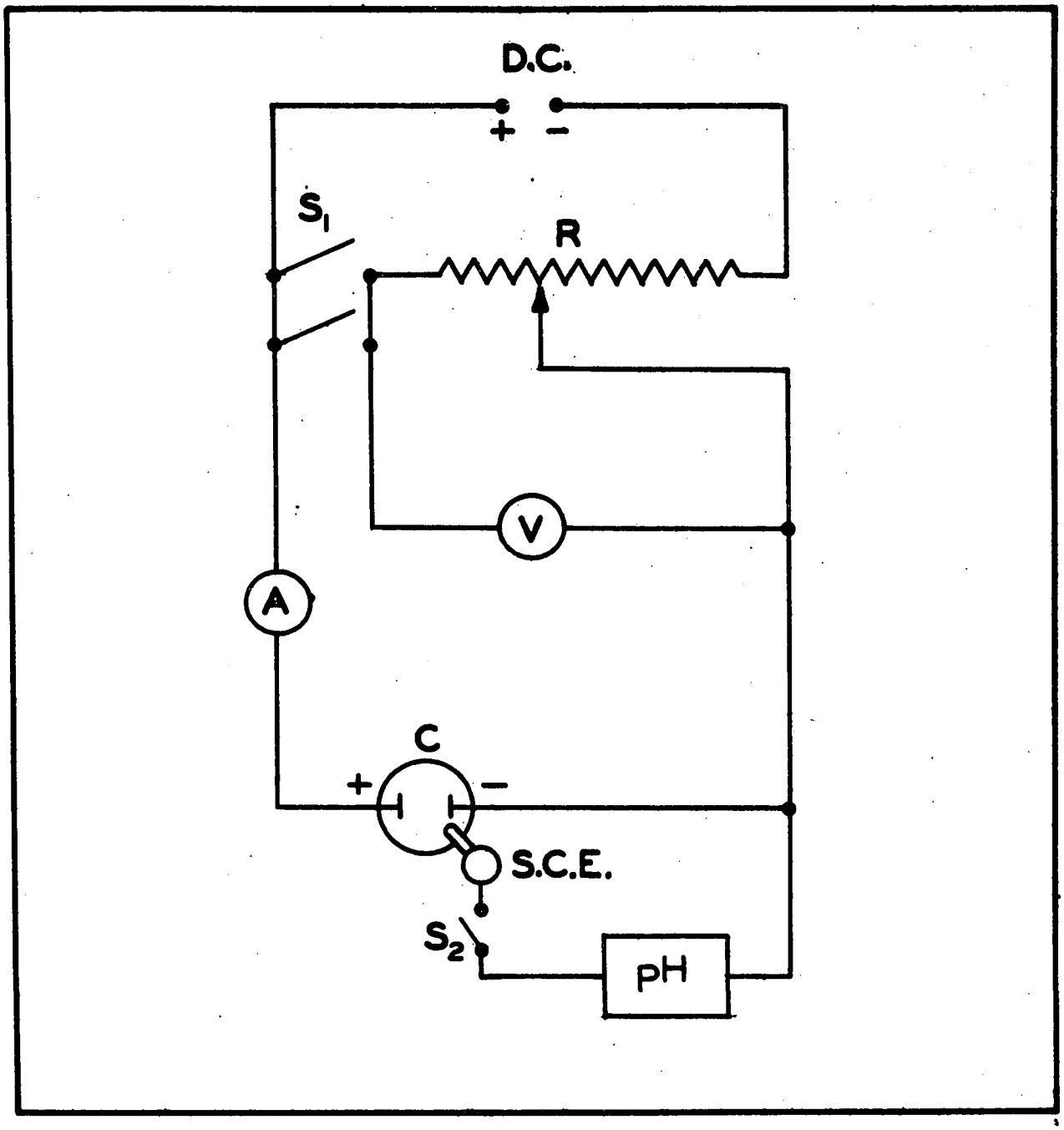
7. Infrared Spectrophotometers

Qualitative infrared spectra of certain metal 8-quinolinates and metal diphenylthiocarbazonates were recorded on Perkin Elmer Model 137B Infracord and Model 521 recording spectrophotometers.

The Infracord is a double-beam instrument. The source produces a continuous spectrum from 2.5 to 15 microns. A sodium chloride prism was used in the monochromator. Before use, the wavelength was calibrated with a polystyrene film.

FIGURE 31

CIRCUIT DIAGRAM OF CONTROLLED-POTENTIAL
ELECTROLYSIS APPARATUS


D.C.
+
−
S1
R
V
A
C
+
−
S.C.E.
S2
pH

The Model 521 is a double-beam instrument capable of scanning from 2.5 to 40 microns (4000 to 250 cm^{-1}). A grating is the dispersing medium. The wavelength was accurate to ± 0.5 cm^{-1} throughout the whole region scanned; the wavelength was calibrated with an indene sample.

The Model 521 was used exclusively for spectra in the 630-250 cm^{-1} region.

Nujol mulls of the samples of metal chelates were prepared. Sodium chloride plates were used with the Infracord, and ceasium bromide plates with the Model 521.

The Model 521 was continuously purged with dry air during a series of measurements in the 630-250 cm^{-1} spectral region.

8. Glassware

All volumetric glassware was calibrated with the solvent used.

Red, low-actinic glass 50- and 100-ml volumetric flasks, and 125-ml separatory funnels were used for metal chelate, 8-quinolinol and diphenylthiocarbazone solutions because these compounds were sensitive to light; the red glassware eliminated photochemical changes. Larger volumetric flasks used with these compounds were coated with black plastic tape.

A special procedure was required for cleaning the glassware. Metal chelates, in particular the metal 8-quinolinates, were difficult to remove by ordinary washing

techniques; a thin film of metal oxinate appeared to adhere strongly to the glass. If the glassware had contained an immiscible organic solvent, it was first rinsed with acetone followed by tap water. The apparatus was then filled with a warm mixture of 4 parts concentrated sulphuric acid, one part concentrated nitric acid solution, and allowed to stand for one hour*. It was then rinsed thoroughly with warm tap water, distilled water and finally ion-exchanged water. The water was washed out with absolute alcohol and the glassware allowed to drain dry. This washing procedure was carried out on all glassware before use. For special solutions employing dried benzene, the glassware was finally flushed with dry nitrogen and allowed to stand in a dry box under dry nitrogen for twenty-four hours.

B. REAGENTS

1. Benzene

The benzene used was Fisher "Spectranalyzed" spectrophotometric grade. Hereinafter, the word "benzene" refers to this spectrophotometric grade, unless otherwise stated. It was used without further purification. Careful studies showed that for the purpose of the present work further purification was in fact unnecessary; proof of this is provided in Appendix VIII. The effects of purified, distilled benzene and spectrophotometric-grade benzene on the

*The 4:1 acid cleaning solution was also an excellent cleansing agent for greasy pipets and burets.

absorbance of a standard diphenylthiocarbazone solution were compared. No detectable difference was observed. The freezing points of the two grades of benzene was found to be the same, within experimental error.

In some of the studies dried benzene was used. Two different methods of drying were employed. In one, the benzene was percolated through a silica gel column, 36 cm long and 3 cm in diameter, at the rate of 25 ml per minute. The silica gel was the indicating variety, 6-16 mesh. This percolation was followed by a second one, this time through fresh silica gel. The water content, determined by a Karl Fisher potentiometric titration (68) was found to be 1.2×10^{-4} M. For some of the work this dried benzene was further dried by calcium hydride (69). No water was detected by the above Karl Fisher titration. These dried benzene products were used only in a dry box under dry nitrogen.

2. Chloroform

The chloroform was "Analar" reagent-grade. It was purified by the method suggested by D. A. Biddle (70). This method consisted of shaking the chloroform with three portions of concentrated sulphuric acid. After washing thoroughly with ion-exchanged water, the chloroform was distilled over CaO under a blanket of dry nitrogen. The middle third fraction boiling at 61°C was collected. One per cent of ethanol was added to the distillate as a preservative.

3. Carbon Tetrachloride

The carbon tetrachloride was "Analar" reagent-grade. It was purified in the same manner as the chloroform (70) except that ethanol was not added.

4. Precautions in the Use of the Solvents

The recommended threshold limit values for benzene, chloroform and carbon tetrachloride adopted by the American Conference of Governmental Industrial Hygienists (1963)(71) are as follows:

Benzene.....25 ppm or 80 mg/m^3 of air
Chloroform.....50 ppm or 240 mg/m^3 of air
Carbon Tetrachloride.....10 ppm or 65 mg/m^3 of air

The threshold limit value is defined as "the condition under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. The values listed refer to time-weighted average concentrations for a normal 8-hour workday".

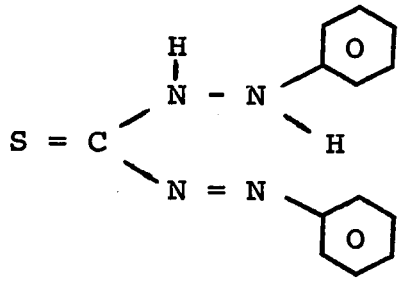
Therefore these solvents were handled only with adequate ventilation and evaporations were carried out in a fume hood. Further, contact with the skin was avoided; this is particularly important in the repetitive handling of benzene.

5. Diphenylthiocarbazone

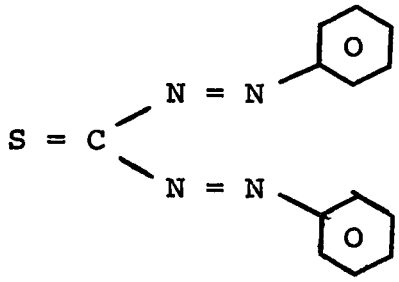
(a) General Description of Reagent

Fisher reagent-grade diphenylthiocarbazone, hereinafter called by its trivial name, dithizone, and given the symbol

H_2Dz was used. Dithizone has the chemical formula



and the major impurity is the oxidation product of dithizone, diphenylthiocarbadiazone



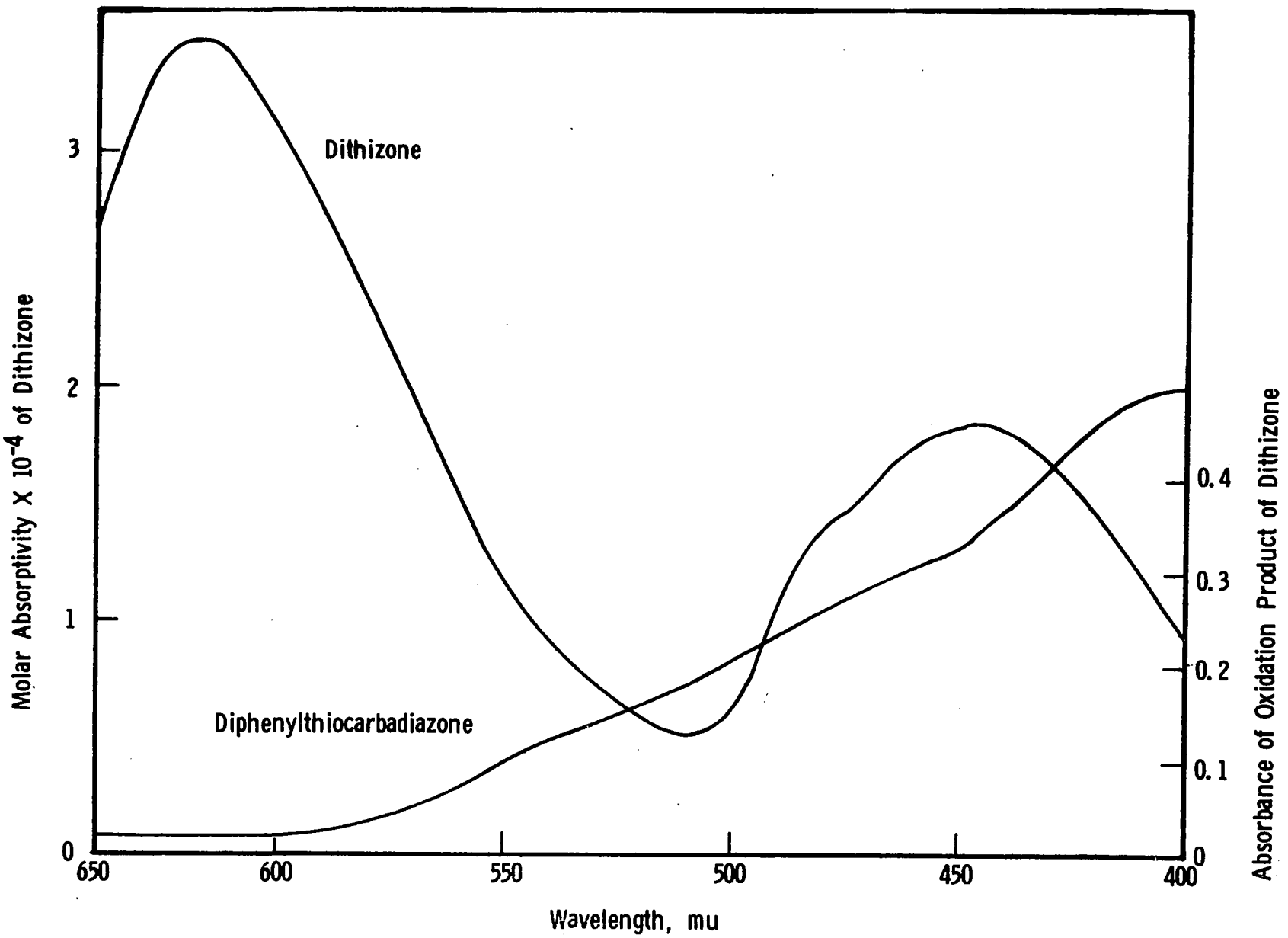
Dithizone was first prepared by Emil Fischer (72) who noted its reaction with heavy metals. It is a black, amorphous solid which decomposes at 165-169°C (73). It is soluble in organic solvents, for example benzene, chloroform and carbon tetrachloride. Its solutions in these three solvents exhibit dichroism. It is insoluble in water and acid solution, but soluble in basic solution (74).

Dithizone solutions are unstable in direct sunlight or in fluorescent light. Therefore, in the present work all solutions were stored in red low-actinic glassware.

The visible absorption spectrum of dithizone has two peaks, one in the region of 620 mμ and the other in the region of 450 mμ (see Figure 32). Solvent shifts are slight. Wavelength maxima and absorptivities in benzene, chloroform

FIGURE 32

MOLAR ABSORPTIVITY CURVE FOR DITHIZONE IN BENZENE
AND A SPECTRAL TRANSMISSION CURVE OF A SOLUTION
OF THE OXIDATION PRODUCT OF DITHIZONE IN BENZENE


Dithizone
Diphenylthiocarbadiazone
Molar Absorptivity X 10^{-4} of Dithizone
Absorbance of Oxidation Product of Dithizone
Wavelength, mu
0
1
2
3
0
0.1
0.2
0.3
0.4
650
600
550
500
450
400

and carbon tetrachloride are given in Table 26 of Section IV C subsection 5 (a).

A more detailed account of the chemistry of dithizone with particular reference to its metal chelates is given later under "Discussion of Results".

(b) The Oxidation Product of Dithizone

The oxidation product is insoluble in water, acid, and basic solutions. Moreover it does not combine with metals (74). In benzene it gives a brown solution. It has no well defined peaks in the visible region. Its absorption in the 620 mμ region is negligible; but it does absorb appreciably in the region of 450 mμ (see Figure 32). These differences in the spectra of dithizone and its oxidation product were useful when checking the purity of dithizone solutions.

(c) The Purification of Dithizone

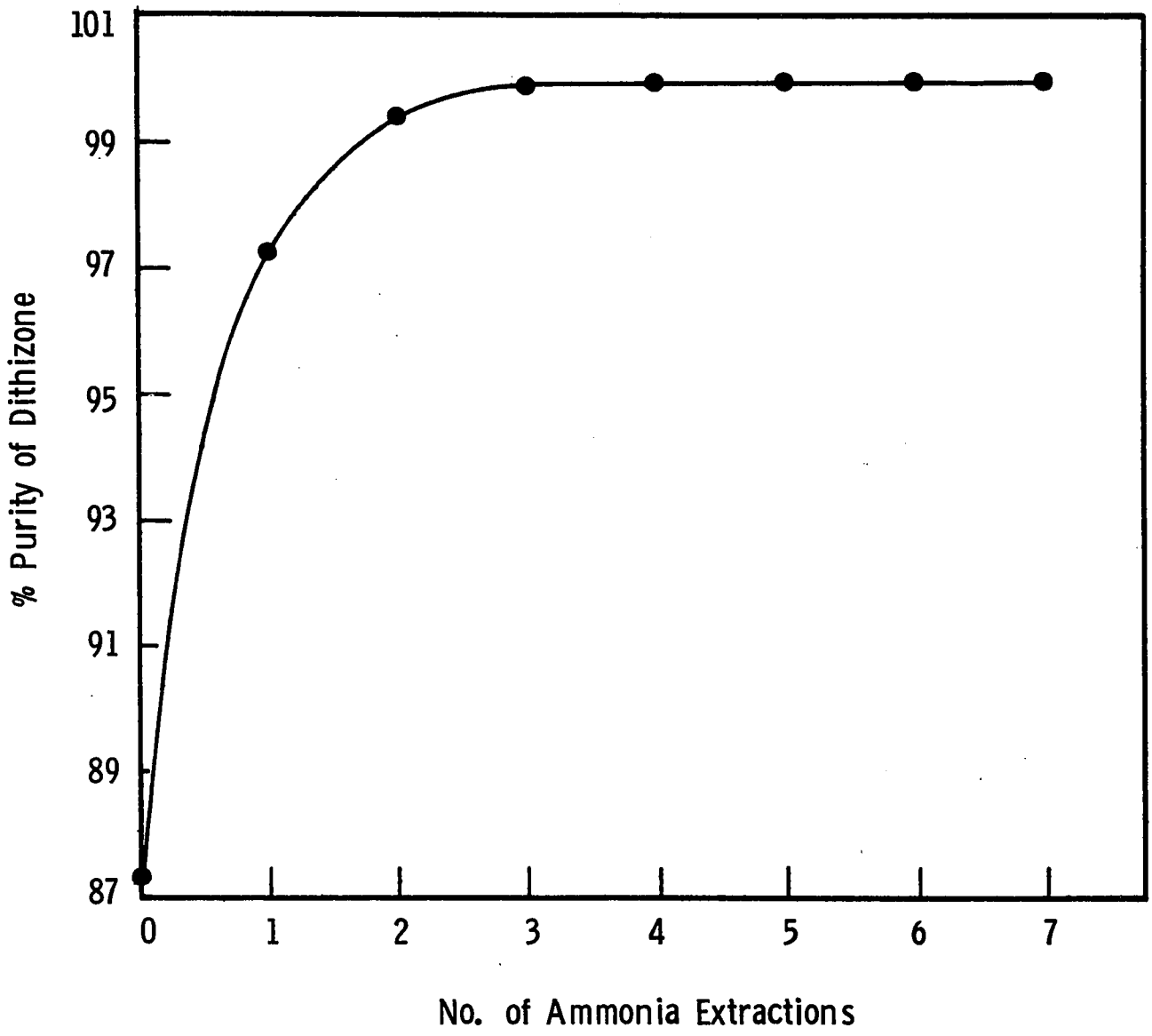
The starting material obtained commercially was not sufficiently pure for use. For example, one batch was found to be 87.3% dithizone. A purification procedure was devised which was based on the method of Mathre and Sandell (75) and on observations by Barnes (76). The method is based on the fact that dithizone is soluble in aqueous ammonia whereas its oxidation product is not. The detailed procedure is given in Appendix IX. It is summarized below.

Two grams of dithizone were dissolved in one litre of chloroform and extracted with a solution containing 5 parts

of purified, concentrated ammonia and 95 parts water. Mathre and Sandell (75) recommended four extractions with 1:100 aqueous ammonia. The aqueous phase was acidified with a solution containing one part of a saturated aqueous solution of SO_2 and five parts of concentrated HCl. Mathre and Sandell recommended using SO_2 to neutralize the aqueous phase. This procedure may be used if small quantities of dithizone are to be prepared. With larger quantities, this procedure is very long, and uses large amounts of SO_2. A pure product of dithizone was obtained with the use of the above acid mixture, provided both were purified. Barnes (76) recommended the use of saturated aqueous SO_2 solution. After neutralization the precipitated dithizone was re-extracted with chloroform. The above procedure was repeated four times. It was established that four extractions were required to obtain the purest dithizone. Figure 33 shows a plot of the found purity of dithizone as a function of the number of extractions. The percent purity at zero extractions was the purity of the starting material. The curve levelled off after three extractions. Four extractions were performed as a precaution. The final chloroform extract was washed with water containing 0.1% of saturated aqueous SO_2 solution. It was filtered through filter paper and one half of the chloroform evaporated in a stream of dry nitrogen. An equal volume of carbon tetrachloride was

FIGURE 33

PER CENT PURITY OF DITHIZONE AS A FUNCTION OF THE NUMBER OF AMMONIA EXTRACTIONS


101
99
97
95
93
91
89
87
% Purity of Dithizone
0
1
2
3
4
5
6
7
No. of Ammonia Extractions

added and again the solution was evaporated to one half the volume. The solution was then immersed in an ice-water bath and after cooling, the crystals of dithizone were filtered onto a sintered-glass filter. The dithizone was first dried in a stream of dry nitrogen and finally under vacuum over potassium hydroxide for two weeks. The entire procedure was carried out in subdued light.

The solid, if stored in the dark and in a tightly sealed bottle, was found to be stable.

(d) Assay Methods for Dithizone

The purity of the solid was determined by two methods:

(i) Spectrophotometric titration of a solution in benzene with standard silver nitrate at 618 mμ.

(ii) Determination of sulphur in the product gravimetrically as $BaSO_4$, after oxidation of five 0.1-gm samples of dithizone with concentrated HNO_3 and potassium chlorate (77).

For procedure (i) five 0.1-gm samples of the purified dithizone were dissolved in benzene in 200-ml calibrated volumetric flasks. Five 0.1-ml aliquots from each volumetric flask were titrated, spectrophotometrically with standard 4×10^{-3} M silver nitrate dissolved in 1:20 methanol:benzene. Details of procedure (i) are given in Section IV C subsection 2 (b).

The assay of the purified solid was found by method (i) to be 99.93 ± 0.22% and by method (ii) calculated for S in $C_{13}H_{12}N_4S$, 12.51%, found S, 12.48 ± 0.06%.

(e) Standard Solutions of Dithizone

The standard solutions of dithizone used as a titrant were solutions of the purified product in benzene. Usually the molarity was 10^{-3} M. The absorbances at 618 mμ and 445 mμ (for benzene) were measured on all fresh solutions and the absorbance ratio was calculated. For very pure dithizone in benzene this ratio had been found to be 1.92 ± 0.04 (see Section IV C subsection 5 (a)). Deviation of any solution from this value indicated that the dithizone solution was impure; it was then discarded.

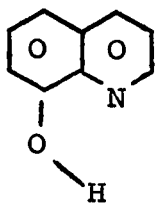
The dithizone solutions themselves were standardized by a spectrophotometric titration at 618 mμ. The titrant was a standard solution of silver nitrate in a 1:20 methanol-benzene solution. The procedure is described in Section IV C subsection 2 (b). Dithizone solutions were always standardized daily before use.

6. 8-Quinolinol

(a) General Description of the Reagent

8-quinolinol, hereinafter called by its trivial name "oxine" and given the symbol HOx, was "Analar" reagent-grade.

Oxine has the chemical formula



It was first prepared by Skraup (78) and Bedall and Fischer (79). It is a white crystalline solid which melts at 75.8°C (80). It is very soluble in benzene, chloroform and carbon tetrachloride, less soluble in ethanol, and practically insoluble in water. It is soluble in dilute aqueous acid and dilute aqueous alkaline solutions (81).

Oxine solutions in benzene, chloroform and carbon tetrachloride were found to be colourless. Oxine, in benzene, had an absorption maximum at 313 mμ (see Section IV C subsection 5 (b)). Oxine solutions in nonaqueous solvents were found to be unstable in direct sunlight and in fluorescent light. Therefore in all experiments, the oxine solutions were stored in red, low-actinic glassware.

A more detailed account of the chemistry of oxine is given under "Discussion of Results".

(b) Purification of Oxine

The starting material obtained commercially was found to be 90.8% oxine. Therefore it was purified by recrystallization from ethanol and the crystals obtained were vacuum sublimed at 100 ± 1°C (82). Details of the sublimation procedure are described in Appendix X. The sublimed crystals were then dried under vacuum over Drierite for two weeks. This purified solid was found to be stable provided the crystals were stored in the dark.

(c) Assay of the Purified Reagent

The dry, purified oxine was assayed by a conventional bromametric method (83) and was found to be 100 ± 0.2% pure.

The melting point was 75.6-76.1°C; the literature value is 75.8°C (80).

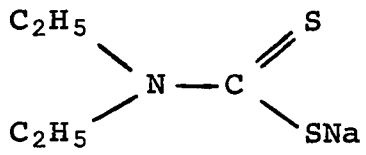
(d) Preparation of Standard Solutions

Standard solutions were prepared in benzene from accurately weighed amounts of the dried solid. A standardization procedure was developed and involved the spectrophotometric titration of oxine with a standard solution of copper in absolute ethanol at 410 mμ. The development of the method is described in Section IV C subsection 3 (b).

7. Sodium Diethyldithiocarbamate

(a) General Description of the Reagent

Sodium diethyldithiocarbamate,



was first prepared by Delepine (84) in 1908 who noted its reaction with copper. It is a white crystalline solid, soluble in water and ethanol but insoluble in carbon tetrachloride, chloroform or benzene.

Sodium diethyldithiocarbamate will hereinafter be given the symbol NaD.

(b) Purification of the Reagent

Fisher reagent-grade sodium diethyldithiocarbamate was used. Its purity was found to be 98.7%. Therefore, the reagent was purified by recrystallization twice from ethanol. The crystals were filtered onto a fritted-glass filter,

washed with ice-cold ethanol, and dried under vacuum over Drierite, for one week (85).

(c) Assay of the Purified Reagent

The purity of the solid was determined by two methods:

(i) Determination of the sodium by the conventional sulphate method (86).

(ii) Determination of the diethyldithiocarbamate radical by precipitation with copper (87).

For procedure (i), five 0.35-gm samples of the purified, dry salt were accurately weighed into porcelain crucibles. The sodium was determined as sulphate by the addition of concentrated sulphuric acid according to the recommended procedure (86). For procedure (ii) five 0.1-gm samples were weighed and dissolved in water. An excess of a standard solution of copper in water was then added. The precipitate was filtered, washed with water, and dried at 110 ± 5°C.

Calculated for Na in $C_5H_{10}NS_2Na$, 13.42, found 13.39 ± 0.08. Calculated for $C_5H_{10}NS_2$, 86.58, found 86.56 ± 0.19.

(d) Preparation of Standard Solutions

Standard solutions for use as a titrant were prepared from the dried solid in absolute ethanol. The solutions were standardized by spectrophotometric titration with a standard solution of copper nitrate in ethanol. The development of this method is described in Section IV C subsection 4. It was found that the solutions of sodium diethyldithiocarbamate in ethanol were not stable for more than 48 hours.

Therefore fresh solutions were prepared and standardized daily.

8. The Metal 8-Quinolinates

(a) Preparation of Solids

The 8-quinolinates of the following metals were prepared according to the methods described by R. G. W. Hollingshead (88):

Pb, Zn, Cd, Co, Ni, Cu, Ag and In

Hereinafter these compounds are given the abbreviated name "metal oxinate" and the abbreviated symbol MOx_n. A detailed, general procedure for their preparation is given in Appendix XI.

Briefly, they were prepared by the addition of a 5% ethanol solution of oxine to pure aqueous solutions of the metal; the aqueous solutions were first adjusted to the pH value prescribed for their precipitation (see Table 1 of Appendix XI). The precipitated metal oxinate was filtered onto a fritted-glass filter, washed with absolute ethanol to remove free oxine, then dissolved in 2N HCl and the metal oxinate reprecipitated by adjustment of the pH. This final filtered product was washed thoroughly with ethanol and then dried at the recommended temperature (see Table 2 of Appendix XI). Hereinafter all references to the metal oxinates are to the dried product.

(b) Some Properties of the Solid Metal Oxinates

The heat stabilities of the solid metal oxinates have been studied by several authors (82,89,90). The metal oxinates are stable up to 300-400°C. They can be vacuum sublimed at 350°C (82). The metal oxinates of copper, nickel, cobalt, cadmium and zinc are known (88) to form hydrates, $CuOx_2 \cdot 1.5H_2O$, $NiOx_2 \cdot 2H_2O$, $CoOx_2 \cdot 2H_2O$, $CdOx_2 \cdot 2H_2O$ and $ZnOx_2 \cdot 2H_2O$. They lose this water in the range 80-140°C, depending on the metal.

Most of the metal oxinates as prepared above were pale-coloured powders. Copper oxinate was dark green, nickel oxinate pale green, cobalt oxinate pale orange, lead, zinc, cadmium, silver and indium oxinates, pale yellow. The approximate solubilities of the metal oxinates in benzene, carbon tetrachloride and chloroform are given in Appendix XII. The solubilities were greatest in chloroform and least in carbon tetrachloride.

(c) Some Properties of the Metal Oxinate Solutions

Solutions of metal oxinates in organic solvents were found to be unstable in direct sunlight and fluorescent light. Therefore, they were always stored in red, low-actinic glassware.

A detailed discussion of the chemistry of the metal oxinates is given later in the Section "Discussion of Results".

(d) Assay of Solid Metal Oxinates

The purity of each metal oxinate was determined by two methods:

(i) Determination of the metal by a standard method after wet oxidation.

(ii) Determination of the oxinate radical by a colorimetric method, after dissolution of the metal chelate in 0.1-N HCl.

The wet oxidation procedure for chelates is described in Appendix XIV. Briefly the sample was treated first with 5 ml of conc. HNO_3, followed by 5 ml of 30 Vol. % hydrogen peroxide. The solution was heated on a hot-plate and evaporated to moist dryness. Subsequent treatment of the residue depended upon the analytical method used to determine the metal.

Details of the colorimetric determination of the oxinate radical are given in Appendix XV. The sample of metal oxinate was dissolved in 0.1-NHCl in a 100-ml red, low-actinic volumetric flask. The solution was diluted ten-fold and the absorbance of the resulting solution measured at 358 mμ. A calibration graph was obtained from standard solutions prepared with purified oxine. To prevent precipitation of silver chloride in the colorimetric determination of the oxinate radical in silver oxinate 2 N HCl was used, instead of 0.1-NHCl.

The results of the analyses of the solid metal oxinates are given in Table 12.

TABLE 12

ANALYSIS OF SOLID METAL OXINATES

Metal Oxinate	Analytical Method for the Metal[1]	Metal, %			Oxinate Radical, %			Purity of Metal Oxinate, %
		Calc.	Found[3]	S[4]	Calc.	Found[3]	S[4]	
$PbOx_2$	Grav. as $PbSO_4$	41.82	41.73	0.14	58.18	58.22	0.11	99.99
	Grav. as $PbCrO_4$		41.80	0.07				
$ZnOx_2$	Titr. with $K_4Fe(CN)_6$	18.48	18.45	0.08	81.52	81.54	0.11	100.04
	Titr. with E.D.T.A.		18.45	0.07				
$CdOx_2$	Electrolytic	28.04	28.01	0.06	71.96	71.94	0.13	99.92
	Titr. with E.D.T.A.		27.95	0.09				
$CuOx_2$	Electrolytic	18.06	18.06	0.03	81.94	81.88	0.15	99.96
	Grav. with α-benzoinoxime		18.11	0.08				
$InOx_3$	Grav. as In_2O_3	20.97	20.95	0.02	79.05	79.09	0.15	100.04
$AgOx \cdot HOx$	Grav. as AgCl	28.46	28.55	0.04	71.49	71.40	0.13	99.95
$CoOx_2$	Electrolytic	16.97	16.94	0.06	83.06	83.07	0.10	100.01
$NiOx_2$	Grav. with dimethylglyoxime	16.92	16.89	0.08	83.08	83.01	0.13	99.90

Continued on next page

TABLE 12 CONTINUED

ANALYSIS OF SOLID METAL OXINATES

[1]Details of all methods are in Reference (86) except for the E.D.T.A. titrations which are in Reference (112).

[2]By the colorimetric procedure described in Appendix XVII.

[3]Mean of 5 determinations.

[4]Standard deviation, based on 4 degrees of freedom.

(e) Preparation and Standardization of Benzene Solutions

Stock solutions of the metal oxinates were prepared from saturated solutions. The saturated solutions were standardized by analyzing an aliquot for the metal by a standard method, after the benzene had been evaporated and the organic part had been decomposed by the procedure in Appendix XIV. It was found that the sodium stannate present as a stabilizer in the hydrogen peroxide interfered in the polarographic determination of zinc. Therefore several oxidations with aqua regia were used to decompose this chelate.

The final treatment of the residues left after evaporation of the benzene and the wet oxidation, and the analytical method used to determine the metal are given in Table 13.

Zinc, cadmium and nickel oxinates form dihydrates, $MOx_2 \cdot 2H_2O$, which were found to be only slightly soluble in benzene. When dried at the recommended temperatures they became anhydrous, and were then quite soluble in anhydrous benzene. They also dissolved initially in undried benzene, but there was sufficient water in the benzene to cause the dihydrate to reform, which then precipitated. Therefore, for the spectrophotometric titrations, stock solutions of these metal oxinates were prepared by dissolving the dried chelates in dried benzene in a dry box flushed with dry nitrogen.

TABLE 13

STANDARDIZATION OF BENZENE SOLUTIONS OF METAL OXINATES AND DITHIZONATES

Metal Chelate	Treatment of Residue after Evaporation of Benzene and Wet Oxidation	Analytical Method for the Metal
$PbOx_2$ $Pb(HDz)_2$	0.1-N HCl	Polarography (113)
$ZnOx_2$ $Zn(HDz)_2$	1 M NH_3/NH_4Cl	Polarography (113)
$CdOx_2$ $Cd(HDz)_2$	0.1-N HCl	Polarography (113)
$CuOx_2$ $Cu(HDz)_2$ CuDz	2 ml conc. HCl, evaporated to dryness, then in 0.1-N HCl	Colorimetrically in CCl_4 with zinc dibenzyl-dithiocarbamate (114)
$InOx_3$ $In(HDz)_3$	4% $NH_2NH_2 \cdot HCl$, 5 ml saturated HCO_2Na, 0.04% starch in 50 ml of 2.5-N HCl	Polarography (115)
$AgOx \cdot HOx$ AgHDz	3 ml H_2O, neutralized with ammonia, made up to volume with 1 M $KNO_3/KSCN$	Polarography (116)
$CoOx_2$		Colorimetrically with Nitroso-R salt (117)
$NiOx_2$	Conc. ammonia	Colorimetrically with dimethylglyoxime (118)

9. Metal Diphenylthiocarbazonates

The metal diphenylthiocarbazonates are hereinafter called "metal dithizonates" and are given the symbol $M(HDz)_n$.

(a) Preparation of the Solids

The solid metal dithizonates were prepared by a solvent extraction procedure based on that recommended by Mathre and Sandell for the preparation of lead dithizonate (75). The detailed procedure is given in Appendix XIII. Briefly, an aqueous solution of the pure metal salt was extracted at the appropriate pH (see Table 1 of Appendix XIII) with a purified chloroform solution of dithizone*. In extractions from alkaline solution, the excess dithizone remained in the aqueous phase. In extractions from acid solutions, a slight excess of metal in the aqueous phase ensured that no excess dithizone was present in the chloroform phase. The water-washed chloroform extracts were filtered, and combined in a 3-litre beaker. Half the chloroform extract was evaporated under a stream of dry nitrogen in a dry box vented to a fume hood. An equal volume of carbon tetrachloride was then added, and the solution evaporated to 200 ± 10 ml. It was then cooled in an ice bath, and the precipitated metal dithizonate filtered onto a fritted-glass filter, washed with ice-cold carbon tetrachloride, and allowed to dry in a

*In order to obtain a sufficient quantity of the chelate, three or more one-litre portions of the chloroform solution were needed.

stream of dry nitrogen in a dry box. All of the above operations were carried out in subdued light. The dithizonates were finally dried under vacuum over potassium hydroxide for two weeks in the dark. The metal dithizonates of

Cu (II), Zn, Pb, Cd, Ag and In

were prepared by the above method. It was found that the solids were stable if they were stored in the dark.

(b) Some Properties of the Prepared Solids

It was found that the solid metal dithizonates decomposed slowly at 110°C, and more rapidly at 150°C. Therefore, they were dried in vacuo. The heat stabilities of the solid metal dithizonates prepared in the present work have not been reported in the literature, nor have any hydrates.

Dithizone is known to form either of two series of metal dithizonates, depending on the conditions of the aqueous solution (72,74). In one series only one of the two replaceable hydrogens on the dithizone molecule is replaced. The resulting dithizonate, $M(HDz)_n$, is called the primary dithizonate. In the other series, both hydrogens of the dithizone molecule are replaced to give the secondary dithizonate. It is well known that for a monovalent metal the formula of the secondary dithizonate is M_2Dz, for a divalent metal it is MDz, and for a trivalent metal it is M_2Dz_3 (74). Of the chelates prepared in the

present work, only copper and silver are known to form secondary dithizonates. In general, metals that form primary dithizonates from acid solution also form secondary dithizonates from alkaline solution.

The prepared metal dithizonates were highly coloured powders. The colour of solid primary copper dithizonate was dark purple (almost black); that of secondary copper dithizonate,dark brown; zinc dithizonate was deep purple; lead dithizonate, carmine red; cadmium dithizonate,orange; indium dithizonate,dark red; and nickel dithizonate,brown. The colour of primary silver dithizonate was orange-yellow, while its secondary dithizonate was purple.

The solubilities of the solid metal dithizonates in benzene, carbon tetrachloride and chloroform are known to vary widely. In general, the solubility decreases from chloroform, to benzene to carbon tetrachloride. The solubilities of primary and secondary copper dithizonates, and of zinc and indium dithizonates are relatively high (about 10^{-3} M-10^{-4} M). The solubilities of lead, cadmium, silver (primary) and nickel dithizonates are lower (about 5×10^{-5} M-10^{-5} M). Secondary silver dithizonate was found to be essentially insoluble ($<10^{-7}$ M) in benzene. Approximate solubilities of the metal dithizonates in benzene, chloroform and carbon tetrachloride are listed in Appendix XII.

(c) Some Properties of Metal Dithizonate Solutions

Solutions of metal dithizonates in benzene, chloroform and carbon tetrachloride were very highly coloured, and sen-

sitive to direct sunlight and to fluorescent light. At all times, solutions of metal dithizonates were stored in red, low-actinic glassware.

For the metal dithizonates there was only one absorption peak in the visible region; for free dithizone there were two, and they were in the region of 620 mμ and 450 mμ. The single peak of the metal dithizonate ranged from 462 mμ for Ag(HDz) to 545 mμ for $Cu(HDz)_2$; for the others, the peak was near 510 mμ. The detailed spectra are given in Section IV C subsection 5 (c). A detailed discussion of the chemistry of the metal dithizonates is given under "Discussion of Results".

(d) Assay of the Solid Metal Dithizonates

The purity of the prepared, solid metal dithizonates was determined by:

(i) Determination of the dithizonate radical.

(ii) Analysis for the metal, after decomposition of the chelate by the wet oxidation procedure in Appendix XIV.

The assay results on the purities of the metal dithizonates are given in Table 14.

Decomposition of the dithizonates by the method prescribed in Appendix XIV was accomplished with difficulty. Whereas the oxinates were decomposed after only one oxidation stage, the dithizonates required repeated oxidation.

TABLE 14

ANALYSIS OF SOLID METAL DITHIZONATES

Metal Dithizonate	Analytical Method[1] for the Metal	Metal, % Calc.	Found[2]	S[3]	Dithizonate Radical, % Calc.	Found[2]	S[3]	Purity of[4] Metal Dithizonate, %
AgHDz	Grav. as AgCl	29.73	29.61	0.03	70.27	70.13	0.13	99.74
$Pb(HDz)_2$	Grav. as $PbSO_4$	28.87	28.75	0.10	71.13	70.90	0.24	99.70
	Grav. as $PbCrO_4$		28.80	0.05				
$Cd(HDz)_2$	Electrolytic	18.04	17.88	0.05	81.96	81.60	0.31	99.89
	Vol. by EDTA		17.93	0.07				
$Zn(HDz)_2$	Vol. by $K_4Fe(CN)_6$	11.35	11.27	0.08	88.65	88.52	0.20	99.79
	Vol. by EDTA		11.20	0.08				
$In(HDz)_3$	Grav. as In_2O_3	13.03	12.86	0.04	86.97	87.00	0.22	99.83
					Sulfur, %			
					Calc.	Found[2]	S[3]	
CuDz	Electrolytic	20.00	19.91	0.03	10.09	10.08	0.11	99.93
	Grav. as α-benzoin-oximate		19.93	0.08				
$Cu(HDz)_2$	Electrolytic	11.08	10.94	0.02	11.18	11.15	0.14	99.90
	Grav. as α-benzoin-oximate		10.98	0.08				

[1]Details of all methods are in Reference (86) except for the E.D.T.A. titrations which are in Reference (112).

[2]Mean of 5 determinations.

[3]Standard deviation, based on 4 degrees of freedom.

[4]Based on the assay result for the dithizonate radical, in the preceding column.

The zinc chelate was decomposed by repeated oxidation with aqua regia*. Indium dithizonate was not completely decomposed even after repeated oxidation with the usual mixture, but the subsequent addition of concentrated sulphuric acid and subsequent evaporation to fumes of SO_3 proved effective.

The dithizonate radical of the dithizonates of lead, zinc, cadmium and indium was determined by reverting a weighed amount of the solid (0.1 gm) with acid. Thus, the solid sample was shaken mechanically in a red, low-actinic flask with 50 ml of 0.1-N hydrochloric acid containing 1% of a saturated solution of SO_3 and 50 ml of benzene. This decomposition required 6-12 hours. The presence of SO_3 prevented the air oxidation of the liberated dithizone (75,76). The benzene solution of the liberated dithizone, after dilution to 250 ml with benzene, was determined by spectrophotometric titration with standard silver nitrate solution (see Section IV C subsection 2 (b)).

As a check, the liberated metal in the aqueous phase was also determined, by using a standard method.

The dithizonate radical in silver dithizonate was determined by reverting a 0.1-gm sample with a 6% solution of potassium iodide in 0.25-N sulphuric acid, as recommended by Irving and Ramakrishna (91). Benzene solutions of primary

*The sodium stannate stabilizer in the hydrogen peroxide was found to interfere in the polarographic determination of zinc.

and secondary dithizonates of copper were found not to be decomposed by acid. Therefore for these dithizonates the sulphur of the dithizonate radical was determined gravimetrically as barium sulphate after oxidation of the chelate.

(e) Discussion of the Assay Results

The purities of the prepared metal dithizonates ranged from 99.5% to 99.9% (see Table 14). An explanation was sought for the 0.5%-0.1% unaccounted for. If this remainder were water, it would not be sufficient to correspond to a hydrate. If metal hydroxide were occluded in those metal dithizonates prepared from alkaline solutions, high results for the metal and low results for the dithizonate radical would have been obtained; this was not observed. Reprecipitation of the solids did not improve their purity.

When chloroform is shaken with an aqueous phase, the ethanol stabilizer dissolves in the water. It is well known that chloroform without the stabilizer partly decomposes into phosgene and hydrochloric acid. The acid would decompose the metal dithizonate. To test this possible source of error, benzene was used instead of chloroform in the preparation. No improvement in the purity of the products was obtained.

An alternate preparative procedure, that of precipitating the metal dithizonate from an alkaline aqueous solution of dithizone (92), gave worse results.

The following explanation is proposed for the 0.5%-0.1% unaccounted for: during the preparation of the metal dithizonate, slight decomposition of the metal dithizonate took place during the lengthy evaporation of the nonaqueous solution to a small volume. Although precautions were taken to avoid this decomposition i.e. subdued lighting and an inert atmosphere were used, a slight amount of decomposition appears to be inherent in the method of preparation. Other workers (74,75,92,93) have also found it impossible to prepare 100% pure metal dithizonates.

(f) Preparation and Standardization of Benzene Solutions

Stock solutions of the metal dithizonates in benzene were prepared from the solids. Where the solubility was low, a saturated solution was prepared. Where the solubility was high an approximate amount of the chelate was weighed and dissolved in the solvent.

Aliquots of the stock solutions were taken for standardization. When the metal dithizonate could be decomposed by dilute acid, the liberated metal was determined in the acid phase by a standard method, and the liberated dithizone in the nonaqueous phase was determined separately by spectrophotometric titration. For copper dithizonate solutions, the chelate had to be decomposed by the wet oxidation procedure, and so only copper was determined.

The final treatment of the residues after evaporation of the aqueous HCl solutions and the method used to determine the metal are given in Table 13.

10. Standard Metal Solutions

Very pure metal solutions were required for the preparation of the metal oxinates and metal dithizonates, and for standard solutions of metals to be used for the analytical methods in Section IV C.

Details for the purification of the reagents and the methods of assay and assay results of the resulting solids are given in Appendix XVI. Also given there are the methods of preparation and standardization of the necessary solutions to be used in the present work. However in Table 15 there is given a summary of these reagents together with their source, methods of purification and the assay method for the solid. As seen in the Appendix the analytical methods indicate that in all cases the metals or their salts were of sufficient purity for the present purposes.

11. General Reagents

(a) Water

Ion-exchanged water was used exclusively in the present work, unless otherwise specified.

Distilled water was passed through Fisher "Rexyn" 1-300 Research Grade mixed-bed ion-exchange resin. The column was 46 cm by 4.5 cm, and contained 450 gm of wet resin. Periodic tests were carried out by shaking the water with 10^{-7} M-10^{-8} M dithizone solution in carbon tetrachloride. The change of absorbance at 620 mμ before and after shaking never exceeded 0.002, and usually was zero for 10-cm cells.

TABLE 15

STANDARD SOLUTIONS OF METALS

Reagent	Source, and Method of Purification	Assay Method
$Pb(NO_3)_2$	"Analar"; recrystallized 3X; dried in vacuo over KOH.	Gravimetrically as chromate.
Zn metal	Fisher analytical grade metal; further purified by electrolysis at constant potential.	
Cd metal	"Analar" metal; further purified by electrolysis at constant potential.	
Cu metal	B.D.H. electrolytic-grade metal.	
In metal	"Analar" metal.	Gravimetrically as In_2O_3
$AgNO_3$	Nicholls; recrystallized 2X, dried at 110°C, then 15 min. at 225°C (M.P.).	
$CoSO_4$	"Analar" $CoSO_4 \cdot 7H_2O$; recrystallized 3X from ethanol; dried at 450°C.	Electrolytically as Co; gravimetrically as $BaSO_4$
$NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$	"Analar" $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$; recrystallized 3X from water.	Gravimetrically by dimethylglyoxime, and gravimetrically as $BaSO_4$

This maximum change would represent, in terms of an equivalent amount of lead, about 40 p.p.b of lead. The pH of the water was 6.5 ± 0.5.

(b) Sodium Hydroxide

Mallinkrodt analytical-grade sodium hydroxide contained a considerable amount of metal impurities, particularly zinc. Where the quantity of sodium hydroxide used was small in the presence of a large amount of metal to be analyzed (i.e. in E.D.T.A. titrations), the reagent-grade chemical was used directly as a 5% solution; but blank titrations were then always performed.

For the preparation of cadmium dithizonates, a solution of specially purified sodium hydroxide was needed. It was prepared by an ion-exchange method. Thus, pure sodium chloride solution was passed through a column of "Amberlite" IRA-410 resin in the hydroxide form (94). The resulting sodium hydroxide solution was stored in a polypropylene bottle.

(c) Ammonia

Purified concentrated ammonia solution was prepared as follows: Anachemia concentrated ammonia was boiled in an all-glass apparatus. The generated ammonia gas was passed through an ice-trap, then a fritted-glass bubbler into 500 ml of water contained in a one-litre polyethylene bottle which had previously been steamed out in order to remove volatile organic residues in the polymer. This purification

operation was then repeated. The solution was assayed for ammonia by conventional potentiometric acid-base titration with 1 N HCl.

Each batch of purified ammonia was tested for heavy metals, by shaking with 10^{-6} M-10^{-8} M dithizone solution in carbon tetrachloride. The absorbance of the organic layer was measured with 10-cm cells at 500 mμ. The maximum absorbance observed was never more than 0.003. Therefore not more than 60 p.p.b. of heavy metals as lead ever were present. Nevertheless, before use the ammonia solution was always shaken with dithizone to remove the last traces of heavy metal impurities.

(d) Hydrochloric Acid

Purified, concentrated hydrochloric acid solution was prepared by double distillation of Anachemia reagent-grade hydrochloric acid by following exactly the procedure described for the preparation of purified ammonia. The resulting hydrochloric acid was stored in polyethylene bottles which had previously been steamed out and was assayed by conventional potentiometric acid-base titration.

The purified hydrochloric acid was tested for the presence of metals with a 10^{-7} M-10^{-8} M dithizone solution in carbon tetrachloride. The change in absorbance was negligible with 10-cm cells. Heavy metals such as lead which extract from alkaline solution were tested by first neutralizing a sample of the purified hydrochloric acid with purified ammonia and then

shaking with 10^{-7} M-10^{-8} M dithizone in carbon tetrachloride. The maximum absorbance was 0.003 in a 10-cm cell.

(e) Nitric Acid

Concentrated (71%) nitric acid (Nichols Chemical Co. Ltd.) was used directly without purification.

Each new bottle of the reagent was tested by the same procedure used for concentrated hydrochloric acid. The maximum absorbance of the carbon tetrachloride phase never exceeded 0.004 in a 10-cm cell, when extractions with dithizone were carried out from an acidic aqueous phase; the absorbance never exceeded 0.007 in a 10-cm cell when extractions were carried out from a basic aqueous phase. An absorbance of 0.007 in a 10-cm cell represents about 0.1 p.p.m. heavy metals as lead.

These results showed that the nitric acid did not require purification. The greatest contamination was introduced when concentrated nitric acid was used to decompose the metal chelates; the maximum amount used was 20 ml. Thus, approximately 2.4 μg of lead would have been introduced. This amount was usually only 0.05% of the amount of metal being determined, and was within the usual standard deviation of the method of analysis.

(f) Sulphuric Acid

Concentrated sulphuric acid (96%) from the Nichols Chemical Co. Ltd. was used without purification.

Tests for the presence of metals were carried out by the procedure described under "Hydrochloric Acid". With sulphuric acid the maximum absorbance never exceeded 0.004-0.005 in a 10-cm cell.

12. Miscellaneous Reagents

The reagents given in Table 16 were used without further purification except where otherwise noted.

C. PROCEDURES

1. Procedure for Spectrophotometric Titrations

(a) With the Use of the 65-ml Titration Cell

A warm-up period of three hours for the Beckmann spectrophotometer, and ten minutes for the tungsten lamp ensured stable absorbance readings. The wavelength was set at either the wavelength of maximum absorption for dithizone, or at the wavelength of maximum absorption of the metal dithizonate (see Appendix XX). The sensitivity potentiometer was set midway between the maximum and minimum positions.

The Koch micro-buret was rinsed and filled with titrant, and the platinum needle attached. An aliquot of the solution to be titrated was transferred by pipet into the 65-ml titration cell. The solution was diluted to 50 ± 0.2 ml with solvent from a 100-ml buret*. The upper edge of the titration cell was smeared with Silicone grease, then transferred to

*In routine practice the volume may be 50 ± 2 ml; the smaller tolerance permitted theoretical interpretation of the titration curves.

TABLE 16

MISCELLANEOUS REAGENTS

Reagent	Source	Form for Use	Use
α-benzoinoxime	Eastman Kodak	1% in absolute ethanol	Precipitant for Cu
Dimethyl-glyoxime	Analar	1% in absolute ethanol	Precipitant for Ni
Zinc dibenzyl-dithiocarbamate	Eastman Kodak	1% in CCl_4	Colorimetric reagent for Cu
K_2CrO_4	Analar	5% in water	Precipitant for Pb
$K_4Fe(CN)_6$	Baker	0.05 N in water	Titrant for Zn
E.D.T.A.*	Matheson, Coleman and Bell	0.01 M in water, stored in polypropylene bottles	Titrant for metals; standardized against Zn metal, with Eriochrome Black T as indicator
KNO_3	Analar	1 M in water	supporting electrolyte in the polarographic determination of Ag
KSCN	Fisher	1 M in water	
Nitroso-R salt**	Fisher	0.1% in water	Colorimetric reagent for Co
$BaCl_2 \cdot 2H_2O$	Analar	5% in water	Precipitant for sulphate

Continued on next page

TABLE 16 CONTINUED

MISCELLANEOUS REAGENTS

Reagent	Source	Form for use	Use
$KBrO_3$	Fisher	0.1-N in water	Primary standard; titrant for oxine by bromatometry
KBr	Fisher		Used with $KBrO_3$ in bromatometry
$Na_2S_2O_3$	Fisher	0.1-N in freshly boiled water	Used to back-titrate excess $KBrO_3$ in bromatometry
KIO_3	Fisher	0.1-N in water	Titrant for standardizing $Na_2S_2O_3$
Methanol	Fisher	Absolute Grade	
Ethanol	Gooderham and Worts Ltd.	Absolute Grade	

*Disodium ethylenediaminetetracetate dihydrate.
**Sodium 1-nitroso-2-hydroxynaphthalene-3:6-disulphonate.

the cell compartment. It was positioned with respect to a line drawn on the floor of the cell housing, at 90° to the light path. Stirring was started, and adjusted to a rapid rate, but wobbling of the magnetic bar was avoided. Stirring was continuous throughout the titration. The titration-cell cover containing the thermocouple was placed on the cell, then the cover of the cell compartment; the platinum needle of the buret was pushed through the Silicone-rubber septum. The tip of the needle was always under the level of the solution.

After about ten minutes, the solution had come to thermal equilibrium with the thermostat at 25°C. For titrations at higher temperatures, the solution in the titration cell was pre-heated. All titrations reported in the present work were performed at 25°C unless otherwise stated. The temperature was kept constant in the present work for purposes of theoretical interpretation; close temperature control would otherwise be unnecessary. In experiments conducted without temperature control variations in temperature of ± 3° did not produce any detectable fluctuations in the results.

In the titration of metal dithizonates with sodium diethyldithiocarbamate, the spectrophotometer was adjusted to zero with a blank of chloroform. In the titration of metal oxinates, the metal oxinate solution itself was used as the photometric blank, since it was transparent at the

wavelengths used. After this adjustment to zero, constant increments of titrant were added, and the absorbance measured after each addition; several increments were also added beyond the end point*. The total volume of the concentrated solution of titrant added was sufficiently low (e.g. 0.25 ml) as not to require a correction to the absorbance due to dilution.

A plot of absorbance against ml of titrant gave the titration graph. By extrapolation of the straight-line portions of the graph, the equivalence point was found. Drawing of the best line by eye gave estimates of the equivalence point that would be adequate for practical use. However, in the present work the equations of the straight lines were calculated by the method of least squares. The point of intersection and hence the equivalence point, was then computed from the two equations. A discussion of the use of least-squares equations is given in Section IV D subsection 2 (c).

(b) With the Use of the 3-ml Titration Cell

The procedure described for the 65-ml titration cell was used, with two modifications:

1) The titration cell was housed in the special cell holder described in Section IV A subsection 1 which was then inserted into the cell compartment.

---

*After use, cells were rinsed clean with acetone, wiped with absorbent tissue, and air-dried.

2) Because there was only 2.5 ml of solution in the cell, the absorbance was corrected for dilution by the titrant, by using the conventional formula $A[v/(V + v)]$.

2. Standardization of Dithizone Solutions by Spectrophotometric Titration

A method was required for the standardization of dithizone solutions in benzene. It had to be accurate, precise, rapid, and convenient.

One method has been reported (75,91,95); it is the so-called "extractive titration", with standard silver solutions. Increasing amounts of silver in 0.1-N nitric acid were extracted with the nonaqueous dithizone solution. The formation of silver dithizonate or the disappearance of dithizone in the organic phase was followed absorptiometrically at 460 mμ or 620 mμ. A plot of absorbance versus the ml of standard silver nitrate gave a change of slope at the equivalence point. Silver dithizonate gives a 1:1 chelate with dithizone (74,96,97).

This long procedure is subject to several errors:

1) Nitric acid in the aqueous phase could oxidize some dithizone.

2) Extraction of the silver can never be complete.

3) A portion of the organic phase must be temporarily removed for the absorbance measurement, and this operation could cause loss of solvent through evaporation.

4) If benzene were the solvent, the mutual solubility of water in benzene would require a volume correction; and the

volume would also change as more silver solution was added to the aqueous solution.

The method developed and used in the present investigation, for the standardization of dithizone, has none of the above errors; yet it is rapid and convenient. It consists of a spectrophotometric titration of the dithizone in benzene with a standard solution of silver nitrate in a 1:20 methanol-benzene mixture.

(a) Standard Metal Solution

A metal salt was sought which would serve as a primary standard for the titration of dithizone, which would dissolve in a nonaqueous solvent mixture which was preponderantly benzene, and which would provide a stable solution.

Salts of lead, copper and silver were studied. Lead nitrate can be obtained pure. It is somewhat soluble in acetone, methanol and ethanol but is insufficiently soluble in their mixtures with benzene. Cupric chloride was also rejected because of its low solubility. Cupric nitrate prepared by the method given in Appendix XVI (d) was soluble in a 1:20 ethanol-benzene mixture. However the precision and accuracy of the titrations was poor.

Silver nitrate was found to meet all the requirements. It was soluble in a methanol-benzene mixture. When dried as described in Section IV B subsection 10 it becomes a primary standard.

For the present work a standard stock solution, 8.0×10^{-3} M in silver nitrate, was prepared in methanol. The molarity of this solution was determined gravimetrically as AgCl and found to correspond to within 1-2 parts per thousand with the molarity calculated from the weight of silver nitrate taken. Accurate dilution of 5 ml of this stock solution to 100 ml with benzene gave the standard solution for use as the titrant. All solutions were stored in red, low-actinic volumetric flasks.

The stock solution of silver nitrate in methanol was very stable. Its molarity as a function of time was measured by high-frequency titration with a standard solution of sodium chloride. Over a period of one month, only random fluctuations occurred for solutions stored in red, low-actinic glassware. Table 17 shows the results. The diluted silver nitrate solutions in 1:20 methanol-benzene were less stable. Its molarity began to change slowly after about 48 hours, as shown in Table 18. The molarity of this solution was also checked every hour for 12 hours and found to be constant within this period; the results are in Table 19. A 1:20 methanol-benzene solution previously stored for a week gave erratic titration graphs. One such graph is illustrated in Figure 34, and compared there with a titration graph obtained with a freshly prepared solution. Therefore fresh 1:20 methanol-benzene solutions of silver nitrate should be prepared from the stock methanol solution, for a standardization of dithizone.

TABLE 17

THE MOLARITY OF A STANDARD SOLUTION OF SILVER NITRATE IN METHANOL, AS A FUNCTION OF TIME

Total volume of solution = 120 ml
Molarity of NaCl = 9.217×10^{-3} M
Initial Molarity from the wt. of silver nitrate taken = 8.103×10^{-3} M
Aliquot of $AgNO_3$ solution taken = 5 ml

Time in Days	Molarity of $AgNO_3$ Soln.* x 10^3 In Low-Actinic Glassware	Molarity of $AgNO_3$ Soln.* x 10^3 In Clear Glassware
0	8.103	8.103
1	8.115	8.103
2	8.109	8.117
4	8.100	8.110
6	8.112	8.099
10	8.115	8.090
14	8.096	8.079
21	8.100	8.066
30	8.109	8.051

*Average of triplicate determinations by high-frequency titration.

TABLE 18

THE MOLARITY OF A STANDARD SOLUTION OF SILVER NITRATE IN 1:20 METHANOL:BENZENE, AS A FUNCTION OF TIME

Total volume of solution = 100 ml
Molarity of NaCl = 9.217×10^{-4} M
Initial molarity from the wt. of silver nitrate taken = 4.052×10^{-4} M
Aliquot of $AgNO_3$ solution taken = 20 ml

Time In Days	Found Molarity of $AgNO_3$ Soln.* x 10^4
0	4.052
1	4.045
2	4.050
3	4.045
4	4.038
6	4.038
10	4.029
14	4.020
21	4.009
30	3.996

*Single determinations.

TABLE 19

MOLARITY OF A STANDARD SOLUTION
OF SILVER NITRATE IN 1:20 METHANOL:BENZENE,
AS A FUNCTION OF TIME OVER A TWELVE-HOUR PERIOD

Total volume of solution = 100 ml
Molarity of NaCl = 1.005×10^{-3} M
Initial molarity from
wt. of silver nitrate taken = 4.119×10^{-4} M
Aliquot of silver nitrate taken = 20 ml

Time In Hours	Found Molarity of $AgNO_3$ Soln.* x 10^4
0	4.119
1	4.111
2	4.106
3	4.118
4	4.110
5	4.127
6	4.119
7	4.130
8	4.126
9	4.101
10	4.120
11	4.120
12	4.106

*Single determinations.

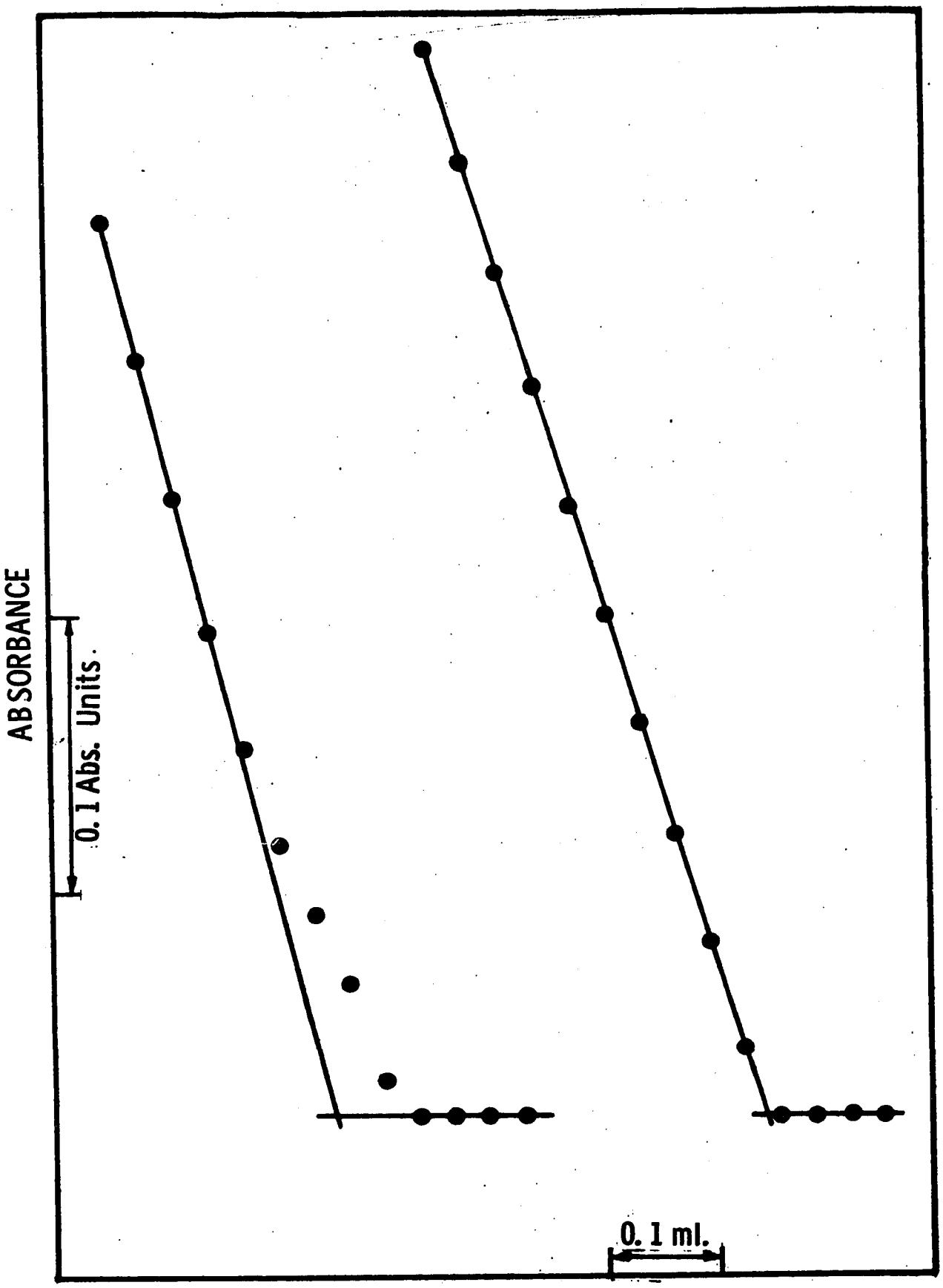
FIGURE 34

TYPICAL TITRATION GRAPHS OF THE SPECTROPHOTOMETRIC TITRATION OF DITHIZONE SOLUTIONS IN BENZENE WITH STANDARD SILVER NITRATE SOLUTION IN 1:20 METHANOL-BENZENE

(a) With Std. $AgNO_3$ solution left standing for 1 week in the dark.

(b) With freshly prepared Std. $AgNO_3$ solution.

Normality of Std. $AgNO_3$ in 1:20 methanol-benzene solution	: 4.13×10^{-4}N
Normality of Std. dithizone solution in benzene	: 1.143×10^{-3}N
µeq of H_2Dz taken	: 0.114 µeq
Initial volume of solution in titration cell	: 50 ml
Wavelength	: 618 mµ



ML. STD. 4×10^{-4} N $AgNO_3$ IN 1:20 METHANOL: BENZENE

(b) Spectrophotometric Titration of Dithizone Solutions in Benzene

In exploratory titrations, the dithizone solution was the titrant. Unfortunately, little or no reaction occurred with the silver nitrate solution. When the nonaqueous solution of silver nitrate was the titrant the reaction with dithizone was rapid and quantitative. The reaction may be written

$$Ag^+ + H_2Dz \rightleftarrows AgHDz + H^+$$

The molar absorptivity of dithizone is 3.47×10^4 at 618 mμ in benzene. Therefore in all standardizations a calibrated, self-filling 100 microlitre micro-pipet was used and reserved exclusively for dithizone solutions. This 100 λ aliquot was diluted in the titration cell to 50 ± 2 ml with benzene. It was then titrated with the silver nitrate solution in a 1:20 methanol-benzene mixture, delivered from a calibrated 1-ml Koch micro-buret.

For a study of the accuracy and precision of a titration, a stock standard solution of dithizone in benzene was prepared by accurately weighing 0.1 gm of purified dithizone into a 200-ml volumetric flask. The flask was made up to volume with benzene, to give a molarity of about 2×10^{-3} M. Solutions of about 2×10^{-4} M and 2×10^{-5} M were then prepared by accurate dilution of this stock solution. The absorbance of the solutions was measured at 618 mμ and 450 mμ. The ratio of these absorbances was calculated.

The concentration was also calculated from the absorbance at 618 mμ and the known molar absorptivity.

Eleven aliquots, each 0.1 ml for the 2×10^{-3} M solution, 1 ml for the 2×10^{-4} M solution and 10 ml for the 2×10^{-5} M solution, were titrated with standard silver nitrate solution, by using the procedure described in Section IV C subsection 1. The wavelength was 618 mμ, in order to follow the disappearance of free dithizone. Since silver dithizonate does not absorb at 618 mμ, the absorbance of the solution at the end of the titration is zero. Thus, the equivalence point of the titration is found at the intersection of the first branch of the titration graph with the abscissa. The equation of the straight line was calculated by the method of least squares and equated to zero to obtain the ml of titrant at the equivalence point.

The measured molarities are given in Table 20 (a typical titration graph is in Figure 34 (b)). The averages for the measured molarities of the three dithizone solutions are also given together with the standard deviations. Table 20 also reports the molarity of the dithizone solution as calculated from the weight of purified dithizone taken and in addition the molarity of the dithizone calculated from the absorbance measured at 618 mμ.

It is clear that the precision and accuracy of this new titration method are excellent. The variation in precision for the three different concentrations of dithizone reflects

TABLE 20

THE ACCURACY AND PRECISION OF THE STANDARDIZATION OF A BENZENE SOLUTION OF DITHIZONE, BY SPECTROPHOTOMETRIC TITRATION WITH A STANDARD SOLUTION OF SILVER NITRATE IN 1:20 METHANOL:BENZENE

Total volume of titration solution = 50 ± 2 ml
Wavelength for the titration = 618 mμ
Path length = 5 cm

Weight of H_2Dz in 200 ml of benzene		0.0993 gm		
Molarity of Std. $AgNO_3$ soln.		4.013×10^{-4} M	4.013×10^{-4} M	4.013×10^{-4} M
Aliquot H_2Dz soln. taken for analysis		0.0978 ± 0.0006	1.000 ± 0.004	9.98 ± 0.02
Found Molarity of H_2Dz	1	1.902×10^{-3}	1.958×10^{-4}	1.950×10^{-5}
	2	1.957	1.962	1.895
	3	1.892	1.925	1.938
	4	1.900	1.938	1.959
	5	1.866	1.904	1.918
	6	1.898	1.883	1.901
	7	1.935	1.888	1.905
	8	1.880	1.967	1.903
	9	1.915	1.899	1.947
	10	1.976	1.910	1.889
	11	1.944	1.952	1.893
Average		1.915×10^{-3}	1.926×10^{-4}	1.918×10^{-5}
S^2		11.56×10^{-10}	9.58×10^{-12}	6.62×10^{-14}
S		$\pm$ 0.034 $\times 10^{-3}$	$\pm$ 0.031 $\times 10^{-4}$	$\pm$ 0.026 $\times 10^{-5}$
Molarity from wt. of H_2Dz taken		1.927×10^{-3}	1.927×10^{-4}	1.927×10^{-5}
Molarity from absorbance @ 618 mμ		1.923×10^{-3}	1.920×10^{-4}	1.929×10^{-5}
% error in Ave. from Molarity from Wt. of H_2Dz taken		- 0.62%	- 0.05%	- 0.47%
% error in Ave. from Molarity from Absorbance @ 618 mμ		- 0.42%	+ 0.31%	- 0.57%
A618/A450		1.90	1.91	1.88

not the difference in concentration but rather the reproducibility of pipetting 0.1, 1.0 and 10.0 ml volume.

A study was also made on the precision of the spectrophotometric titration of dithizone as a function of time. Determinations in quintuplicate were made on each of ten different days, over a period of one month. Fresh 1:20 methanol-benzene standard solutions of silver nitrate were used each day. Table 21 shows the results. The variances were found to be homogeneous at the 95% level, with the use of Bartlett's criterion.

3. Standardization of Oxine Solutions by Spectrophotometric Titration

A spectrophotometric titration procedure proved to be convenient for the standardization of oxine solutions in benzene. It was similar to the one developed for the standardization of dithizone. The titrant was a standard solution of cupric nitrate in ethanol.

The titration was based on the reaction

$$Cu(NO_3)_2 + 2HOx \rightleftarrows CuOx_2 + 2HNO_3$$

The formation of copper oxinate at 420 mμ was followed absorptiometrically.

(a) Standard Copper Solution

The preparation of the standard 0.04-N copper stock solution is described in Appendix XVI (d). This stock solution was used as is. For some titrations it was diluted tenfold with ethanol before use, to give a 4.0×10^{-3} N standard solution of copper.

TABLE 21

VARIATION IN THE PRECISION OF THE SPECTROPHOTOMETRIC TITRATION OF A BENZENE SOLUTION OF DITHIZONE, WITH A STANDARD SOLUTION OF SILVER NITRATE IN 1:20 METHANOL:BENZENE, AS A FUNCTION OF TIME

Time In Days	Average Found* Molarity of H_2D_Z Soln. x 10^3	Variance** x 10^{11}	Std. Deviation** x 10^3
1	1.089	8.48	0.009
2	1.042	4.22	0.006
7	1.076	13.79	0.012
14	1.030	12.65	0.012
18	1.029	2.72	0.005
19	1.033	3.25	0.006
21	1.040	5.93	0.008
25	1.053	18.6	0.014
27	1.043	2.65	0.005
32	1.053	9.54	0.010

*The average is for five trials.
**The variance and standard deviation were calculated for 4 degrees of freedom.

Copper was chosen as the titrant metal for the following reasons:

1) The pure metal is a primary standard.

2) Cupric nitrate is readily soluble in ethanol and these solutions are stable.

3) Cupric oxinate in benzene has a well defined absorption peak at 420 mμ, with an absorptivity of 5.9×10^3, which is sufficiently high to permit the titration of dilute solutions of oxine.

Other metals have disadvantages as titrants:

1) The absorptivities of lead and zinc oxinates are too low.

2) Indium salts are relatively insoluble in alcohols.

3) Cobalt and nickel salts are difficult to prepare with the purity required of a primary standard.

(b) Spectrophotometric Titration of Oxine

The precision and accuracy of the method were determined. Thus, an accurately weighed amount of purified oxine which assayed 100% by bromatometric titration*, was dissolved in benzene to give a standard solution of 10^{-2} M. Solutions of 10^{-3} M and 10^{-4} M were prepared by accurate dilution with benzene. Five aliquots of each of these three solutions were suitably diluted with benzene, and titrated spectrophotometrically against a 4×10^{-3} N standardized solution of copper nitrate in ethanol. The procedure is described in Section IV C subsection 1; the wavelength was 420 mμ. A

*Section IV B subsection 6 (b).

typical titration graph is in Figure 35.

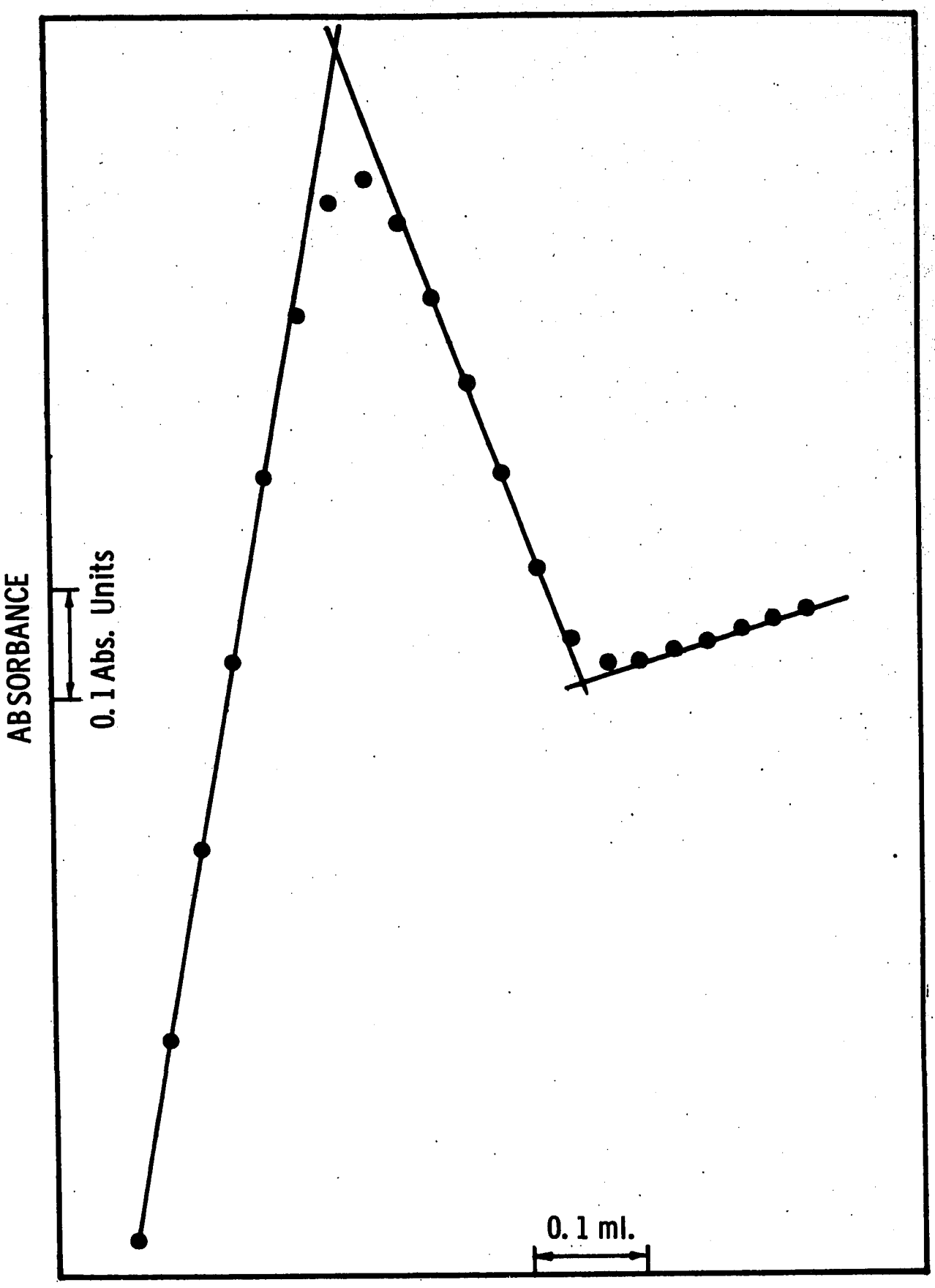
There was some concern that the probable low solubility of $Cu(NO_3)_2$ in benzene would cause spurious breaks in the titration graph. The solubility of $Cu(NO_3)_2$ in benzene has not been measured. At the second end point in Figure 35, 0.4 ml of standard 0.04-N Cu solution in ethanol has been added to the benzene solution in the titration cell. This volume corresponds to 0.8% ethanol in the benzene solution. The solubility of $Cu(NO_3)_2$ in ethanol is 78 gm/100 ml of ethanol at 12.5°C (51). Thus in the increment of ethanol solution added 312 mg of $Cu(NO_3)_2$ would dissolve. If none of the copper added reacted with the oxine, there would be 3 mg of free $Cu(NO_3)_2$ present in the solution. Therefore, the solubility would have to be decreased by a factor of one-hundred in the presence of benzene. This is unlikely, because the copper would be in the form of an alcoholate complex of cupric nitrate which would be expected to be soluble to some extent in benzene. Furthermore, it was observed that in the first part of the titration $CuOx_2$ was formed immediately on addition of $Cu(NO_3)_2$ solution and the absorbance of the resulting solution indicated the complete reaction to $CuOx_2$.

The first of the two breaks in the curve was taken as the equivalence point. It was found by solving the least-squares equations of the relevant two linear arms of the titration graph.

FIGURE 35

A TYPICAL TITRATION GRAPH OF THE SPECTROPHOTOMETRIC TITRATION OF OXINE IN BENZENE WITH A STANDARD SOLUTION OF COPPER NITRATE IN ETHANOL

Normality of Standard $Cu(NO_3)_2$ solution	:	0.0402 N
Normality of HOx solution	:	0.0155 N
µeq HOx taken	:	7.75 µeq
Initial volume of solution	:	50 ml
Wavelength	:	420 mµ


ABSORBANCE
0.1 Abs. Units
0.1 ml.
ML. STD. 0.04-N Cu SOLN.

The results and relevant statistics are given in Table 22. It is evident that the precision and accuracy of the method are excellent.

The existence of two breaks in the titration graphs (e.g. Figure 35) requires comment. The first break occurred at a molar ratio of copper:oxine of 1:2 and the second at a ratio of 1:1. The slope of the first line of the titration graph corresponds to the absorptivity of cupric oxinate. Therefore it is proposed that the first equivalence point represents the formation of $CuOx_2$ from oxine. The addition of a second equivalent of cupric nitrate may then convert the $CuOx_2$ to ion pairs $[CuOx^+, NO_3^-]$. That the absorbance at the second equivalence point is one half that at the first equivalence point seems to indicate that the molar absorptivity of $CuOx^+$ is one half that of $CuOx_2$. However, this must be considered a tentative explanation.

4. Standardization of Sodium Diethyldithiocarbamate Solutions by Spectrophotometric Titration

A spectrophotometric titration procedure, similar to that developed for the standardization of dithizone and oxine solutions, was developed for the standardization of ethanol solutions of sodium diethyldithiocarbamate.

Cupric nitrate in ethanol was chosen for the standardization. Copper forms a complex with diethyldithiocarbamate which is soluble in chloroform and carbon tetrachloride (84). Bode (98) found that this chelate has the formula CuD_2, with

TABLE 22

THE ACCURACY AND PRECISION OF THE STANDARDIZATION OF BENZENE SOLUTION OF OXINE BY SPECTROPHOTOMETRIC TITRATION WITH A STANDARD SOLUTION OF COPPER NITRATE IN ETHANOL

Initial volume of titration solution = 50 ± 2 ml
Wavelength for the titration = 420 mμ
Path length = 5 cm

Weight of HO_x taken in 100 ml of benzene		0.1554 gm	-	-
Molarity of Std. Cu soln. in ethanol		2.08×10^{-3}	2.08×10^{-3}	2.08×10^{-3}
Aliquot HO_x soln. taken		0.196 ± 0.001	1.000 ± 0.004	1.998 ± 0.007
Found Molarity of HO_x	1	1.050×10^{-2}	1.077×10^{-3}	1.069×10^{-4}
	2	1.054	1.077	1.053
	3	1.076	1.055	1.064
	4	1.096	1.043	1.038
	5	1.054	1.043	1.041
Average (n = 5)		1.066×10^{-2}	1.059×10^{-3}	1.053×10^{-4}
S^2		3.88×10^{-8}	1.94×10^{-10}	1.66×10^{-12}
S		$\pm 0.020 \times 10^{-2}$	$\pm 0.014 \times 10^{-3}$	$\pm 0.013 \times 10^{-4}$
Molarity from wt. of HO_x taken		1.070×10^{-2}	1.070×10^{-3}	1.070×10^{-4}
% error in Ave. from Molarity from wt. of HO_x taken		- 0.37%	- 1.03%	- 1.59%

an absorption spectrum in carbon tetrachloride that had a well-defined maximum at 435 mμ. The chelate in ethanol has an absorption peak at the same wavelength. The preparation of the standard solution of copper in ethanol is described in Appendix XVI (d).

It was found possible to use NaD in ethanol as the titrant, and to titrate it into aliquots of the standard ethanol solution of cupric nitrate. This proved to be more convenient than the reverse operation which had to be used for the standardization of dithizone and oxine solutions.

To test the precision and accuracy of the standardization, a 2.5×10^{-2} N standard solution of NaD in ethanol was prepared from an accurately weighed amount of the dried salt. This solution was diluted ten and one-hundred times with ethanol. Ten, 5 and 0.5 ml aliquots of a standard 3.5×10^{-4} N solution of cupric nitrate in ethanol were titrated spectrophotometrically with the two diluted solutions of NaD respectively, according to the procedure outlined in Section IV C subsection 1. The results are reported in Table 23.

Agreement between the molarity found by titration and the molarity calculated from the weight of NaD was good; and the precision was excellent. A typical titration graph is illustrated in Figure 36.

The sodium diethyldithiocarbamate solutions in ethanol were not stable for longer than 48 hours; Table 24 shows the

TABLE 23

THE ACCURACY AND PRECISION OF THE STANDARDIZATION OF ETHANOL SOLUTIONS OF SODIUM DIETHYLDITHIOCARBAMATE, WITH A STANDARD SOLUTION OF COPPER IN ETHANOL, BY SPECTROPHOTOMETRIC TITRATION

Initial volume of solution in titration cell: 50 ± 2 ml
Wavelength for the titration : 435 mμ
Path length : 5.0 cm

Weight of NaD in 100 ml of ethanol	0.4491 gm	
Normality of Std. Cu soln.	3.525×10^{-4} N	
Aliquot of Cu soln. taken, ml	1.98 ± 0.02	0.197 ± 0.002
Found Molarity of NaD soln.*	2.346×10^{-3}	2.344×10^{-4}
S^2	2.26×10^{-10}	8.35×10^{-12}
S	0.015×10^{-3}	0.029×10^{-4}
Molarity from wt. of NaD taken	2.373×10^{-3}	2.373×10^{-4}
% Difference**	- 1.14	- 1.22

*Mean of 10 samples.
**Calculated from the found molarity and that from the wt. of NaD taken.

FIGURE 36

A TYPICAL TITRATION GRAPH OF THE SPECTROPHOTOMETRIC TITRATION OF AN ETHANOL SOLUTION OF CUPRIC NITRATE, BY AN ETHANOL SOLUTION OF SODIUM DIETHYLDITHIOCARBAMATE, AT 435 mμ

Normality of Standard $Cu(NO_3)_2$ solution	:	3.525×10^{-4} N
Normality of Standard NaD solution	:	2.373×10^{-3} N
μeq of Cu taken	:	0.705 μeq
Initial volume of solution	:	50 ml
Wavelength	:	435 mμ

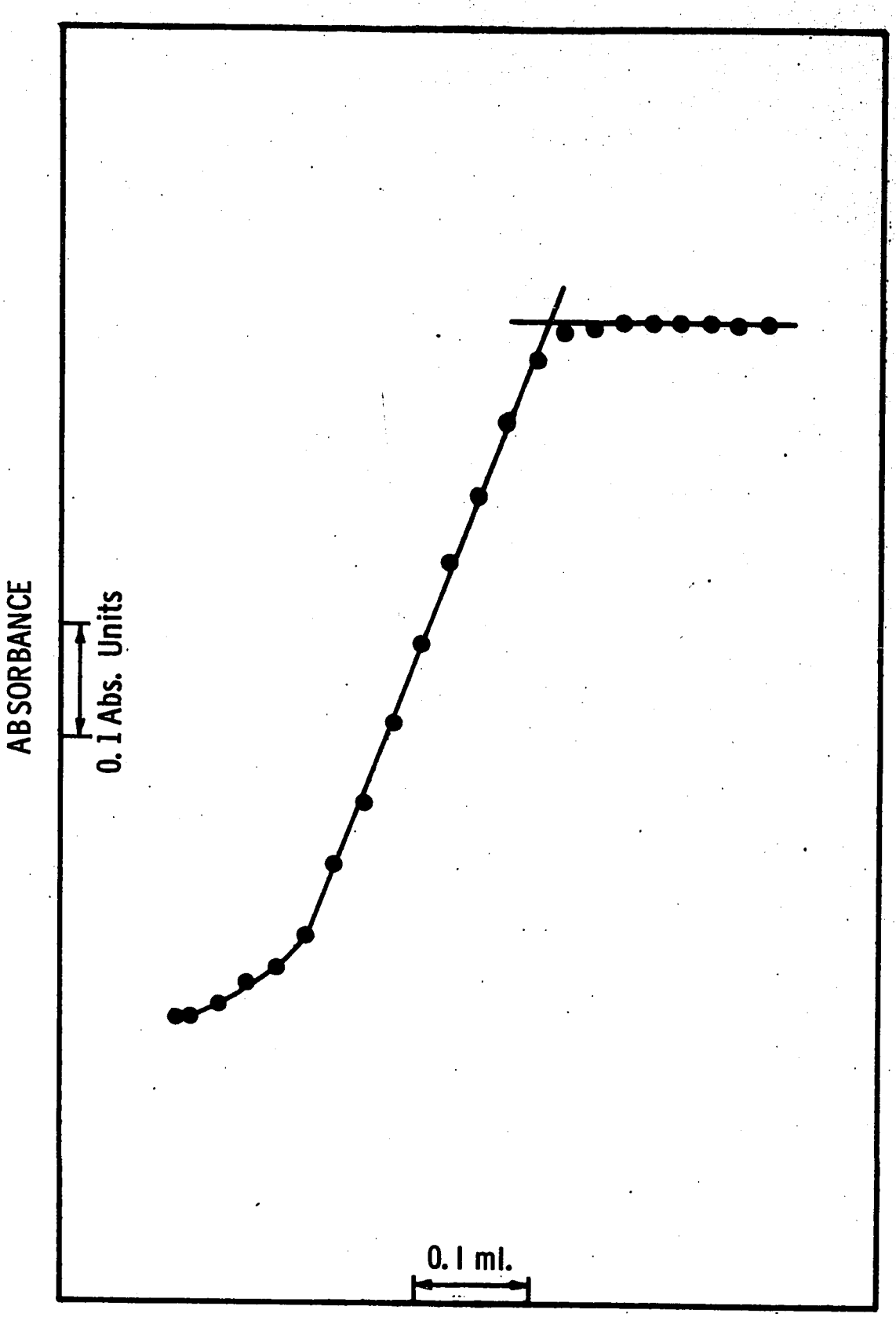

ABSORBANCE
0.1 Abs. Units
0.1 ml.
ML. STD. 2.4 X 10^-3 N NaD

TABLE 24

THE STABILITY OF ETHANOL SOLUTIONS OF SODIUM DIETHYLDITHIOCARBAMATE, OVER A PERIOD OF ONE WEEK

Time In Days	Molarity* x 10^3
0	2.411
1	2.418
2	2.418
3	2.390
4	2.341
5	2.276
6	2.157
7	1.982

*Mean of 3 samples.

change in molarity observed in daily titrations performed over a period of one week. Titrations were also performed every hour for twelve hours; these results are shown in Table 25. The molarity remained constant over this 12-hour period, within experimental error. Bode (99) found that aqueous solutions of NaD decomposed rapidly at low pH and less rapidly at higher pH. The half-life of the salt at pH 2 was 0.3 sec., at pH 7, 8.3 hours, and at pH 8, 3.5 days. However, the ethanol solutions were found in the present investigation to be more stable than aqueous solutions. Fresh solutions of sodium diethyldithiocarbamate in ethanol should therefore be prepared daily.

5. Determination of Molar Absorptivities*

(a) Dithizone

The pronounced tendency of dithizone to be oxidized demands that great care be taken in the preparation of a sufficiently pure solution for measurement. Wide variations in literature values (75,95,100,101) of the absorptivity of dithizone (see Table 26) may be attributed to differences in the purity of the dithizone.

Several procedures have been reported (91,95,101) for the determination of the absorptivity of dithizone in non-aqueous solvents. Of published methods that attempt to eliminate or avoid the error due to instability of dithizone

*Hereinafter the word "absorptivity" will refer to molar absorptivity in litres $mole^{-1}$ cm^{-1}.

TABLE 25

FLUCTUATIONS IN THE MOLARITY OF AN ETHANOL SOLUTION OF SODIUM DIETHYLDITHIOCARBAMATE, OVER A TWELVE-HOUR PERIOD

Time In Hours	Molarity* x 10^3
0	2.879
1	2.832
2	2.833
3	2.848
4	2.887
5	2.867
6	2.840
7	2.894
8	2.882
9	2.887
10	2.855
11	2.825
12	2.816

*Mean of 3 samples.

TABLE 26

COMPARISON OF THE ABSORPTIVITY OF DITHIZONE IN BENZENE AT 618 mμ AND AT 450 mμ DETERMINED BY TWO DIFFERENT METHODS

	Molar Absorptivity at 25°C			
	Reversion Technique		Spectrophotometric Titration	
	From Pb Solutions n = 18	From Zn Solutions n = 18	Freshly Prepared n = 18	From Solid Dithizone n = 18
618 mμ	3.44×10^4	3.50×10^4	3.49×10^4	3.45×10^4
$S^2 \times 10^{-4}$	64.0	46.5	49.6	33.8
$S \times 10^{-4}$	0.08	0.07	0.07	0.06
450 mμ	1.82×10^4	1.84×10^4	1.83×10^4	1.87×10^4
$S^2 \times 10^{-4}$	30.4	29.6	27.5	22.4
$S \times 10^{-4}$	0.06	0.05	0.05	0.04

VALUES FOR a_{H_2Dz} IN OTHER SOLVENTS

SOLVENT		REFERENCE
CCl_4	: $3.17 \pm 0.02 \times 10^4$ at 620 mμ; $1.90 \pm 0.02 \times 10^4$ at 450 mμ:	(1)
CCl_4	: $3.64 \pm 0.01 \times 10^4$ at 620 mμ; $2.14 \pm 0.02 \times 10^4$ at 450 mμ:	(2)
CCl_4	: $3.46 \pm 0.09 \times 10^4$ at 620 mμ; $2.03 \pm 0.08 \times 10^4$ at 450 mμ:	(3)
CCl_4	: 3.04×10^4 at 620 mμ; 1.90×10^4 at 450 mμ:	(4)
$CHCl_3$	: $4.15 \pm 0.05 \times 10^4$ at 605 mμ; 1.60 ± 0.02 at 440 mμ	: (3)
$CHCl_3$	: $4.37 \pm 0.10 \times 10^4$ at 615 mμ; 1.71 ± 0.04 at 445 mμ	: This work

(1) O. B. Mathre and E. B. Sandell, Talanta, 11, 295 (1964).
(2) O. A. Weber and V. B. Vouk, Analyst, 85, 40 (1960).
(3) S. S. Cooper and M. L. Sullivan, Anal. Chem., 23, 613 (1951).
(4) H. A. Liebhafsky and E. H. Winslow, J. A. C. S. 59, 1966 (1937).

solutions, the most popular is the "reversion" technique developed by Irving, Risdon and Andrew (102), and extended by Cooper and Sullivan (100). In it, a known quantity of a metal dithizonate is first extracted into a nonaqueous solvent, then is decomposed by a "reversion" reagent, and the absorbance of the fresh, pure dithizone is measured. However, an error may arise in their initial step, the preparation of the nonaqueous solution of the metal dithizonate. They extract the excess free dithizone from that solution with a dilute aqueous solution of ammonia; but possibly some of the metal dithizonate will thereby be decomposed.

Weber and Vouk (95) used a direct method. They prepared the nonaqueous solution of free dithizone, measured its absorbance, then weighed the dithizone left after careful evaporation of the solvent. They claim that even if oxidation of the dithizone occurs during the evaporation, it would change the weight by only one percent. The method is cumbersome; 100 mg of dithizone requires 700 ml of benzene for solution (the absorbance at 618 mμ would then be 1.94 in a 0.1-cm cell).

In the present work, two procedures were used:

1) The "reversion" procedure described above.

2) Measurement of the absorbance of a dithizone solution which had been standardized by titration with a standard solution of silver nitrate in 1:20 methanol-benzene,

shown in Section IV C subsection 2 to be an accurate, precise method.

All dithizone solutions were stored in red, low-actinic glassware, to ensure their stability.

(i) The reversion technique

In the present work, the procedure of Cooper and Sullivan (100) was followed with minor changes, lead and zinc dithizonates being used as the sources of dithizone. They determined the concentration of liberated metal colorimetrically with dithizone; in the present work the metals were determined polarographically. They liberated the dithizone with 0.1-N HNO_3; in the present work it was liberated by a solution containing one part of a saturated SO_2 solution to 99 parts of 0.1-N HCl. Dilute HNO_3 is a mild oxidizing agent, so that some oxidation of the dithizone seemed possible in their method.

The detailed procedure is in Appendix XVII; a summary follows. Aliquots of 5×10^{-4} M aqueous solutions of lead and of zinc were separately diluted to 50 ml in red, low-actinic separatory funnels, and then adjusted by addition of buffers to pH 8. Aliquots of 10^{-4} M benzene solutions of freshly purified dithizone were added to the funnels, and diluted to 30 ml with benzene. After equilibration, the aqueous phase was discarded. (A sufficient amount of dithizone had been added to ensure a 1% excess in that

phase.) The benzene phase was washed with diluted ammonia, and the washings discarded. The metal from the dithizonate was then extracted quantitatively into 10 ml of 0.1-N HCl containing 0.1 ml of a saturated solution of SO_2.

The aqueous layer was quantitatively transferred to a beaker, evaporated to dryness to remove SO_2, taken up again in 0.1-N HCl and determined polarographically.

The benzene layers were transferred quantitatively to 50-ml red, low-actinic volumetric flasks, diluted to the mark, and spectral transmission curves run at 25°C from 750-350 mμ, by using a Perkin Elmer Model 350 Spectrophotometer. The final dithizone concentrations covered the concentration range 10^{-4} M-10^{-6} M. From the measured concentrations of the metals, the concentrations of the dithizone in the benzene solutions were found. Then together with their measured absorbances, the absorptivities were calculated.

The average absorptivities at 618 mμ and 450 mμ obtained from the lead and zinc solutions are compared in Table 26. The variances were homogeneous at the 95% level, by Bartlett's criterion (103); and the means were not significantly different at the 95% level. Beer's Law was obeyed over the concentration range 10^{-4} M to 10^{-6} M.

(ii) Direct measurement of absorptivities of dithizone solutions

1) From freshly purified solutions

Six freshly purified solutions of dithizone covering

the concentration range 5 x 10^{-4} to 5 x 10^{-6} M, were prepared in triplicate by the procedure in Appendix IX. Each solution was diluted to the mark with benzene in 50-ml, red, low-actinic volumetric flasks. The concentration of each solution was determined by spectrophotometric titration as described in Section IV C subsection 2. Five replicate titrations were performed on each solution.

The spectral transmission curves were measured at 25°C as previously described, and the absorptivities calculated from 750 mμ to 350 mμ at 5 mμ intervals. The values obtained at 618 mμ and 450 mμ are entered in Table 26.

2) From purified solid

Six solutions of dithizone in replicates of three and having a concentration range of 5 x 10^{-4} M to 5 x 10^{-6} M were prepared directly from the solid. The concentration of each solution was determined by spectrophotometric titration. The spectral transmission curves were measured at 25°C and the absorptivities calculated, as before. The values obtained at 618 mμ and 450 mμ are compared with other values in Table 26.

Except for solutions prepared from the solid, the solutions used to measure absorptivities of dithizone were saturated with water. To determine if water had any effect on the absorptivity, three solutions having concentrations of 10^{-4} M, 10^{-5} M and 10^{-6} M were prepared in triplicate

from the dried solid. Benzene dried by percolation through a silica gel was used. The solid had been dried under vacuum over KOH for two weeks. The solutions were prepared in a dry box under a blanket of dry nitrogen. The concentration of each solution was determined, and the spectral transmission curves measured, as described above. The absorptivities found for the dried benzene solutions were not significantly different (at the 95% level) from the other values reported in Table 26.

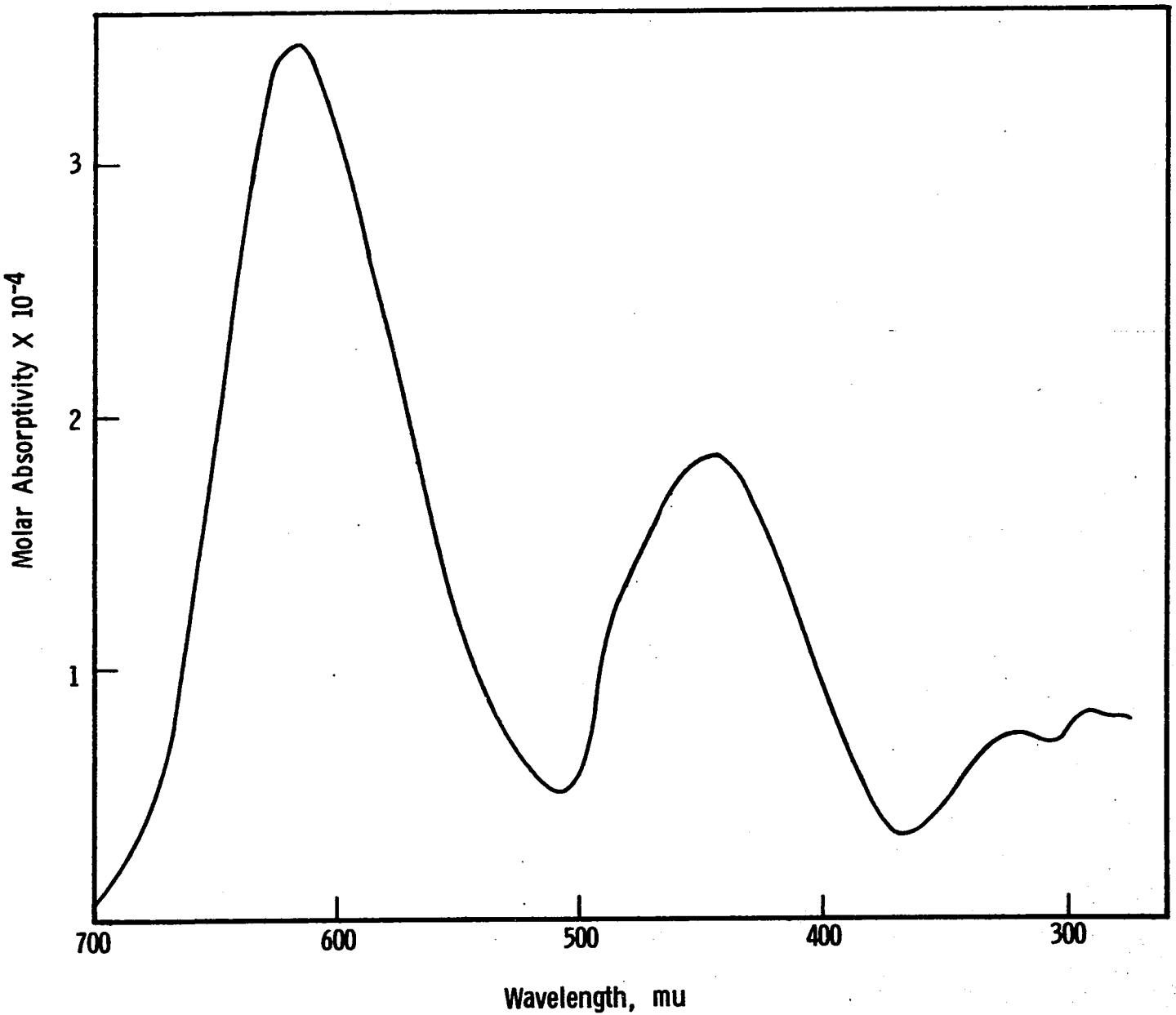
The variances are reported in Table 26 for the four different methods of determination of the absorptivity of dithizone; they proved to be homogeneous by Bartlett's criterion (103) at the 95% level. Moreover, an analysis of variance showed that the mean values of the absorptivities were not significantly different at the 95% level. Therefore pooled estimates of the mean and the variances could be reported. These pooled estimates for 81 solutions are given in Table 1 of Appendix XVIII, for the absorptivity of dithizone at 10 mμ intervals from 700 to 350 mμ. The curve of absorptivity versus wavelength is given for dithizone in Figure 37.

Over the range of dithizone concentrations used, 10^{-6}-10^{-4} M, Beer's Law was obeyed at each wavelength studied, from 700 to 350 mμ.

The absorptivities for dithizone at 25°C in the ultraviolet region were determined from six solutions having a concentration range of 5×10^{-4} to 5×10^{-6} M. These solu-

FIGURE 37

THE ABSORPTIVITY OF DITHIZONE IN BENZENE AT 25°C,
AS A FUNCTION OF WAVELENGTH


Molar Absorptivity X 10^{-4}
3
2
1
700
600
500
400
300
Wavelength, mu

tions were prepared from the solid, and the concentrations determined by spectrophotometric titration. The values at 5 mμ intervals are given in Table 2 of Appendix XVIII. The ultraviolet spectrum in benzene is shown in Figure 37.

A useful check on the purity of dithizone solutions is the ratio of the absorbance at 618 mμ to that at 450 mμ. The average value of this ratio for all solutions described above was found to be 1.92 with a standard deviation of 0.04 (80 degrees of freedom).

(b) Oxine

It was necessary in the present work to be able to measure approximately the concentration of free oxine in the presence of a metal oxinate dissolved in a nonaqueous solvent. Solutions of oxine in benzene, carbon tetrachloride and chloroform absorb only in the ultraviolet region. By measuring the absorptivities of oxine and the metal oxinates in the ultraviolet region, a colorimetric procedure was developed for the purpose of determining the free oxine content.

The absorptivity of oxine in benzene was determined from standard solutions prepared by dissolving the pure dried solid. Six standard solutions having a concentration of 7.0×10^{-3} M oxine were prepared. A further six solutions, each in triplicate, and covering the concentration range from 1.4×10^{-3} M to 1.4×10^{-5} M were prepared by accurately diluting appropriate aliquots of the six stock solutions.

The spectral transmission curves were measured from 400 to 270 mμ at 25°C with the Perkin Elmer Model 350 spectrophotometer described in Section IV A subsection 2 with pure solvent as the photometric blank. The absorptivities were calculated at 2.5 mμ intervals. The values at 5 mμ intervals are in Appendix XIX. The absorptivity versus wavelength curve is shown in Figure 38. The absorption maximum of oxine in benzene was 313 mμ and the absorptivity at this wavelength was 2.50×10^3 ($S = 0.05 \times 10^3$, $n = 24$).

Beer's Law was obeyed at all measured wavelengths, for the concentration range 7.0×10^{-3} M to 1.4×10^{-5} M.

(c) The Metal Dithizonates

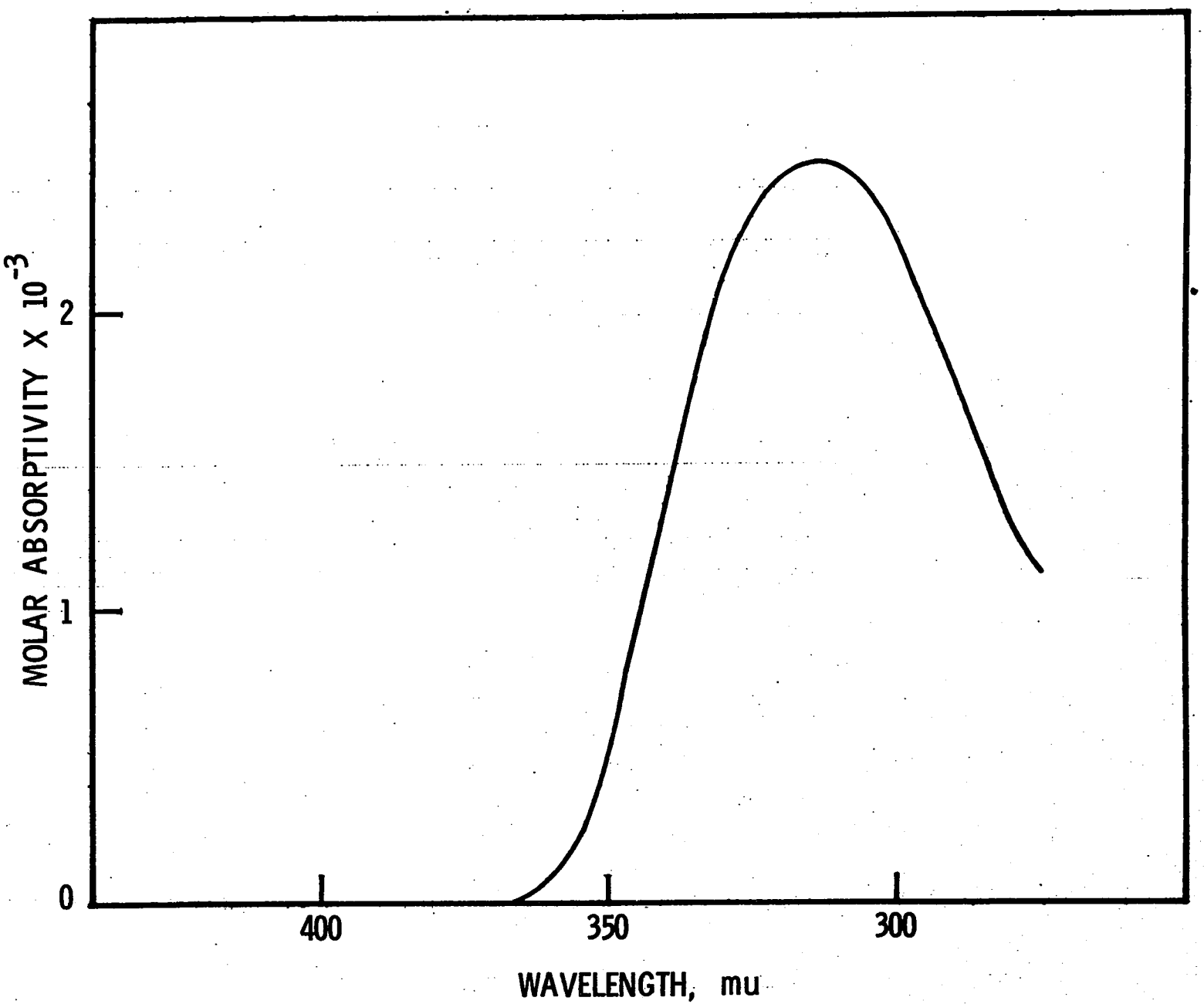
(i) Visible spectra

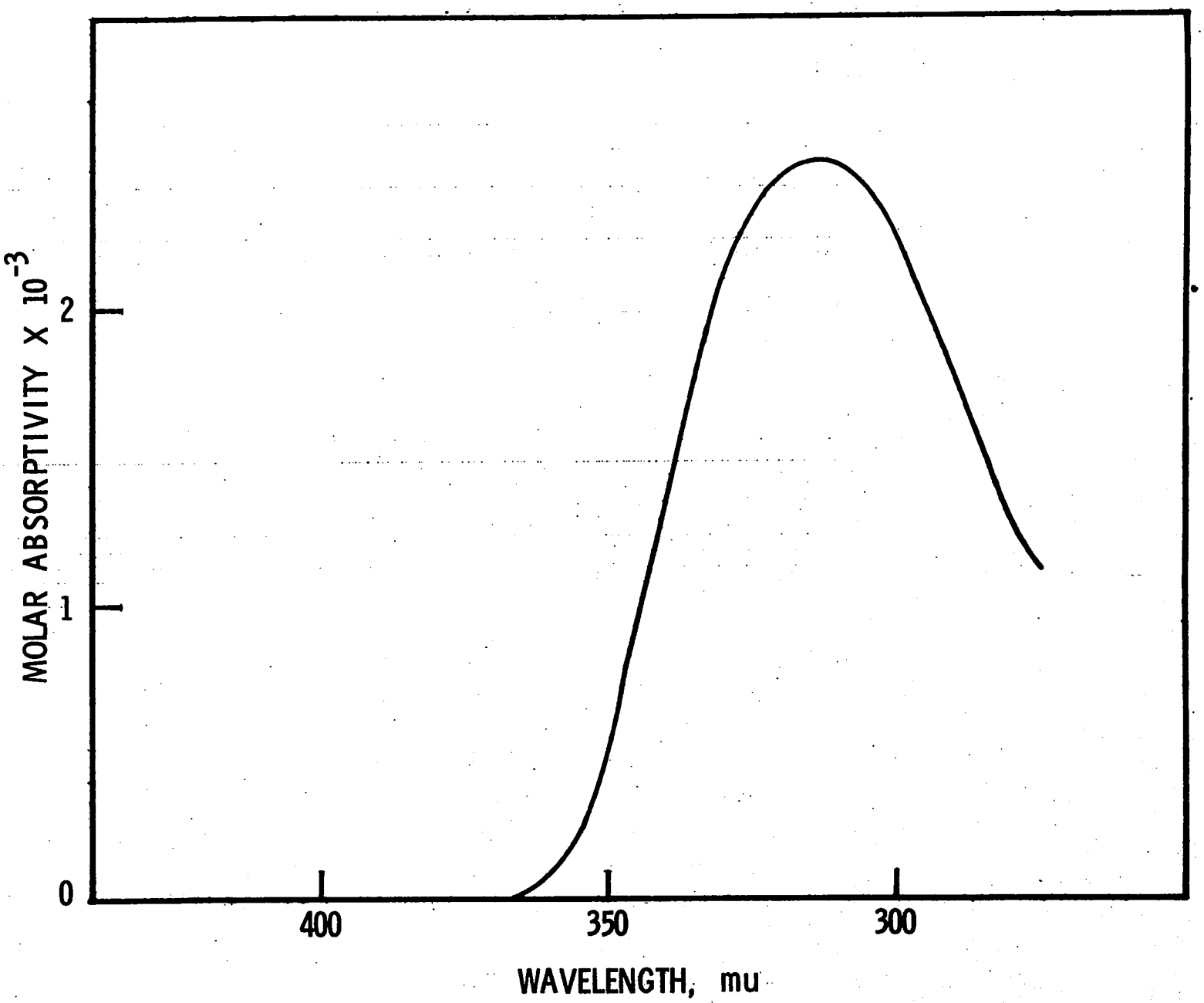
The absorptivities of the dithizonates of Pb, Zn, Cd, Cu (11), Ag and In were determined in benzene at 25°C.

Solutions of these metal dithizonates were prepared by two different methods. In the first, solutions were prepared directly from the purified solids, and the solutions subsequently standardized by analysis of the liberated metal after decomposition of the chelate. Weber and Vouk (95), and Mathre and Sandell (75) used this method in their determination of the absorptivity of lead dithizonate. Geiger and Sandell (93) used it for the determination of the absorptivities of primary and secondary copper dithizonates.

FIGURE 38

ABSORPTIVITY OF OXINE IN BENZENE AT 25°C,
AS A FUNCTION OF WAVELENGTH


MOLAR ABSORPTIVITY X 10^{-3}
2
1
0
400
350
300
WAVELENGTH, mu


MOLAR ABSORPTIVITY X 10^{-3}
2
1
0
400
350
300
WAVELENGTH, mu

In the second method, a solution of the metal dithizonate was prepared by extracting a known amount of metal with a benzene solution of dithizone (100).

Irving and Ramakrishna (91) criticised the first method, because light-absorbing impurities in the solution are ignored. Therefore in the present work, an independent test was made of the purity of each metal dithizonate used.

Now Irving and Ramakrishna showed that "the extinction coefficient obtained experimentally, when a sample of dithizone having a purity of only 85% was used, is less than 5% greater than the value obtained with the purest available dithizone". The purities of the metal dithizonates used in the present work are listed in Table 14 of Section IV B subsection 9 (d). All metal dithizonates were found to be at least 98% pure. According to the findings of Irving and Ramakrishna, the impurities in these products would therefore produce an error in the absorptivity that was in fact lower than the standard deviation found for the determination of those absorptivities.

The second method required caution in order to prevent decomposition of the metal dithizonate solution during washing. Care was also taken to ensure that the reagents used were extremely pure. A 1.0 ± 0.2% excess of dithizone was always present after extraction, to ensure complete extraction of the metal dithizonate. In extractions from alkaline solution, the excess dithizone remained in the

aqueous phase and only a very small amount remained in the organic phase. One washing with 1:100 ammonia solution was sufficient to remove this amount. The aqueous phase was always tested for complete extraction by shaking with 10^{-7} M dithizone solution in benzene and observing the change in absorbance.

Only the first method was used to prepare solutions of primary and secondary copper dithizonates*. The solutions were freshly prepared and the spectral transmission curves measured immediately, because primary copper dithizonate solutions disproportionate into secondary copper dithizonate and dithizone on standing (93).

Solutions of silver dithizonate were prepared by both methods. In the second, the silver dithizonate was extracted from an acid aqueous solution, and the excess dithizone was allowed to remain in the organic phase**. Since a

---

*Primary copper dithizonate is usually prepared by extraction from acid solution and any excess dithizone must be removed by shaking with alkali (93). This is impossible, because primary copper dithizonate is changed to secondary copper dithizonate in neutral or alkaline solutions (93).

**Cooper and Sullivan (100) removed this excess by washing with 1:100 ammonia solution, but some of the silver dithizonate could then be decomposed into secondary silver dithizonate.

known concentration of silver was extracted with a known concentration of dithizone, the amount of excess dithizone was known. The composite spectral transmission curve was measured. The absorbance due to dithizone was then subtracted, to yield the spectral transmission curve of silver dithizonate alone. The variances of the absorptivities were significantly higher than those obtained by the first method. Therefore these measurements were rejected and only those obtained by the first method were used in the evaluation of the absorptivity of silver dithizonate.

Absorptivities of the metal dithizonate solutions were measured over as wide a concentration range as possible. These ranges are given in Table 27. In general the concentration from solution to solution varied by a factor of about 2.5. Each solution was prepared in triplicate.

The same aqueous-phase conditions as those reported in Table 1 of Appendix XIII were used for the extraction procedure. The required concentration ranges were obtained by taking appropriate aliquots of the standard metal solutions. Each solution was shaken for ten minutes to ensure complete extraction. For solutions prepared from the purified solids, the required concentration range was obtained by accurate dilution of the standardized stock solution of metal dithizonate. The methods of analysis for the metal after decomposition of the chelate were the same as those reported in Section IV B subsection 9 for the individual

TABLE 27

THE CONCENTRATION RANGES USED FOR THE DETERMINATION OF THE MOLAR ABSORPTIVITIES OF METAL DITHIZONATES IN BENZENE

Metal Dithizonate	Solution Prepared by Extraction		Solution Prepared from Pure Solid	
	Concentration Range	Total No. Of Solns.	Concentration Range	Total No. Of Solns.
$Pb(HDz)_2$	5×10^{-5} M - 5×10^{-7} M	27	5×10^{-5} M - 5×10^{-7} M	21
$Zn(HDz)_2$	10^{-4} M - 2.5×10^{-7} M	36	5×10^{-5} M - 2.5×10^{-7} M	30
$Cd(HDz)_2$	10^{-5} M - 5×10^{-7} M	21	2×10^{-5} M - 5×10^{-7} M	21
$Cu(HDz)_2$	-	-	10^{-4} M - 10^{-6} M	36
CuDz	-	-	10^{-4} M - 10^{-6} M	36
AgHDz	-	-	5×10^{-5} M - 10^{-6} M	21
$In(HDz)_3$	10^{-4} M - 2.5×10^{-7} M	36	10^{-4} M - 2.5×10^{-7} M	36

metal dithizonates. A summary of the methods is given in Table 28.

Solutions of lead and indium dithizonates, and primary and secondary cupric dithizonates were also prepared in dried benzene from the purified, dried solids, in order to determine the effect, if any, of the presence of water on the absorptivity. No effect was observed.

The spectral transmission curves of all solutions were measured from 750 to 350 mμ on the Perkin Elmer Model 350 Spectrophotometer. Spectral transmission curves measured with the use of 1-cm and 5-cm cells were thermostated at 25 ± 0.1°C; those obtained with the use of 0.1-cm and 10-cm cells could not be temperature-controlled and were at ambient temperature. The effect of temperature on the absorptivities of metal dithizonates was determined; no changes were observed when the temperature was raised from 25°C to 40°C. Therefore ambient temperatures were satisfactory. The values of the absorptivities were calculated at 5 mμ intervals from the measured absorbance and the concentration of metal dithizonate in the benzene solutions. Tables1-7 of Appendix XX give the average numerical values and the variances of the absorptivities at 10 mμ intervals from the individual metal dithizonates in benzene at 25°C*. Beer's Law was found to be obeyed for all the metals, over

*The values in chloroform and carbon tetrachloride are not much different from those in benzene. A comparison of values at the wavelength peaks is given in Appendix XXI.

TABLE 28

METHODS OF ANALYSIS FOR THE LIBERATED METALS AFTER DECOMPOSITION OF THE METAL DITHIZONATES

Metal	Procedure Used
Pb	Polarography in 0.1 N HCl
Zn	Polarography in 1 M NH_3/1 M NH_4Cl
Cd	Polarography in 0.1 N HCl
In	Polarography in 2.5 N HCl, sat. sodium formate 5% hydrazine hydrochloride
Ag	Polarography in 1 M KNO_3, 1 M KSCN
Cu	Colorimetrically as Dibenzyldithiocarbamate

the concentration ranges studied. The absorptivity curves for the individual metal dithizonates in benzene are illustrated in Figure 39 (a)-(g). Figure 40 shows all the curves on one scale.

(ii) Statistical treatment of absorptivity data

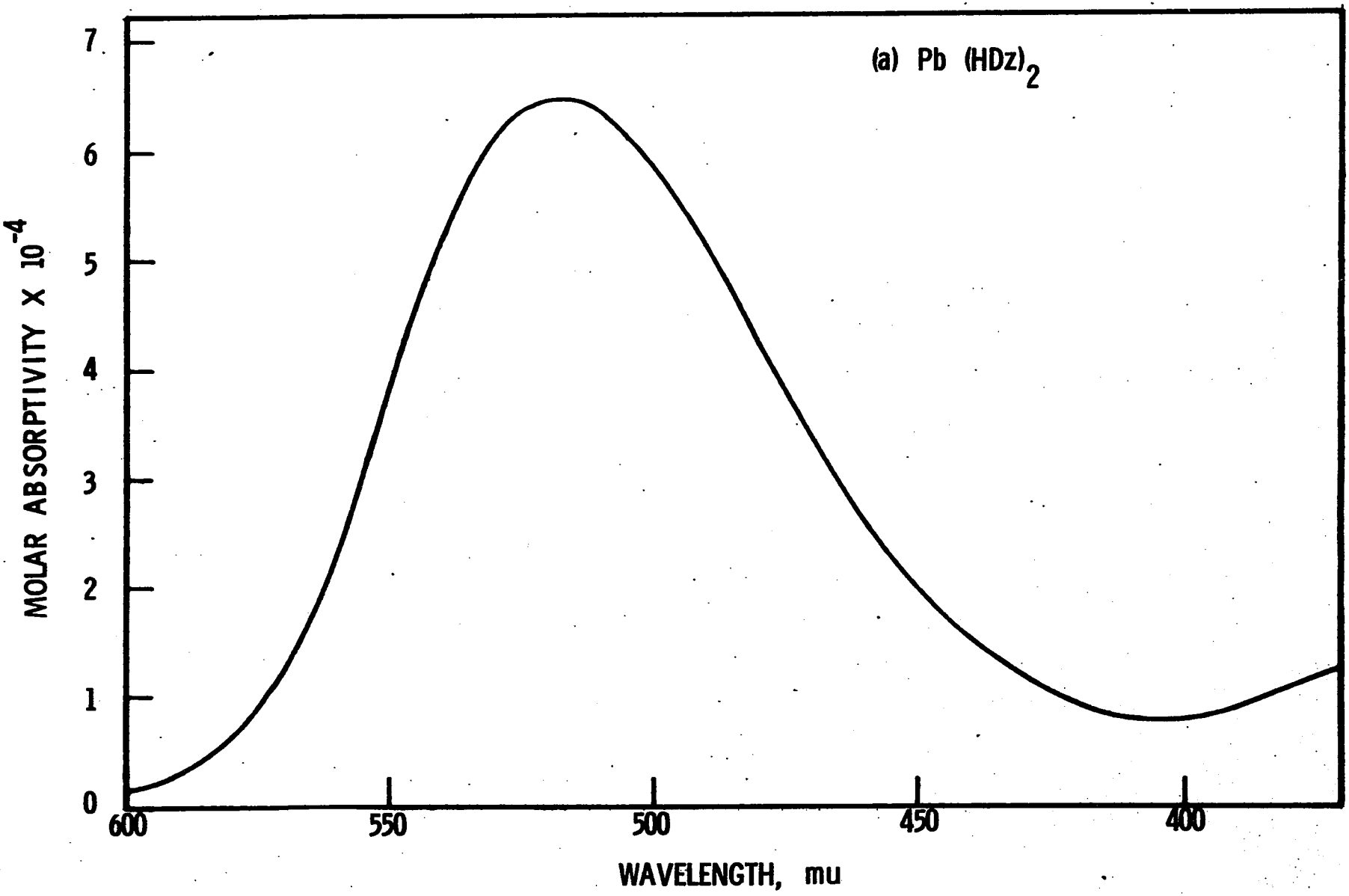
It was found with the use of Bartlett's criterion that the variances at the different wavelengths were not homogeneous at the 95% level. As expected the variances on the high-wavelength side of the absorption peak were higher than those on the low-wavelength side. The absorption curves are not symmetrical and rise more steeply on the high-wavelength side. Therefore the small deviations in the tabulated concentrations of the solutions will produce proportionately larger deviations in the absorbance there. However, at the absorption maxima and minima the variances are at a minimum. The above described inhomogeneity of variance with wavelength is important in calculations using absorptivities.

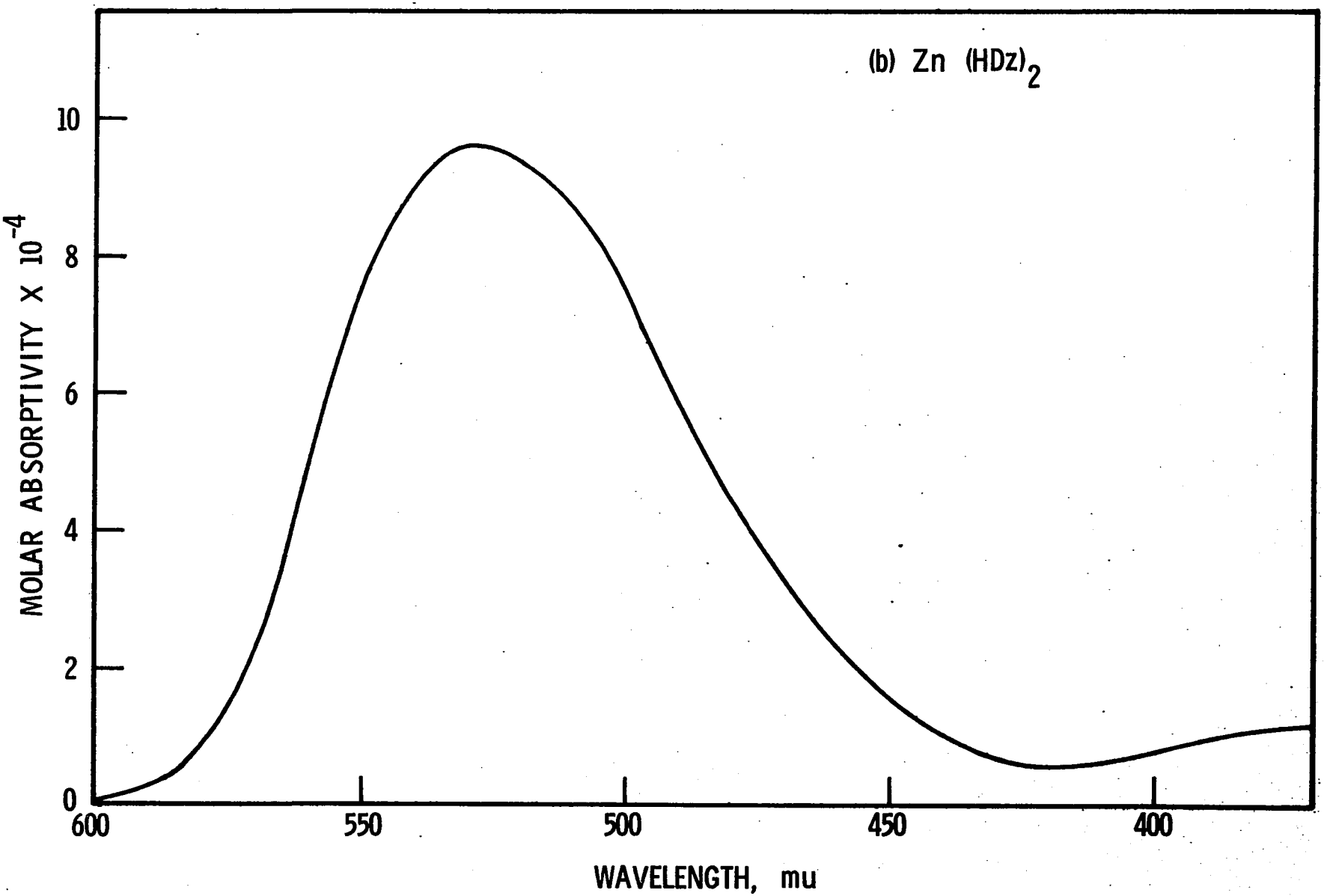
The absorptivity data of all the metal dithizonates was statistically evaluated with the use of analysis of variance. This analysis gave an estimate of the variance associated with changing the concentration which could then be compared with the variance due to reproducibility at an individual concentration. Where two methods (i.e. preparation of solutions from the purified solid and by extraction) were used to measure absorptivities, the variances associated with each method were compared.

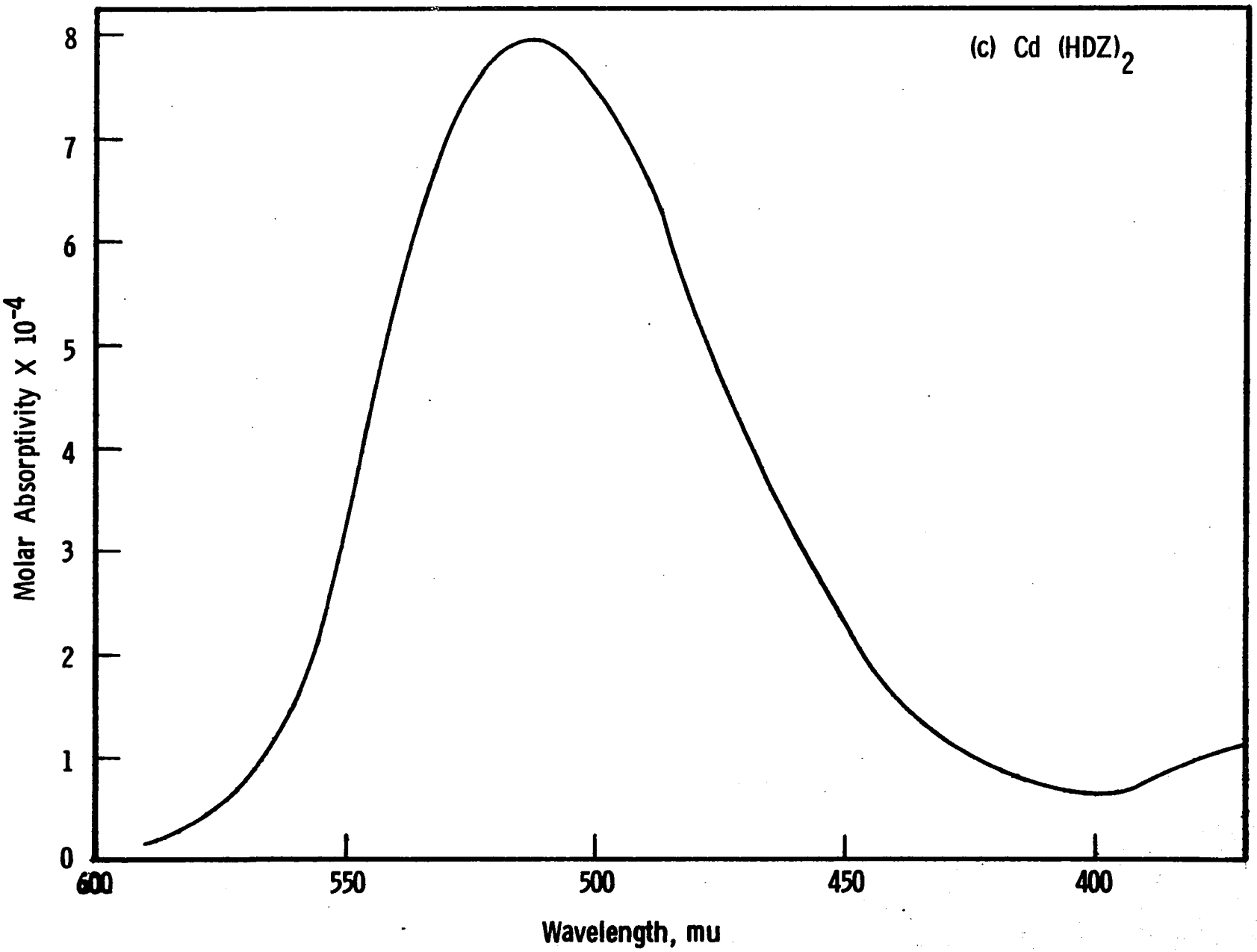
FIGURE 39

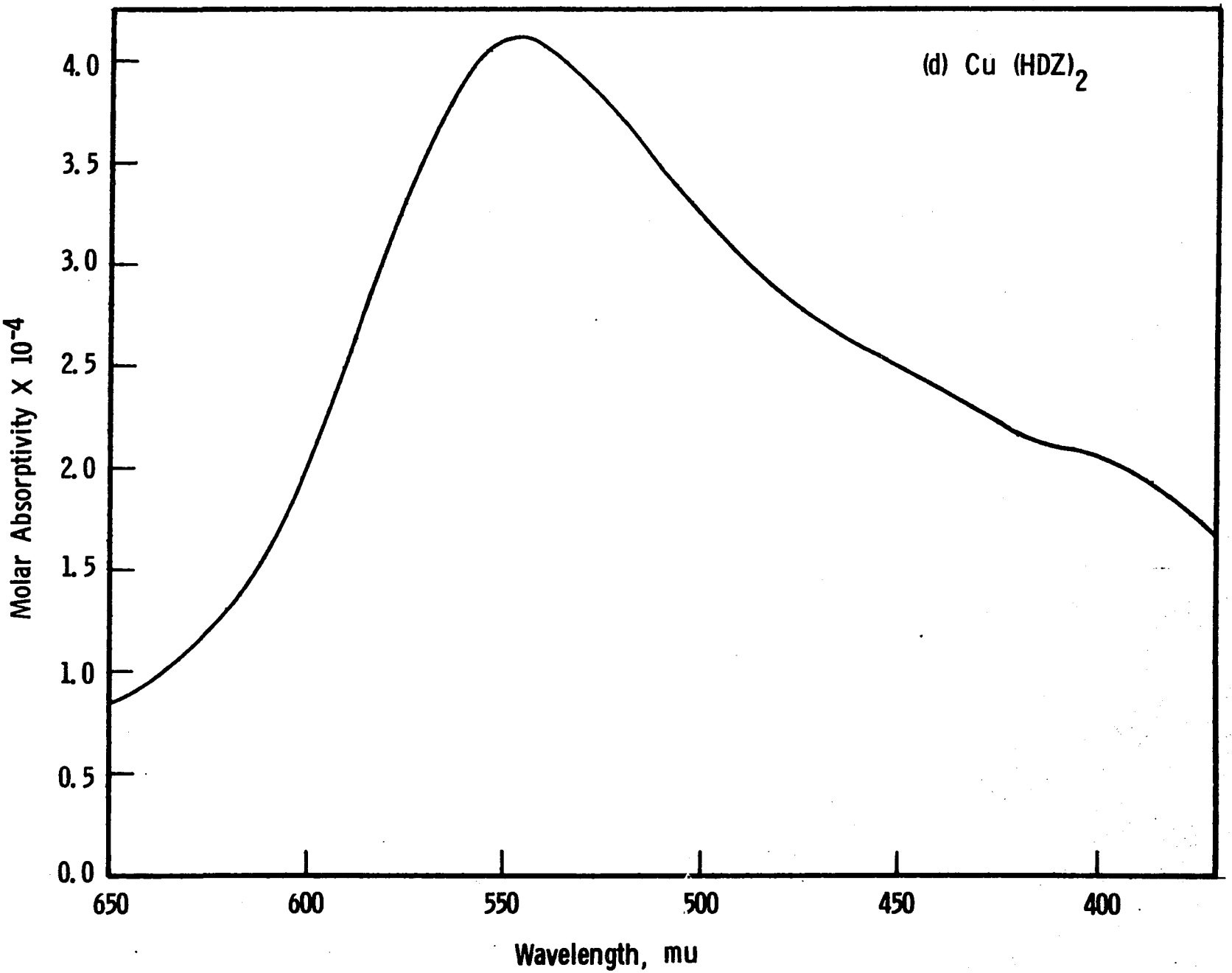
THE MOLAR ABSORPTIVITY CURVES OF THE METAL DITHIZONATES IN BENZENE AT 25°C

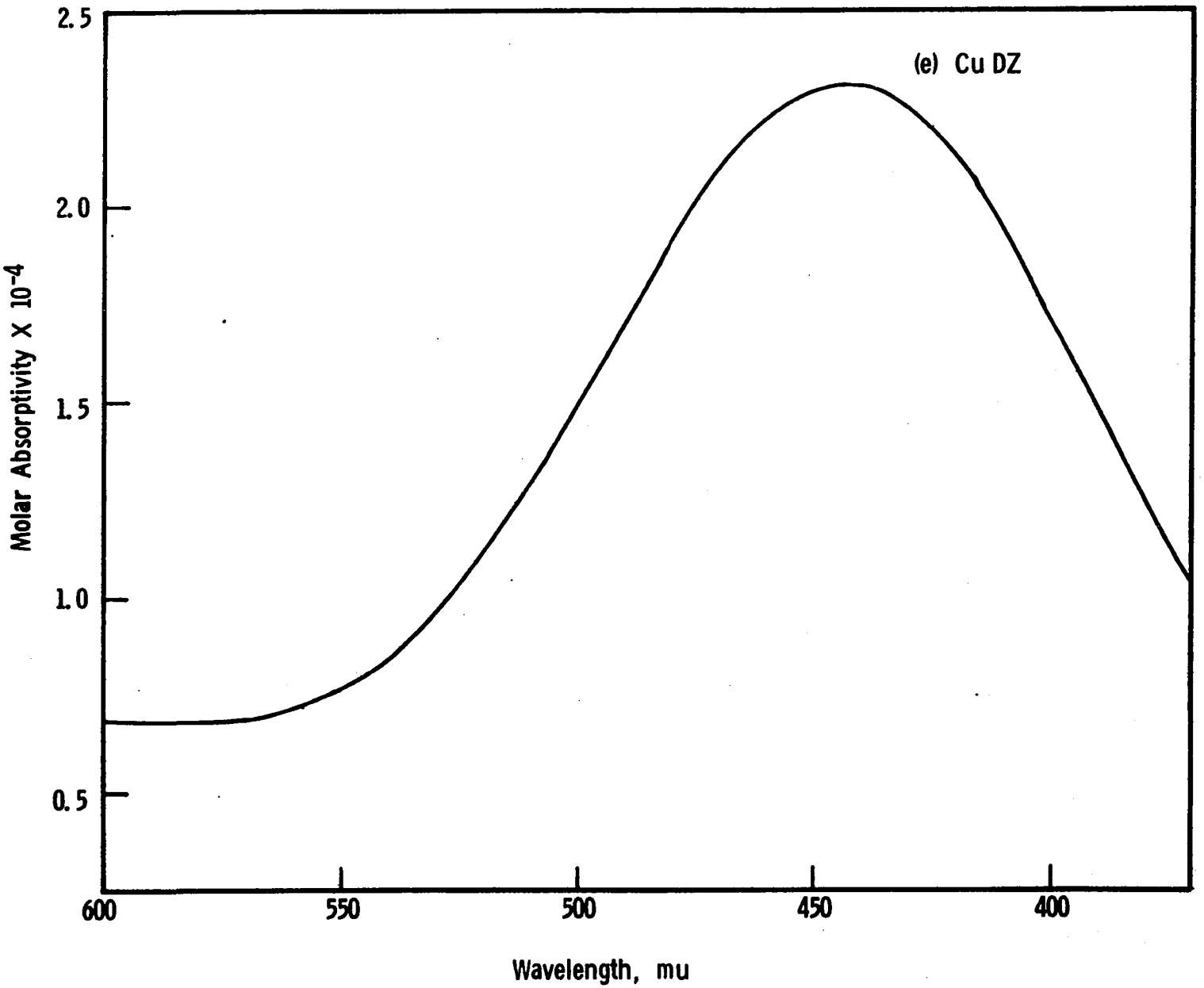
(a) $Pb(HDz)_2$
(b) $Zn(HDz)_2$
(c) $Cd(HDz)_2$
(d) $Cu(HDz)_2$
(e) CuDz
(f) AgHDz
(g) $In(HDz)_3$

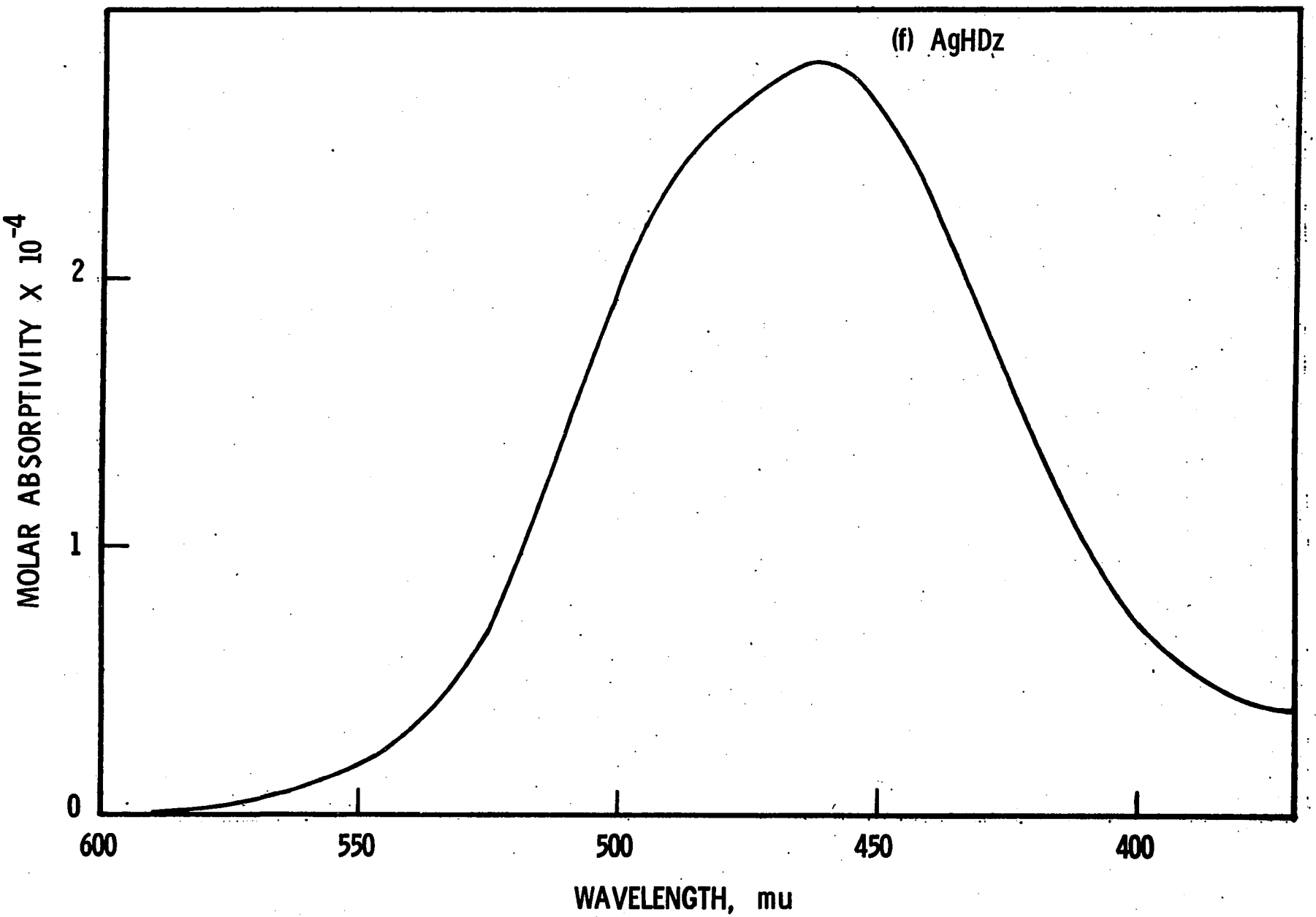

(a) Pb (HDz)2
MOLAR ABSORPTIVITY X 10-4
0
1
2
3
4
5
6
7
600
550
500
450
400
WAVELENGTH, mu


(b) Zn (HDz)2
MOLAR ABSORPTIVITY X 10-4
0
2
4
6
8
10
600
550
500
450
400
WAVELENGTH, mu


(c) Cd (HDZ)2
Molar Absorptivity X 10-4
0
1
2
3
4
5
6
7
8
600
550
500
450
400
Wavelength, mu


(d) Cu (HDZ)2
Molar Absorptivity X 10-4
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
650
600
550
500
450
400
Wavelength, mu


(e) Cu DZ
2.5
2.0
1.5
1.0
0.5
Molar Absorptivity X 10^{-4}
600
550
500
450
400
Wavelength, mu


(f) AgHDz
MOLAR ABSORPTIVITY X 10^{-4}
2
1
0
600
550
500
450
400
WAVELENGTH, mu

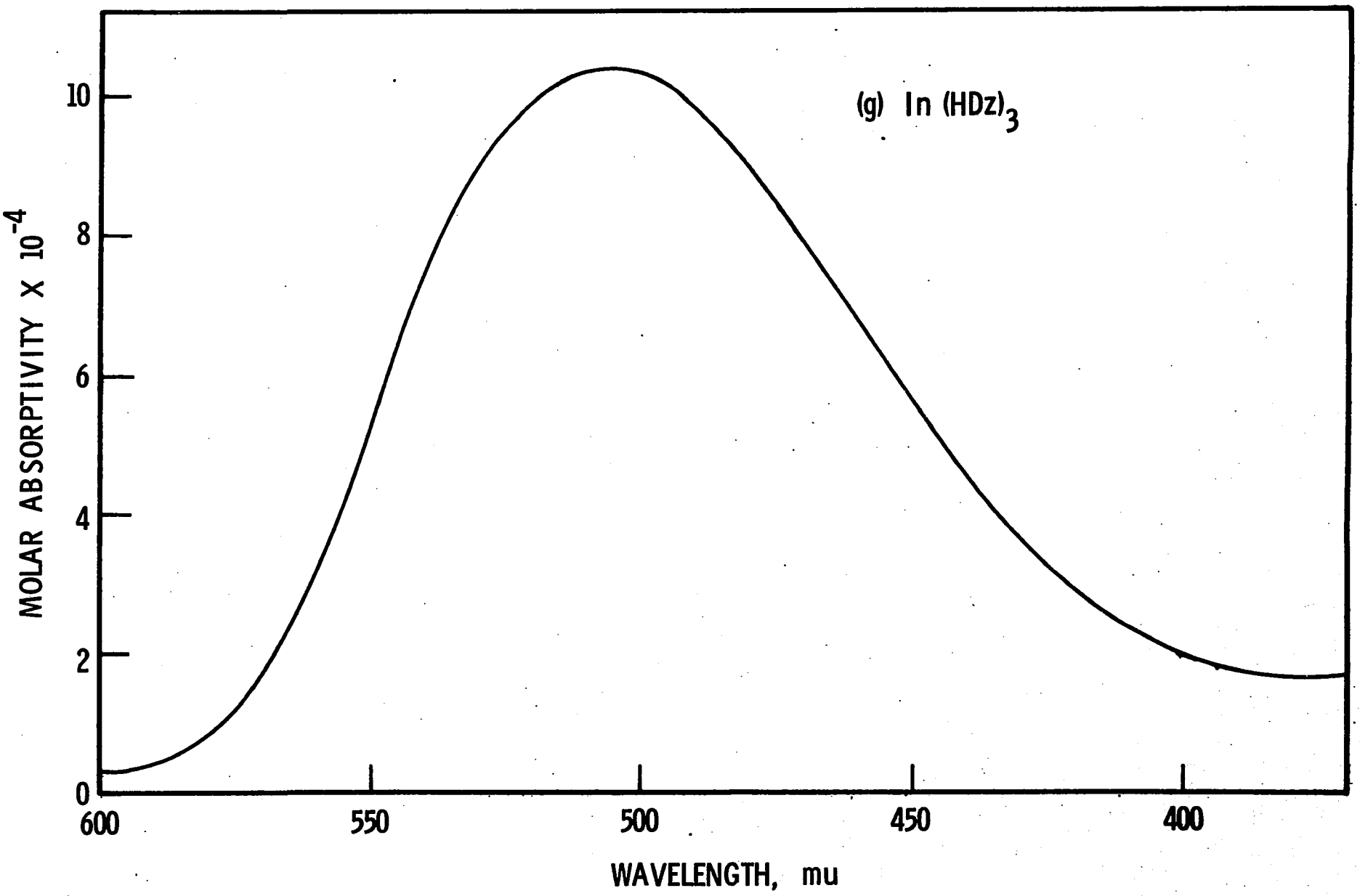
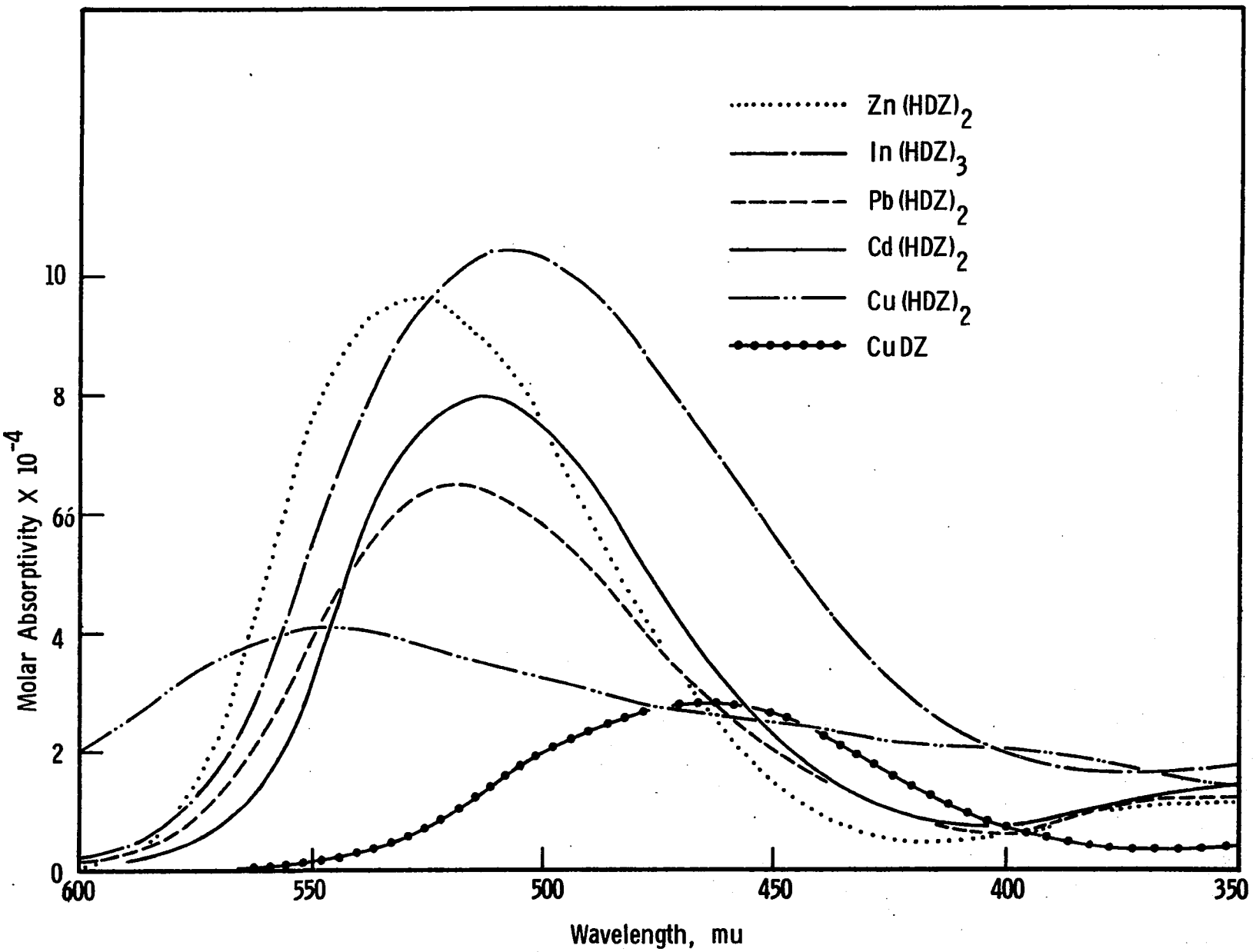

(g) In (HDz)3
MOLAR ABSORPTIVITY X 10-4
0
2
4
6
8
10
600
550
500
450
400
WAVELENGTH, mu

FIGURE 40

COMPARISON OF THE ABSORPTIVITY CURVES
OF THE METAL DITHIZONATES IN BENZENE AT 25°C


Zn (HDZ)2
In (HDZ)3
Pb (HDZ)2
Cd (HDZ)2
Cu (HDZ)2
Cu DZ
Molar Absorptivity X 10-4
0
2
4
6
8
10
600
550
500
450
400
350
Wavelength, mu

As an example, the statistical treatment of the data for lead dithizonate is presented in Table 29. It was found by Bartlett's criterion that the variances obtained at individual concentrations were homogeneous at a given wavelength. The variances were then pooled to give one variance. It was found that the differences between the variances associated with using the different starting materials (solutions by extraction and solutions from pure solid) were insignificant at the 95% level. These two variances were then pooled to give one grand variance. The grand mean was also calculated.

The same results were found when the absorptivity data of all metal dithizonates studied was statistically evaluated. Thus in the tables of Appendix XXII the overall means and pooled variances are reported.

(iii) Ultraviolet spectra

In exploratory studies, the ultraviolet spectra of the metal dithizonates were measured. However, there were no peaks characteristic of the compounds. For all the metal dithizonates studied, the absorptivity in the ultraviolet region was much lower than that in the visible region.

(d) The Metal Oxinates

The oxinates of lead, zinc, cadmium and indium had peaks on the edge of the visible region; those of copper, cobalt and nickel had peaks in the visible region. The

TABLE 29

STATISTICAL TREATMENT OF THE DATA FOR THE DETERMINATION OF THE ABSORPTIVITY OF LEAD DITHIZONATE AT 517 mμ IN BENZENE

Data From Solutions Prepared From Purified Solid

Molar Conc. $Pb(HDz)_2$	5.070×10^{-5}	5.111×10^{-5}	1.014×10^{-5}	5.111×10^{-6}	2.028×10^{-6}	1.008×10^{-6}	5.070×10^{-7}
$a \times 10^{-4}$	6.48	6.40	6.48	6.55	6.62	6.48	6.58
	6.38	6.44	6.56	6.54	6.57	6.51	6.52
	6.63	6.48	6.46	6.47	6.51	6.45	6.70
Total $\times 10^{-4}$	19.49	19.32	19.50	19.56	19.70	19.44	19.80
Mean $a \times 10^{-4}$	6.50	6.44	6.50	6.52	6.57	6.48	6.60
$S^2 \times 10^{-4}$	1.58	0.16	0.28	0.19	0.31	0.09	0.84

Test for homogeneity of S_i^2[1]

$$B = \chi^2 = 8.3 < \chi^2_{0.05}\ (6) = 12.6$$

Pooled Variance $\overline{S}_1^2 = 6.05 \times 10^5$

Mean of all values of absorptivity, $a_{11} = 6.51 \times 10^4$

Data From Solutions Prepared by Extraction

Molar Conc. $Pb(HDz)_2$	4.963×10^{-5}	2.482×10^{-5}	9.926×10^{-6}	7.44×10^{-6}	4.963×10^{-6}	2.482×10^{-6}	9.926×10^{-7}	7.44×10^{-7}	4.963×10^{-7}
$a \times 10^{-4}$	6.28	6.61	6.38	6.55	6.45	6.35	6.43	6.37	6.57
	6.31	6.52	6.50	6.50	6.38	6.26	6.30	6.46	6.40
	6.43	6.46	6.65	6.36	6.52	6.35	6.41	6.37	6.44
Total $\times 10^{-4}$	19.02	19.59	19.53	19.41	19.35	18.96	19.14	19.20	19.41
Mean $a \times 10^{-4}$	6.34	6.53	6.51	6.47	6.45	6.32	6.38	6.40	6.47
$S^2 \times 10^{-4}$	0.63	0.57	1.83	0.97	0.49	0.27	0.49	0.27	0.79

Test for homogeneity of S_i^2[1]

$$B = \chi^2 = 4.1 < \chi^2_{0.05}\ (8) = 15.5$$

Pooled Variance $\overline{S}_2^2 = 9.12 \times 10^5$

Mean of all values of absorptivity, $a_{12} = 6.43 \times 10^4$

Tests of Significance between Methods

Variances

$F = \overline{S}_2^2/\overline{S}_1^2 = 1.51 < F_{0.05}\ (26,20) = 2.07$

∴ Variances not significantly different

Means

$t = 1.79 < t_{0.05}\ (14) = 2.14$

∴ Means not significantly different

Grand Mean of Absorptivity = 6.47×10^4

Grand Variance = 7.79×10^5

Standard Deviation = 8.8×10^2 (47 degrees of freedom)

[1] Bartlett's Criterion (119).

207

absorptivities of the oxinates of Pb, Zn, Cd, Cu (11) and In were determined in benzene at 25°C*.

The solutions of the metal oxinates were prepared from the pure solids. Stock saturated solutions were prepared in replicate, and standardized by the methods reported in Section IV B subsection 8. From these standard solutions working solutions were prepared in triplicate by accurate dilution. As wide a concentration range as possible was used. The absorbance of the most dilute solution was in no case less than 0.200 in a 10-cm cell, at the wavelength of maximum absorption. The concentration ranges used for the metal oxinates are given in Table 30.

The absorptivities of copper, lead and indium oxinates were measured both in spectrophotometric-grade benzene and in specially dried benzene; with dried solids. The values of the absorptivities were found not to depend on drying the solvent. However, the absorptivities of $ZnOx_2$ and $CdOx_2$ were determined exclusively in dried benzene.

The spectral transmission curves of each solution were recorded with a Perkin Elmer Model 350 spectrophotometer. Both visible and ultraviolet regions were scanned. The temperature of the solution was kept at 25 ± 0.1°C except when 10-cm cells were used. Tests showed that there was no change in absorbance when the temperature was raised from 25°C to 40°C. Absorptivities were then calculated at 5 mμ

*The very low solubility of silver oxinate in benzene prevented measurements on it.

TABLE 30

CONCENTRATION RANGES USED FOR THE DETERMINATION OF THE ABSORPTIVITIES OF METAL OXINATES IN BENZENE

Metal Oxinate	Concentration Range	Total No. Of Solns.
$PbOx_2$	5×10^{-5} M - 2.5×10^{-6} M	19
$ZnOx_2$	10^{-4} M - 5×10^{-6} M	22
$CdOx_2$	5×10^{-5} M - 5×10^{-6} M	16
$CuOx_2$	10^{-4} M - 2.5×10^{-6} M	25
$InOx_3$	2×10^{-3} M - 5×10^{-6} M	37

intervals in the visible region, and 2.5 mμ intervals in the ultraviolet region. They are tabulated for 10 mμ and 5 mμ intervals respectively, together with the variances in Tables 1-5 of Appendix XXII. For all metal oxinates studied, Beer's Law was obeyed over the concentration range used. The absorptivity curves are shown in Figure 41 (a) to (e) and all on one scale in Figure 42 for comparison.

The absorptivities of the metal oxinates in the ultraviolet region were important when the concentration of excess oxine was determined in the organic phase after solvent extraction. In general, the absorptivities of the metal oxinates in benzene at 313 mμ, the absorption maximum of oxine, are of the same order of magnitude as that of oxine (see Figure 42). Hence, for low concentrations of metal oxinate and an excess of oxine large in comparison, a reasonable estimate of the concentration of oxine was feasible.

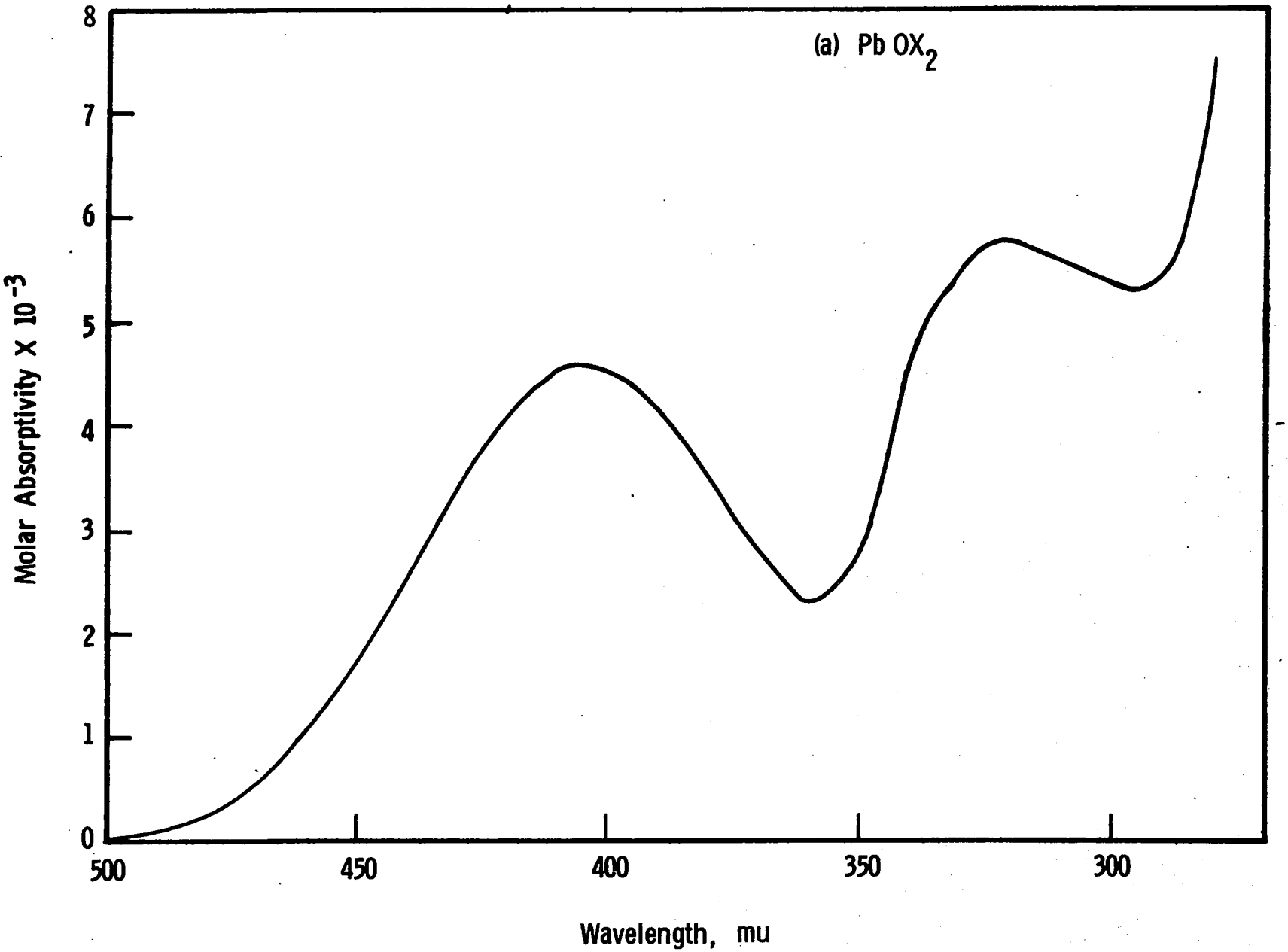
6. Procedures for Spectrophotometric Study of Reactions of Lead, Copper and Indium Oxinates with Dithizone in Benzene at 25°C

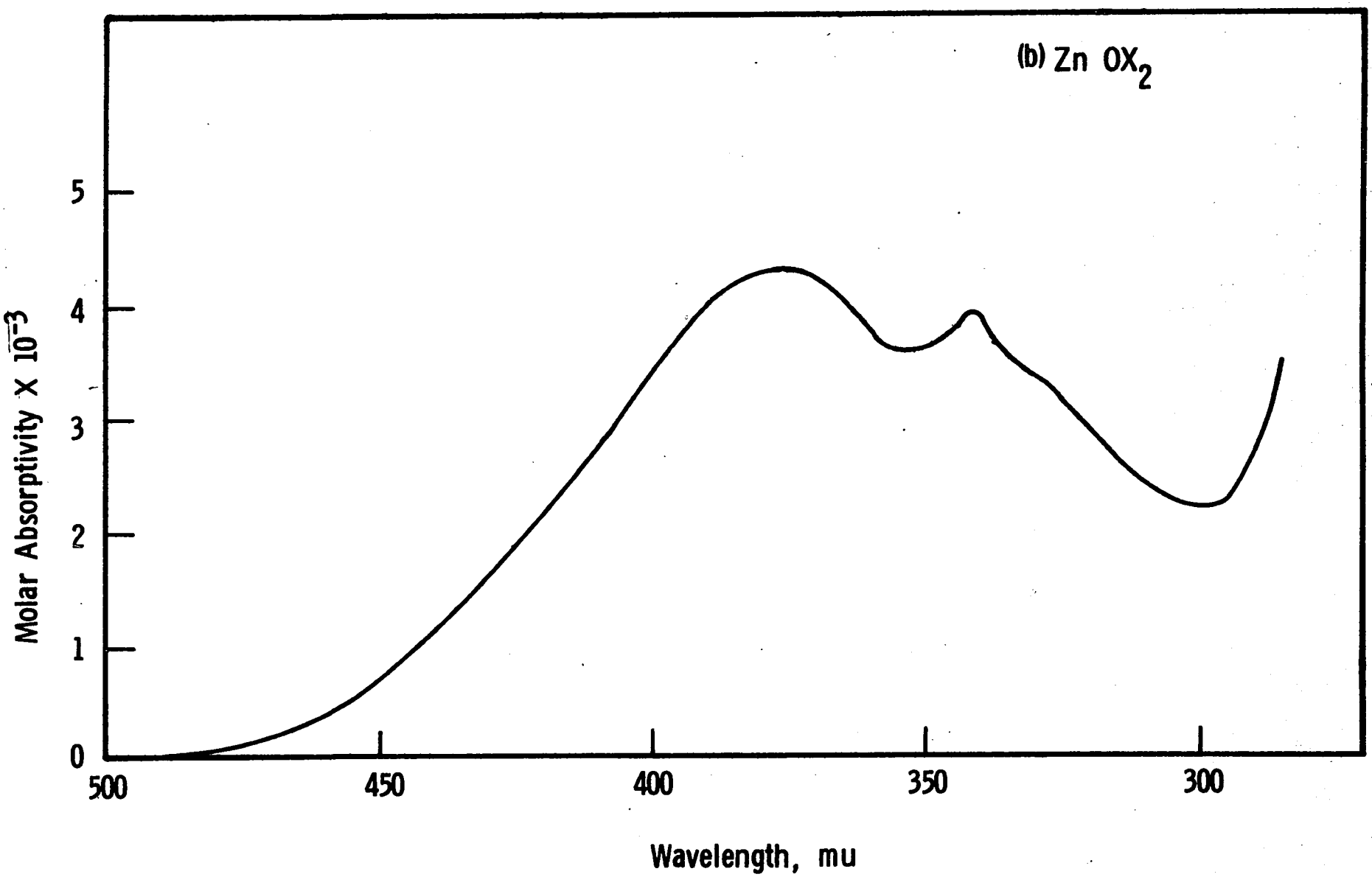
In order to calculate the theoretical titration graph for the titration of a metal oxinate with dithizone in benzene, it was necessary to measure the equilibrium constants for that reaction. Thus, a detailed study was made of the reactions in benzene between dithizone and the individual oxinates of lead, copper and indium. The relevant equili-

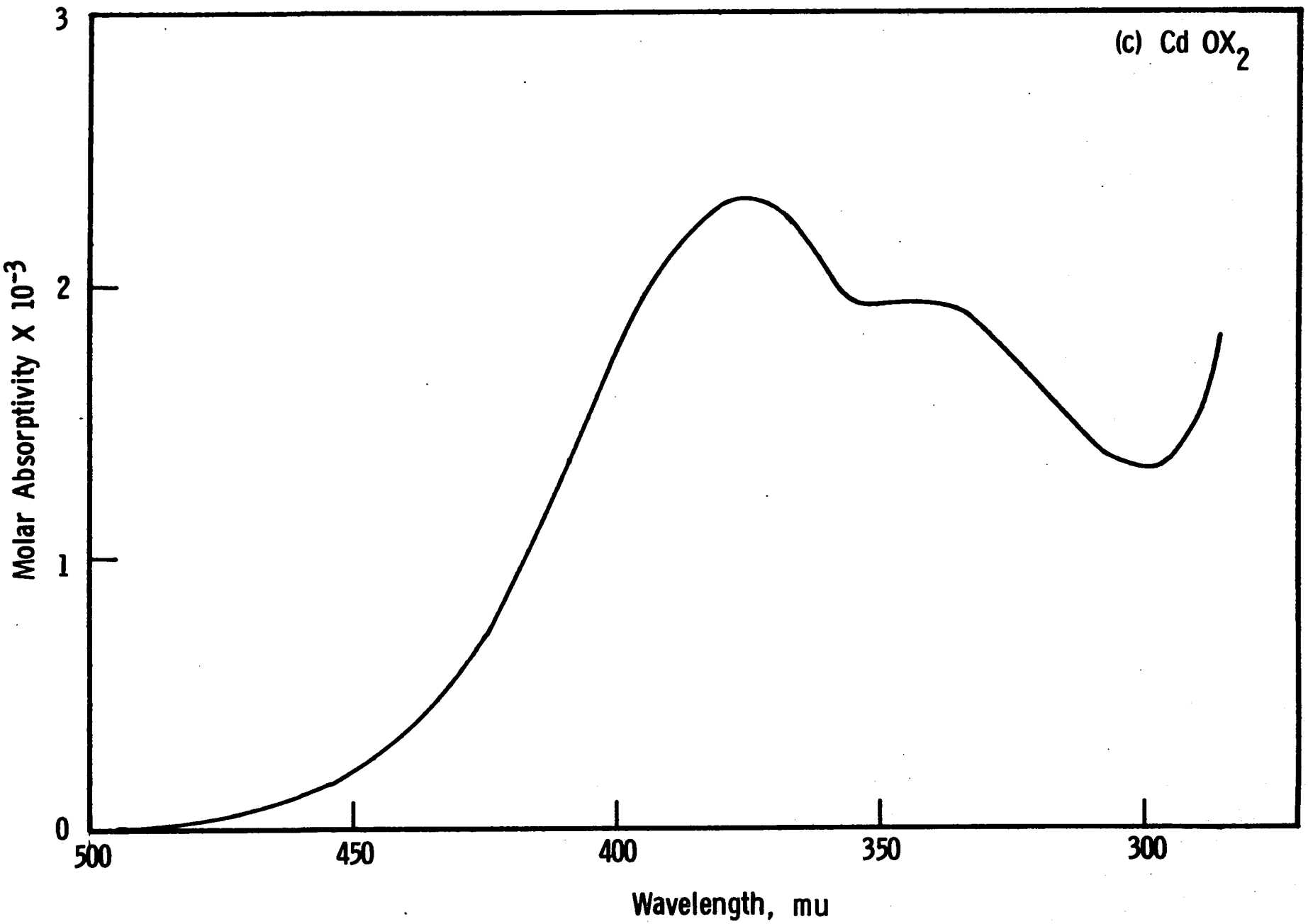
FIGURE 41

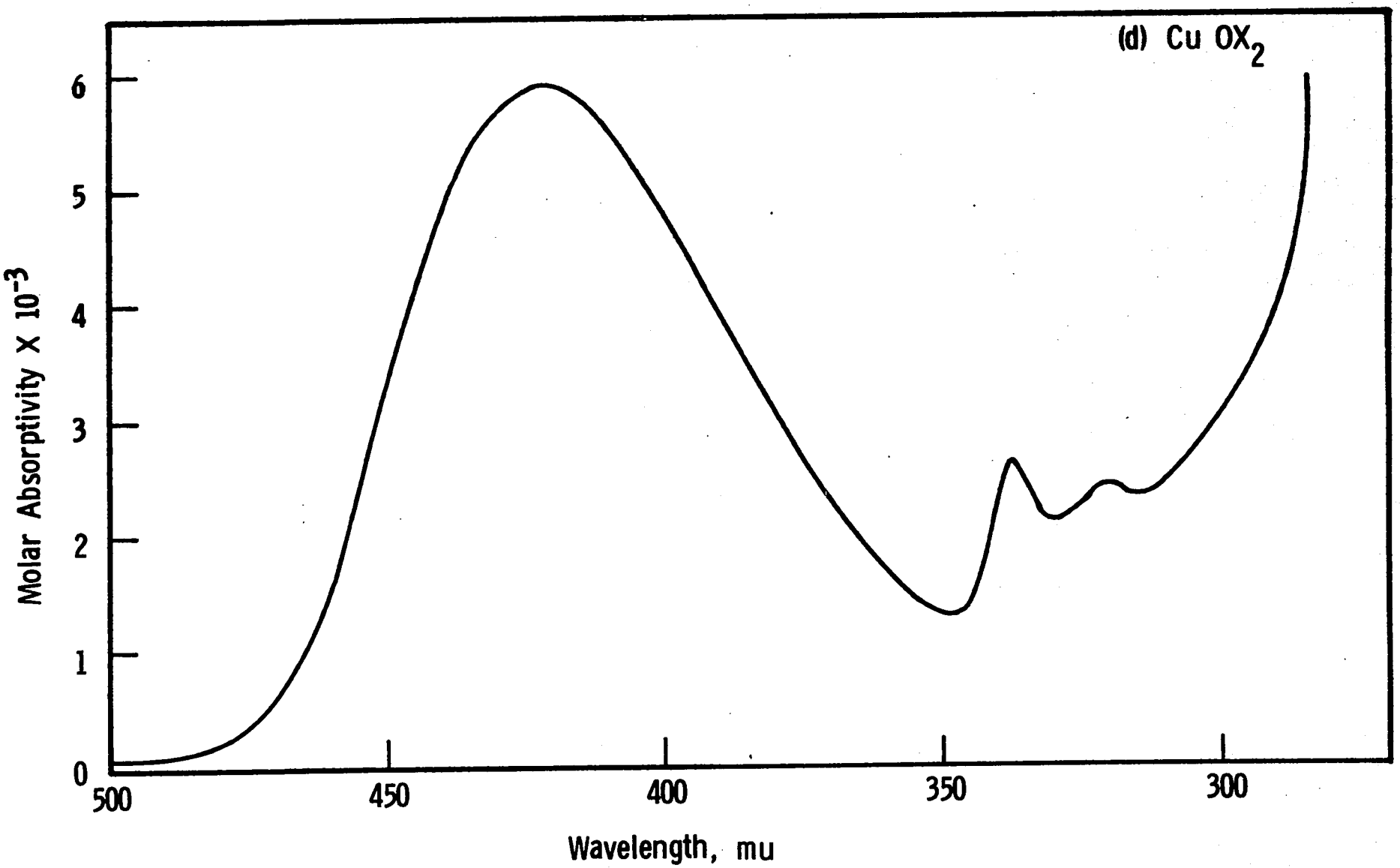
MOLAR ABSORPTIVITY CURVES FOR THE METAL OXINATES IN BENZENE AT 25°C

(a) $PbOx_2$
(b) $ZnOx_2$
(c) $CdOx_2$
(d) $CuOx_2$
(e) $InOx_3$


(a) Pb OX_2
Molar Absorptivity X 10^{-3}
8
7
6
5
4
3
2
1
0
500
450
400
350
300
Wavelength, mu


(b) Zn OX_2
Molar Absorptivity X 10^{-3}
0
1
2
3
4
5
500
450
400
350
300
Wavelength, mu


(c) Cd OX2
Molar Absorptivity X 10-3
3
2
1
0
500
450
400
350
300
Wavelength, mu


(d) Cu OX_2
Molar Absorptivity X 10^{-3}
6
5
4
3
2
1
0
500
450
400
350
300
Wavelength, mu

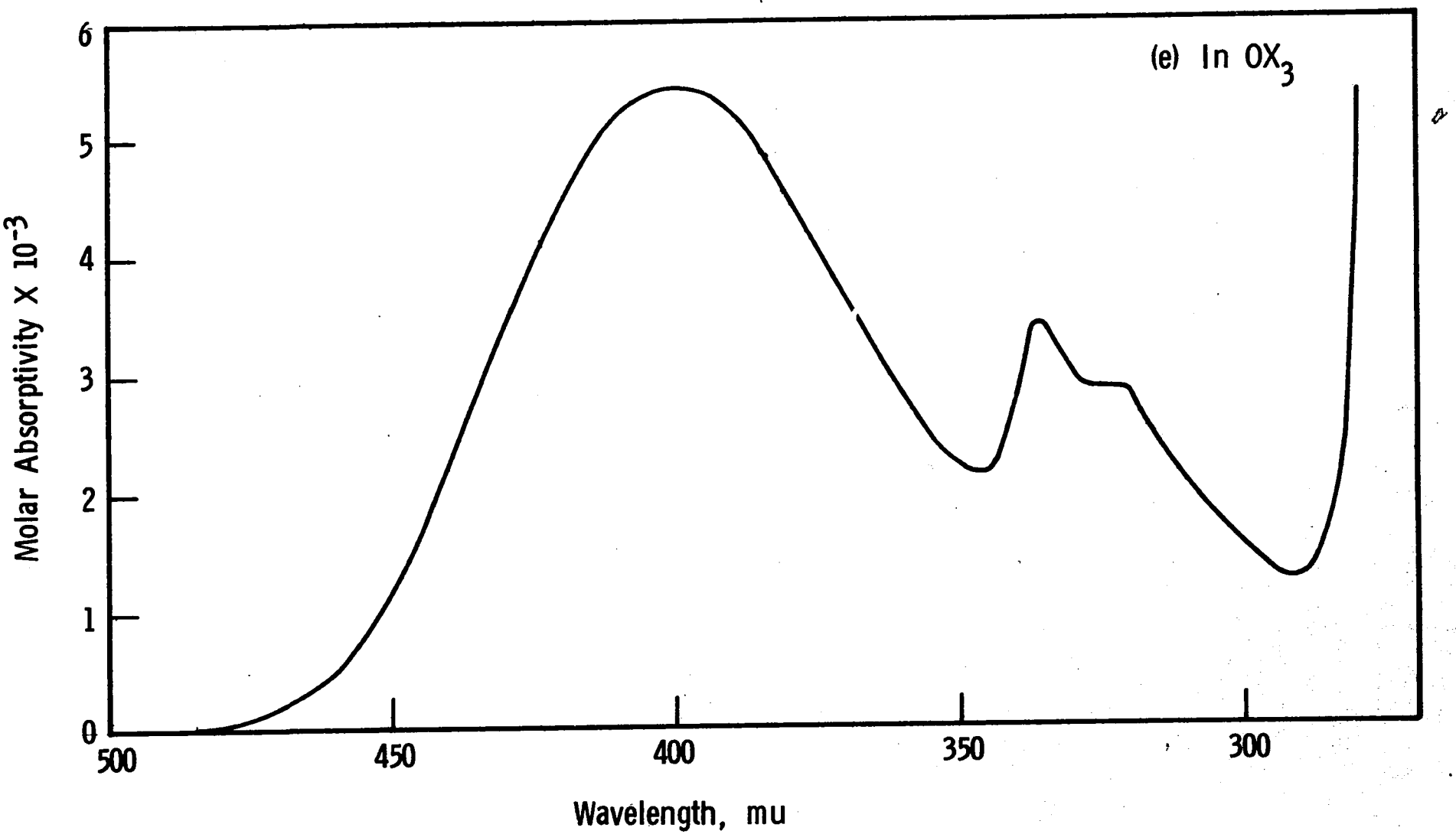
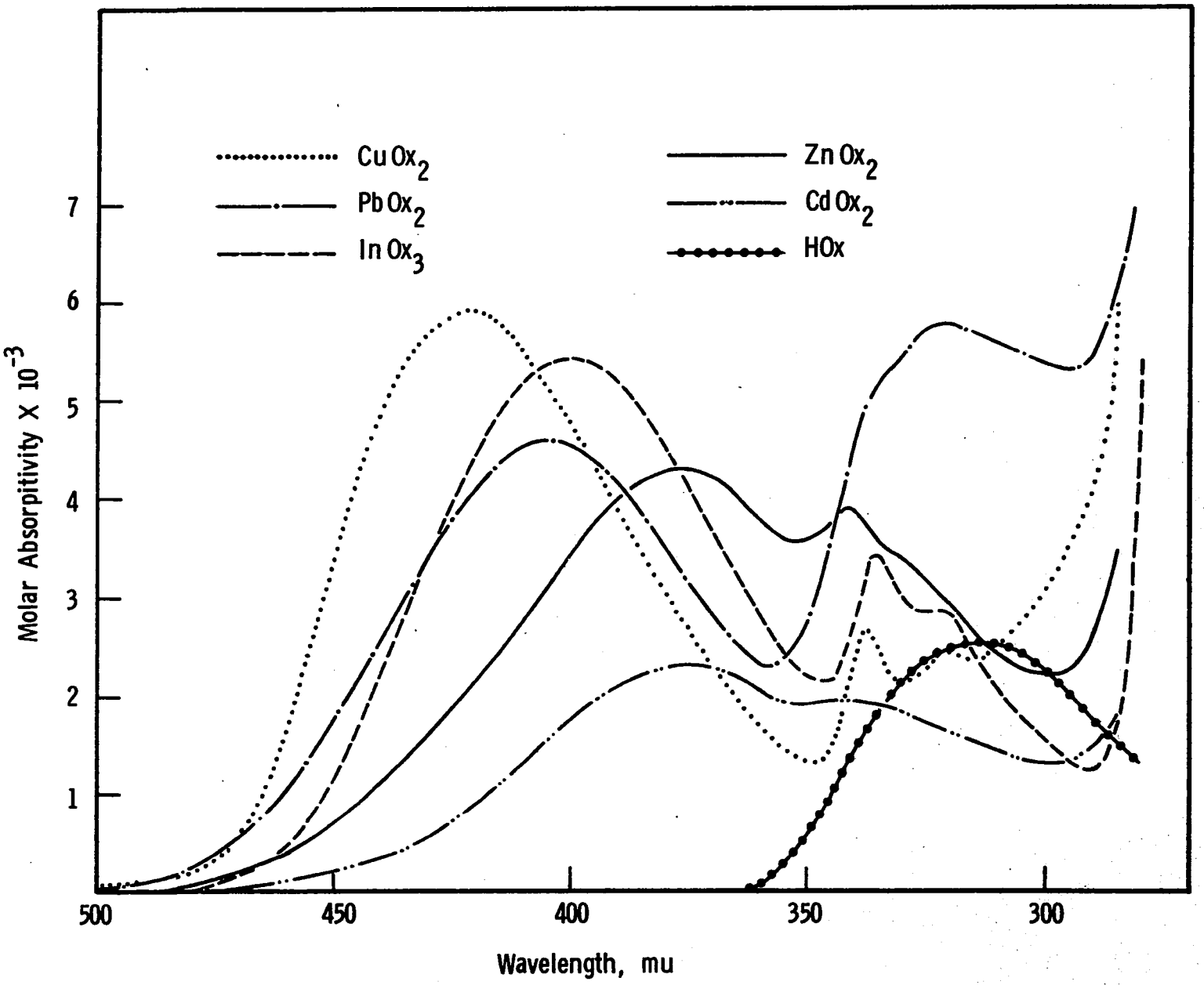

(e) In OX_3
Molar Absorptivity X 10^{-3}
6
5
4
3
2
1
0
500
450
400
350
300
Wavelength, mu

FIGURE 42

COMPARISON OF THE MOLAR ABSORPTIVITY CURVES
OF THE METAL OXINATES AND OXINE,
IN BENZENE AT 25°C


Cu Ox2
Pb Ox2
In Ox3
Zn Ox2
Cd Ox2
HOx
Molar Absorptivity X 10-3
7
6
5
4
3
2
1
500
450
400
350
300
Wavelength, mu

brium constants were measured by using two different spectrophotometric techniques; namely the Method of Continuous Variations, and the Ratio Method. Measurements were made with the Perkin Elmer Model 350 spectrophotometer.

(a) Method of Continuous Variations (62,63)

In the Method of Continuous Variations, the sum of the concentrations of reactants is kept constant, while the ratio of the individual concentrations are varied. In the present work, the total concentrations of the copper and indium systems were 10^{-4} M and 10^{-5} M. In the lead system, because of the lower solubility of lead chelates, the total concentration was about 10^{-5} M. "Job Plots" were constructed from 21 points, each point representing a solution. The concentration of reactants in a given series of solutions was varied in 0.5 concentration units. Thus, for a total concentration of 10^{-4} M, the concentration of one reactant was in steps 10^{-4} M, 9.5×10^{-5} M, 9.0×10^{-5} M, 8.5×10^{-5} M ..... and the concentration of the other reactant was in corresponding steps 0, 0.5×10^{-5} M, 1.0×10^{-5} M, 1.5×10^{-5} M .....

In practice accurately measured volumes of the standardized solutions of the reactants (dithizone and metal oxinate) in benzene were delivered from 5-ml Koch micro-burets into volumetric flasks of red, low-actinic glass. The solutions were prepared in subdued light in a

room in which the temperature was kept constant at 23 ± 2°C. The solutions were then allowed to stand for one week*.

In some series the sum of the concentrations of dithizone and of metal oxinates were kept constant and the ratio of the individual concentrations varied as described above. But, in addition, for each set of solutions a constant excess of free oxine was also added. This excess was of the order of 10-100 times the total concentration of reactants. For these solutions, of course, the plots were no longer the conventional continuous variation type of plot.

Some series were prepared in dried benzene in order to determine the effect of a slight amount of moisture in the spectrophotometric-grade benzene. Precautions were taken to prevent the dried benzene and solutions from absorbing moisture by carrying out most of the operations in a dry box. However the initial dispensing of the very small volumes of reactants into the volumetric flasks was done in air so that a very slight amount of moisture may have been picked up. For every series of solutions prepared for the method of continuous variations, replicates (n = 5) were prepared for those ratios of reactants of 4:1, 1:1 and 1:4.

(b) Ratio Solutions

For some of the dithizone-metal oxinate reactions, particularly those for which the equilibrium constant was

*This length of time was not entirely necessary, but was governed by the amount of time that was required to prepare the large number of solutions made up at one time.

low, so-called Ratio Solutions were prepared. In them the concentration of one of the reactants was kept constant and that of the other was varied in known steps.

Aliquots of the standardized solution of one reactant were delivered from pipets into volumetric flasks of red, low-actinic glass. The other reactant was then added either by pipet or from a 5-ml Koch micro-buret. All solutions prepared in dried benzene were manipulated in a dry box. All solutions were prepared in a darkened room at 23 ± 2°C. The solutions were then allowed to stand for one week. In those ratio solutions in which dithizone was one of the reactants, an auxiliary set of solutions containing the same amount of dithizone initially added, were also prepared. The absorbance of these solutions was measured at the same time as those containing both reactants. This precaution was necessary to rule out the possibility that the dithizone had decomposed on standing. The found concentration of dithizone after standing one week should have been, within experimental error, the same as the known, original concentration of dithizone added. Similarly, pure solutions of the other reactants were used as checks.

In every series of ratio solutions prepared, selected solutions were prepared in replicate (n = 5). A high and low ratio of one reactant to the other was selected as well as a solution when the ratio was approximately equal.

The reactions studied are listed in the following subsections (see Appendix XXIV for a detailed description

of the preparation of solutions to study these reactions).

(a) Lead

The following reactions were studied:

1) Lead oxinate with dithizone in wet and dried benzene.

2) Lead oxinate with dithizone in which there was a constant amount of free oxine in excess, in wet and dried benzene.

3) Lead oxinate with lead dithizonate in dried benzene.

4) Lead oxinate with lead dithizonate in the presence of excess free oxine in dried benzene.

5) Lead dithizonate and dithizone in dried benzene.

6) Lead dithizonate and oxine in dried benzene.

(b) Indium

The following reactions were studied in benzene:

1) Indium oxinate with dithizone.

2) Indium oxinate with dithizone in the presence of excess free oxine.

3) Indium dithizonate and oxine.

4) Indium dithizonate and indium oxinate in dried benzene.

5) Indium dithizonate and dithizone.

(c) Copper

The following reactions were studied:

1) Cupric oxinate with dithizone in wet and dried benzene.

2) Cupric oxinate with dithizone in the presence of excess free oxine, in wet and dried benzene.

3) Secondary* cupric dithizonate and dithizone in wet and dried benzene.

4) Secondary cupric dithizonate and oxine in benzene.

5) Primary* cupric dithizonate and dithizone in wet and dried benzene.

6) Primary cupric dithizonate and cupric oxinate.

7) Primary cupric dithizonate and oxine.

The spectra transmission curves of the solutions were measured with the Perkin Elmer Model 350 spectrophotometer. Solutions in 1-cm and 5-cm cells were thermostated at 25 ± 0.1°C. The effect of temperature on the absorbance of the solutions was checked. From 25°C to 40°C, a maximum change of 5% in the absorbance was observed for certain solutions; in a majority of cases, the absorbance changed by only 2-3%.

The absorbances of the solutions at selected wavelengths as required were read off the recorded spectra transmission curves. These and other data necessary for the study of the aforementioned reactions are in Appendices XXVI - XXVIII. From (i) the numerical values of the absorbance, (ii) the known initial concentrations of the reactants and (iii) the absorptivities of the species in solution, the required

---

*Primary cupric dithizonate referes to the dithizonate formed by displacing one of the two replaceable hydrogens on the dithizone molecule, designated $Cu(HDz)_2$. Secondary cupric dithizonate refers to the chelate formed by replacing both hydrogens, designated CuDz.

equilibrium constants could be calculated (see Section IV D, subsection 3 for the calculated values and Section V subsection D for a discussion of the calculations).

7. Infrared Spectra: Preparation of Samples and Results

The infrared spectra of the following compounds were recorded

Lead oxinate	Lead Dithizonate	Oxine
Cupric oxinate	Silver Dithizonate	Dithizone
Cadmium oxinate	Primary Cupric Dithizonate	
Zinc Oxinate	Secondary Cupric Dithizonate	
Indium oxinate		

In addition, the following samples were prepared:

(a) A 1:1 Molar Mixture of Lead Oxinate and Lead Dithizonate

This solid was prepared by dissolving 15 mg of lead dithizonate and 10 mg of lead oxinate in 200 ml of benzene. The benzene was slowly evaporated in the dark in a dry box. Four batches were prepared.

(b) A 1:1 Molar Mixture of Primary Cupric Dithizonate and Dithizone

This sample was prepared by dissolving 28.7 mg of primary cupric dithizonate and 12.8 mg of purified dithizone in 100 ml of dried benzene in a dry box. The solution was evaporated slowly to dryness in the dark and in a dry box under nitrogen.

The spectra were recorded on Nujol mulls of the solids, with a Perkin Elmer Model 521 infrared spectrophotometer

(Section IV A subsection 7). The caesium bromide region, from 750 to 250 cm^{-1} was scanned. Water vapour was removed from the instrument with the use of the pump and drying tower provided with the instrument.

The spectra of dithizone and oxine were recorded in the NaCl, KBr and CsBr regions. Nujol mulls of the solids, and also 5×10^{-4} M solutions in carbon tetrachloride were used.

Information on metal-oxygen, metal-sulphur and metal-nitrogen bonds was sought. Their vibrations occur in the KBr and CsBr regions (104-106). The spectra of metal oxinates in the 4000-750 cm^{-1} region (107-110) and in the 4000-450 cm^{-1} region (111) have been reported. Although "metal-sensitive" bands, attributed to C-O stretching were found, the published data did not provide the sought-for information.

The absorption maxima of the metal oxinates, metal dithizonates, dithizone, oxine and the 1:1 mixtures are given in Table 31. A comparison of the spectra of lead oxinate, lead dithizonate and the corresponding mixture is shown in Figure 43.

The spectra obtained for primary and secondary cupric dithizonate and the 1:1 mixture of cupric dithizonate and dithizone were very poor. It was not possible to grind the solids to a fine powder and this caused too great a reflection of the infrared radiation. Thus, the bands appeared only as weak signals and no conclusive data was

TABLE 31

INFRARED ABSORPTION FREQUENCIES OF OXINE, DITHIZONE, AND OF SOME METAL OXINATES AND METAL DITHIZONATES IN THE CAESIUM BROMIDE REGION

Absorption Frequency*, cm^{-1}								
HOx	Assignment	$Cd(Ox)_2$	$Zn(Ox)_2$	$Pb(Ox)_2$	$In(Ox)_3$	$Cu(Ox)_2$	Tentative** Assignment	Ref.
690 (sh)	i.p. ring def.	694 (s)	686 (s)	690 (s)	700 (s)	680 (v.s)	i.p. ring def. + M-O str.	(1),(4)
677 (s)	C-N	680 (v.s)	680 (v.s)	680 (v.s)	686 (v.s)	611 (m)	C-N str.	(2)
636 (sh)	i.p. ring def.	615 (m)	615 (m)	613 (m)	610 (m)	600 (s)	i.p. ring def.	(1)
606 (m)								
					594 (m)			
					568 (w)			
552 (s)	o.p. ring	575 (m)	573 (m)	571 (m)	548 (m)	559 (m)	M-N str.	(3)
525 (m)	def.	544 (w)	549 (m)	535 (m)	500 (s)	502 (s)	M-N str.	
476 (w)		483	478 (s)	478 (s)	497 (sh)	480 (sh)	M-O str. +	(4)
456 (sh)		428	421 (v.w)	468 (s)	479 (w)	432 (v.w)	ring def.	
450 (m)	i.p. C-O bend.			417 (v.w)	423 (v.w)			
413 (w)								
300 (w)		398	382 (s)	354 (m)	386 (s)	398 (s)	M-O	(4)
		384		343 (s)		320 (v.s)	str.	
						286 (m)		

Absorption Frequency, cm^{-1}						
H Dz / H_2Dz	Assignment	$Pb(HDz)_2$	AgHDz	Tentative Assignment**	Ref.	1:1 Mixture $PbOx_2$ + $Pb(HDz)_2$***
701 (s)	i.p. ring def. + C-S	709 (m)	704 (m)	i.p. ring def. + C-S	(5)	710
691 (s)	" + C-S	691 (s)	690 (s)	" + C-S	(5)	689 (s)
677 (s)	C-N str. + C-S	677 (s)	677 (s)	C-N str. + C-S	(2),(5)	677 (s)
636 (m)	C-S	639 (s)	640 (s)	C-S	(5)	641 (m)
						609 (w)
576 (w)		588 (w)	588 (w)			586 (w)
552 (m)	C-N str.	571 (s)	569 (s)	M-N str.	(3)	571 (m)
521 (w)			531 (s)	+ C-N str.		535 (w)
500 (w)	C-S	506 (s)	501 (m)	C-S	(5)	500 (m)
488 (m)		474 (s)	478 (s)	C-S str.	(5)	479 (m)
478 (s)		411 (m)	410 (m)	M-S str.	(6),(7)	473 (m)
430 (w)						410 (w)
		392		M-S str.	(6),(7)	356 (v.b.,w)
		314	320	M-S str.	(6),(7)	
294 (m)	C-S	276		C-S str.	(5)	

Footnote to Table

The following symbols are used in the table: o.p., out-of-plane; i.p., in-plane; str., stretching; def., deformation; s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

References

(1) J. E. Tackett and D. T. Sawyer, Inorg. Chem., 3, 692 (1964).

(2) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd Ed., Methwen and Co. Ltd., London (1960).

(3) D. B. Powell and N. Sheppard, J. Chem. Soc., 3108 (1956, K. Nakamoto, J. Fujita and H. Murata, J. Am. Chem. Soc. 80, 4817 (1958).

(4) J. Fujita, A. E. Martell and K. Nakamoto, J. Chem. Phys. 36, 324, 331 (1962).

(5) N. B. Calthup, L. H. Daly and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, N. Y. (1964).

(6) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley and Sons, Inc., N. Y. (1963).

(7) D. M. Adams and J. [illegible], J. Chem. Soc. (A) 1299 (1968).

*Samples were as Nujol mulls.

**Note: These assignments are entirely speculative and are based on assignments made to other chelate compounds by the authors given in the references. The infrared spectra of metal oxinates and dithizonates in the CsBr region have not been reported in the literature.

***See text page 216.

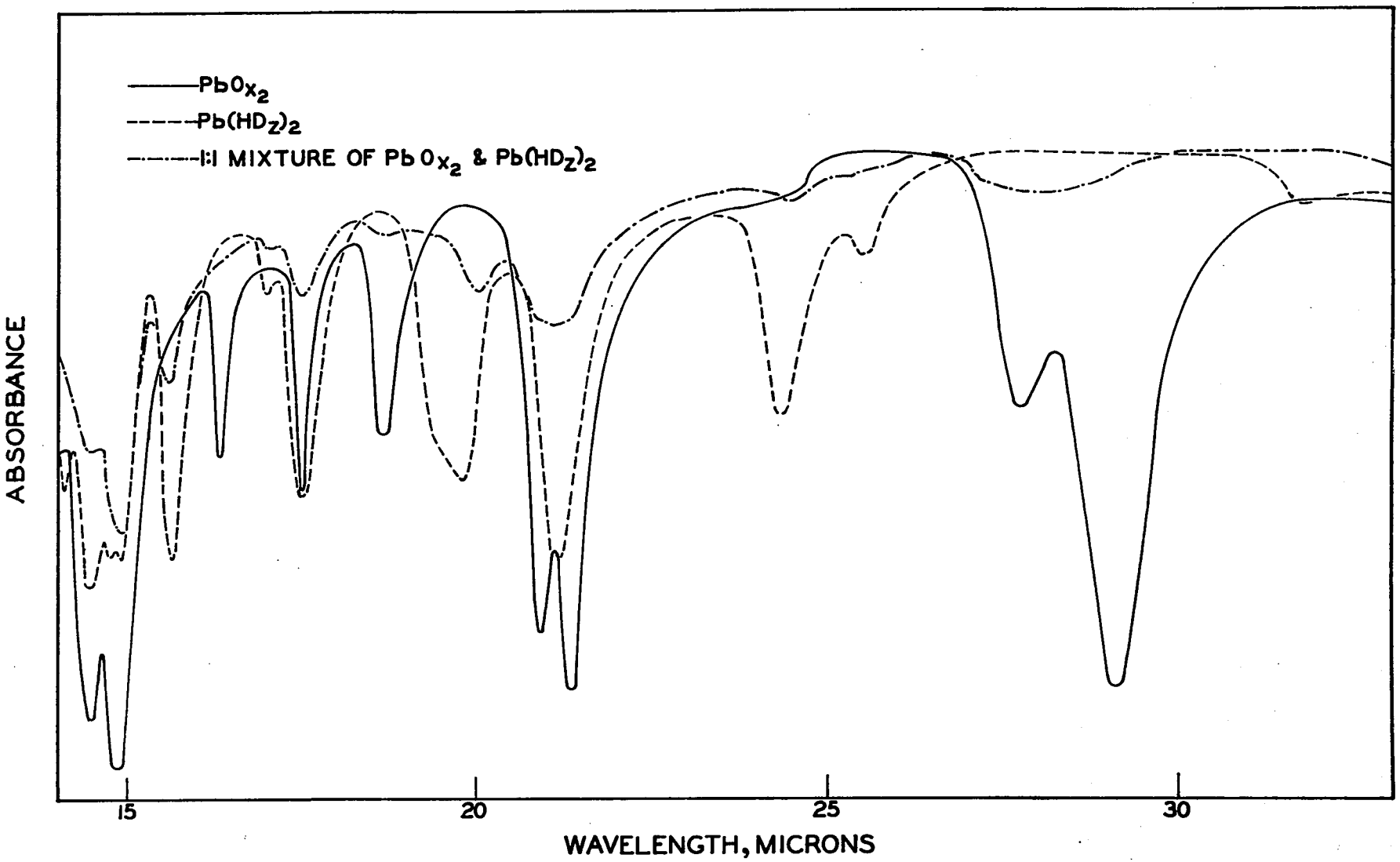
FIGURE 43

INFRARED SPECTRA FROM 14 TO 33 MICRONS OF LEAD OXINATE, LEAD DITHIZONATE AND THE 1:1 MOLAR MIXTURE OF LEAD OXINATE AND LEAD DITHIZONATE

Samples were as Nujol mulls between CsBr plates.

See text, page 216 for the preparation of the 1:1 mixture.

See Table 31 for a list of the absorption maxima.


PbOx2
Pb(HDZ)2
1:1 MIXTURE OF PbOx2 & Pb(HDZ)2
ABSORBANCE
15
20
25
30
WAVELENGTH, MICRONS

obtained. Potassium bromide pellets were prepared with the solids in an attempt to solve the problem. However, the attempt was unsuccessful.

8. X-Ray Diffraction Patterns: Preparation of Samples and Results

The following samples were prepared for x-ray analysis:

(1) Lead oxinate

(2) Lead dithizonate

(3) 1:1 Molar Mixture of Lead Oxinate and Lead Dithizonate*

(4) Primary cupric dithizonate

(5) Dithizone

(6) 1:1 Molar Mixture of Primary Cupric Dithizonate and Dithizone*

The lead samples were prepared for analysis by making a mull with acetone and then "painting" it onto a "Mylar" film. The copper samples were made into powder rods.

The x-ray diagrams for the lead compounds were obtained with the use of unfiltered cobalt x-radiation. They were irradiated for 10 hours. The extinctions were recorded with a Debye-Scherer camera. The copper compounds were irradiated with nickel-filtered copper Kα x-radiation. The extinctions were recorded with a Guinier camera. They were irradiated for 24 hours.

The powder patterns obtained are shown in Figure 44.**

*Prepared by the same method used for the infrared samples.

**Only the powder patterns for (4), (5) and (6) have been reproduced in the Figure.

FIGURE 44

X-RAY POWDER PATTERNS OF DITHIZONE, CUPRIC DITHIZONATE AND THE 1:1 MOLAR MIXTURE OF CUPRIC DITHIZONATE AND DITHIZONE

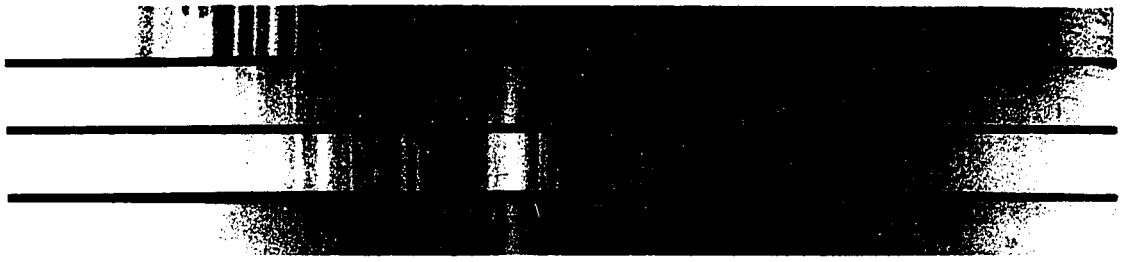
(a) $Cu(HDz)_2$

(b) H_2Dz

(c) 1:1 Molar Mixture of $Cu(HDz)_2$ and H_2Dz

Camera: Guinier
Samples irradiated for 24 hrs. with nickel-filtered copper Kα x-radiation.

See text page 216 for the preparation of the 1:1 molar mixture.


A
B
A
C

D. RESULTS

1. Spectrophotometric Titrations

(a) Introduction

The dithizonates of Ag, Pb, In, Cu (11), Zn and Cd in chloroform were titrated with a standard solution of sodium diethyldithiocarbamate in ethanol; and the oxinates of Pb, Cu (11), Zn, Cd and In in benzene were titrated with a standard solution of dithizone in benzene. End points were determined spectrophotometrically. The titration procedure has been described in Section IV C subsection 1; and the preparation and standardization of solutions has been described in Section IV B subsections 5-9.

In the development of these spectrophotometric titration methods, the following topics were investigated:

(1) The rate of attainment of equilibrium after addition of titrant.

(2) The effect of reducing the metal concentration by a factor of 10.

(3) Comparison of data obtained from titrations performed at 618 mμ and at the wavelength of maximum absorption of the metal dithizonate.

(4) The effect of an initial excess of free dithizone or of free oxine in the solution for titration when metal dithizonates or metal oxinates, respectively, were titrated.

(5) The effect of changing the temperature of the titration solution.

(6) The titration of mixtures of metal dithizonates.

(b) Titration of Metal Dithizonates by Diethyldithiocarbamate.

The metal dithizonates of Ag, Pb, In, Cu (II), Zn and Cd in chloroform were titrated with a 2.5×10^{-3} N standard solution of sodium diethyldithiocarbamate in ethanol. The metal dithizonate stock solutions were 5×10^{-5} N. Five, and 0.5-ml aliquots were diluted to 50.0 ± 0.2 and 2.50 ± 0.01 ml respectively, for the titrations. Each titration was in replicate (n = 4 or 6).

Cobalt, nickel, bismuth and mercury dithizonates gave titration graphs with arms which could not be extrapolated to a precise intersection point because of curvature. Therefore their study was not pursued.

Each metal dithizonate-diethyldithiocarbamate system was tested over a two-hour period for the rate of attainment of equilibrium. For the study, increments of NaD solution corresponding to 0.5, 1.0 and 1.5 equivalents were added to the metal dithizonate solution in the titration cell. In every case equilibrium was established almost instantaneously, and there was no change in absorbance with time. All titrations were performed at 25.0 ± 0.1°C; the effect of temperature was not studied.

The titration results of single metal dithizonates are given in Tables 32-37. Typical titration graphs for titrations performed at the wavelengths of maximum absorption

TABLE 32

SPECTROPHOTOMETRIC TITRATIONS OF SILVER DITHIZONATE IN CHLOROFORM WITH STANDARD SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL AT 25°C

Normality of standard solution of NaD in ethanol,	MACRO:	2.346×10^{-3} N	MICRO:	2.346×10^{-4} N
Normality of silver dithizonate solution in titration cell,	MACRO:	4.571×10^{-6} N	MICRO:	9.142×10^{-6} N
Initial volume of solution in titration cell,	MACRO:	50 ± 0.2 ml	MICRO:	2.50 ± 0.01 ml
Path length of titration cell,	MACRO:	5.0 cm	MICRO:	1.0 cm

Initial Molar Ratio[1]	0				2				4			
	MACRO		MICRO		MACRO		MICRO		MACRO		MICRO	
Conc. of H_2Dz in solution	-	-	-	-	1.091×10^{-5}M		2.188×10^{-5}M		4.365×10^{-5}M		2.182×10^{-5}M	4.365×10^{-5}M	8.730×10^{-5}M
Wavelength, mμ	615	465	615	465	615	465	615	465	615	465	615	465
μeq. AgHDz taken	0.2286	0.2286	0.02286	0.04572	0.2286	0.2286	0.02286	0.04572	0.2286	0.2286	0.02286	0.04572
μeq. AgHDz found[2]	0.2310	0.2299	0.02333	0.04663	0.2340	0.2338	0.02350	0.04711	0.2368	0.2356	0.02410	0.04787
% Error in μeq. found[3]	+1.05	+0.57	+2.06	+1.99	+2.36	+2.27	+2.80	+3.04	+3.59	+3.08	+5.42	+4.70
Variance, $S^2 \times 10^6$	78.0	85.1	1.25	0.71	10.9	42.4	1.48	0.35	39.4	17.2	1.48	1.14
Std. Dev., $S \times 10^2$	0.88	0.92	0.11	0.08	0.33	0.65	0.12	0.06	0.63	0.42	0.12	0.12

[1]Approximate molar ratio of initial concentration of dithizone with respect to the initial concentration of AgHDz present in the titration solution.
[2]Mean of 6 titrations (MACRO). Mean of 4 titrations (MICRO).
[3]Calculated as the percentage difference between the μeq. found and μeq. taken.

TABLE 33

SPECTROPHOTOMETRIC TITRATIONS OF LEAD DITHIZONATE IN CHLOROFORM WITH STANDARD SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL AT 25°C

Normality of standard solution of NaD in ethanol,	MACRO:	2.188×10^{-3} N	MICRO:	2.188×10^{-4} N
Normality of lead dithizonate solution in titration cell,	MACRO:	4.572×10^{-6} N	MICRO:	9.144×10^{-6} N
Initial volume of solution in titration cell,	MACRO:	50 ± 0.2 ml	MICRO:	2.50 ± 0.01 ml
Path length of titration cell,	MACRO:	5.0 cm	MICRO:	1.0 cm

Initial Molar Ratio[1]	0				2				4			
	MACRO		MICRO		MACRO		MICRO		MACRO		MICRO	
Conc. of H_2Dz in solution	-	-	-	-	5.584×10^{-6} M		1.117×10^{-5} M		1.117×10^{-5} M		2.234×10^{-5} M	
Wavelength, mμ	615	510	615	510	615	510	615	510	615	510	615	510
μeq. $Pb(HDz)_2$ taken	0.2286	0.2286	0.02286	0.02286	0.2286	0.2286	0.02286	0.02286	0.2286	0.2286	0.02286	0.02286
μeq. $Pb(HDz)_2$ found[2]	0.2306	0.2257	0.02284	0.02225	0.2290	0.2396	0.02238	0.02262	0.2257	0.2332	0.02248	0.02201
% Error in μeq. found[3]	+0.87	-1.27	-0.10	-2.67	+0.61	+4.81	-2.11	-1.05	-1.27	+2.01	-1.66	-3.72
Variance, $S^2 \times 10^6$	48.4	31.3	1.20	1.00	46.3	76.2	1.57	0.81	1.09	21.2	1.08	1.34
Std. Dev., $S \times 10^2$	0.70	0.56	0.11	0.10	0.68	0.87	0.12	0.09	1.04	0.46	0.10	0.12

[1]Approximate molar ratio of initial concentration of dithizone with respect to the initial concentration of $Pb(HDz)_2$ present in the titration solution.
[2]Mean of 6 titrations (MACRO). Mean of 4 titrations (MICRO).
[3]Calculated as the percentage difference between the μeq. found and μeq. taken.

TABLE 34

SPECTROPHOTOMETRIC TITRATIONS OF INDIUM DITHIZONATE IN CHLOROFORM WITH STANDARD SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL AT 25°C

Normality of standard solution of NaD in ethanol,	MACRO: 2.309×10^{-3} N	MICRO: 2.309×10^{-4} N
Normality of indium dithizonate solution in titration cell,	MACRO: 5.622×10^{-6} N	MICRO: 1.124×10^{-5} N
Initial volume of solution in titration cell,	MACRO: 50 ± 0.2 ml	MICRO: 2.50 ± 0.01 ml
Path length of titration cell,	MACRO: 5.0 cm	MICRO: 1.0 cm

Initial Molar Ratio[1]	0				3				6			
	MACRO		MICRO		MACRO		MICRO		MACRO		MICRO	
Conc. of H_2Dz in solution	-	-	-	-	5.584×10^{-6} M		1.117×10^{-5} M		1.117×10^{-5} M		2.234×10^{-5} M	
Wavelength, mμ	615	510	615	510	615	510	615	510	615	510	615	510
μeq. $In(HDz)_3$ taken	0.2811	0.2811	0.02811	0.02811	0.2811	0.2811	0.02811	0.02811	0.2811	0.2811	0.02811	0.02811
μeq. $In(HDz)_3$ found[2]	0.2783	0.2783	0.02735	0.02675	0.2754	0.2817	0.02632	0.02721	0.2777	0.2712	0.02679	0.02670
% Error in μeq. found[3]	-1.00	-1.00	-2.70	-4.84	-2.03	+0.21	-6.37	-3.20	-1.21	-3.52	-4.70	-5.02
Variance, $S^2 \times 10^6$	1.21	49.3	1.11	0.94	69.9	83.7	1.86	1.03	31.7	52.8	1.44	0.77
Std. Dev., $S \times 10^2$	1.10	0.70	0.10	0.10	0.84	0.92	0.14	0.10	0.56	0.73	0.12	0.09

[1]Approximate molar ratio of initial concentration of dithizone with respect to the initial concentration of $In(HDz)_3$ present in the titration solution.
[2]Mean of 6 titrations (MACRO). Mean of 4 titrations (MICRO).
[3]Calculated as the percentage difference between the μeq. found and μeq taken.

TABLE 35

SPECTROPHOTOMETRIC TITRATIONS OF ZINC DITHIZONATE IN CHLOROFORM WITH STANDARD SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL AT 25 ± 0.1 °C

Normality of standard solution of NaD in ethanol : 2.409×10^{-3} N
Normality of zinc dithizonate solution in titration cell : 5.892×10^{-6} N
Initial volume of solution in titration cell : 50 ± 0.2 ml
Path length of titration cell: 5.0 cm

Initial Molar Ratio[1]	0		2		4	
Conc. of H_2Dz in solution	-		6.00×10^{-6} M		1.20×10^{-5} M	
Wavelength mμ	615	530	615	530	615	530
μeq. $Zn(HDz)_2$ taken	0.2946	0.2946	0.2946	0.2946	0.2946	0.2946
μeq. $Zn(HDz)_2$ found[2]	0.2898	0.2794	0.2880	0.2794	0.2861	0.2867
% Error in μeq. found[3]	-1.63	-5.16	-2.24	-5.16	-2.88	-2.68
Variance $S^2 \times 10^6$	34.7	43.0	79.1	182.0	67.2	101.0
Std. Deviation $S \times 10^2$	0.59	0.66	0.89	1.35	0.82	1.00

[1]Approximate molar ratio of initial concentration of dithizone with respect to the initial concentration of $Zn(HDz)_2$ present in the titration solution.
[2]Average of 4 titrations.
[3]Calculated as the percent difference between the μeq. found and μeq. taken.

TABLE 36

SPECTROPHOTOMETRIC TITRATIONS OF CADMIUM DITHIZONATE IN CHLOROFORM WITH STANDARD SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL AT 25 ± 0.1°C

Normality of standard solution of NaD in ethanol : 2.375×10^{-3} N
Normality of cadmium dithizonate solution in titration cell : 5.680×10^{-6} N
Initial volume of solution in titration cell : 50 ± 0.2 ml
Path length of titration cell : 5.0 cm

Initial Molar Ratio[1]	0		2		4	
Conc. of H_2Dz in solution	-		5.374×10^{-6} M		1.075×10^{-5} M	
Wavelength mμ	615	518	615	518	615	518
μeq. $Cd(HDz)_2$ taken	0.2840	0.2840	0.2840	0.2840	0.2840	0.2840
μeq. $Cd(HDz)_2$ found[2]	0.2862	0.2802	0.2830	0.2779	0.2779	0.2765
% Error in μeq. found[3]	+0.77	-1.34	-0.35	-2.15	-2.15	-2.64
Variance $S^2 \times 10^6$	55.0	45.0	46.9	94.0	25.9	67.3
Std. Deviation $S \times 10^2$	0.74	0.67	0.68	0.97	0.51	0.82

[1]Approximate molar ratio of initial concentration of dithizone with respect to the concentration of $Cd(HDz)_2$ present in the titration solution.
[2]Average of 4 titrations.
[3]Calculated as the percent difference between the μeq. found and μeq. taken.

TABLE 37

SPECTROPHOTOMETRIC TITRATIONS OF COPPER DITHIZONATE IN CHLOROFORM WITH STANDARD SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL AT 25 ± 0.1°C

Normality of standard solution of NaD in ethanol : 2.502×10^{-3} N
Normality of copper dithizonate solution in titration cell : 5.236×10^{-6} N
Initial volume of solution in titration cell: 50 ± 0.2 ml
Path length of titration cell : 5.0 cm

Initial Molar Ratio[1]	0		2		4	
Conc. of H_2Dz in solution	-		5.374×10^{-6} M		1.075×10^{-5} M	
Wavelength mμ	615	545	615	545	615	545
μeq. $Cu(HDz)_2$ taken	0.2618	0.2618	0.2618	0.2618	0.2618	0.2618
μeq. $Cu(HDz)_2$ found[2]	0.2631	0.2677	0.2665	0.2627	0.2610	0.2702
% Error in μeq. found[3]	+0.50	+2.25	+1.81	+0.34	-0.31	+3.21
Variance $S^2 \times 10^6$	111	40.4	34.1	38.8	38.6	102.0
Std. Deviation $S \times 10^2$	1.05	0.64	0.58	0.62	0.62	1.00

[1]Approximate molar ratio of initial concentration of dithizone with respect to the initial concentration of $Cu(HDz)_2$ present in the titration solution.
[2]Average of 4 titrations.
[3]Calculated as the percent difference between the μeq. found and μeq. taken.

of the metal dithizonate, are shown in Figure 45 (a)-(g). Figure 45 (h) illustrates the titration curve obtained in all cases for a titration carried out at 615 mμ (one of the wavelengths of maximum absorption of dithizone in chloroform).

The effect of initial free dithizone in excess in the titration of silver dithizonate is illustrated in Figure 45 (d) and (e). The maximum initial excess of dithizone that could be used was four-fold with respect to the initial concentration of metal dithizonate, because at higher concentrations the absorbance of the solution in the titration cell increased beyond 2.0. Of the metal dithizonates studied, silver showed the most sensitivity to initial excesses of dithizone, copper the least. The order of increasing curvature at the end-point was found to be

$AgHDz > Zn(HDz)_2 \approx Cd(HDz)_2 > Pb(HDz)_2 > In(HDz)_3 > Cu(HDz)_2$

A statistical analysis of the data is given in Section IV D subsection 2(f).

In exploratory studies, several binary and ternary mixtures of metal dithizonates were titrated with NaD. The following mixtures gave indefinite end-points due to curvature of the graphs:

$AgHDz + Zn(HDz)_2$	$AgHDz + Zn(HDz)_2 + Cd(HDz)_2$
$AgHDz + Cd(HDz)_2$	$AgHDz + Zn(HDz)_2 + Pb(HDz)_2$
$Zn(HDz)_2 + Cd(HDz)_2$	$AgHDz + Zn(HDz)_2 + Cu(HDz)_2$
$Zn(HDz)_2 + Pb(HDz)_2$	$AgHDz + Cd(HDz)_2 + Pb(HDz)_2$
	$Zn(HDz)_2 + Cd(HDz)_2 + Pb(HDz)_2$

FIGURE 45

TYPICAL TITRATION GRAPHS OF SPECTROPHOTOMETRIC TITRATIONS OF SINGLE METAL DITHIZONATES IN CHLOROFORM AT 25°C WITH A STANDARD SOLUTION OF SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL

(a) $Pb(HDz)_2$ at 510 mμ

(b) $Cu(HDz)_2$ at 545 mμ

(c) $In(HDz)_3$ at 510 mμ

(d) AgHDz at 465 mμ

(e) $1:4(AgHDz)_i:(H_2Dz)_i$ Mixture at 465 mμ

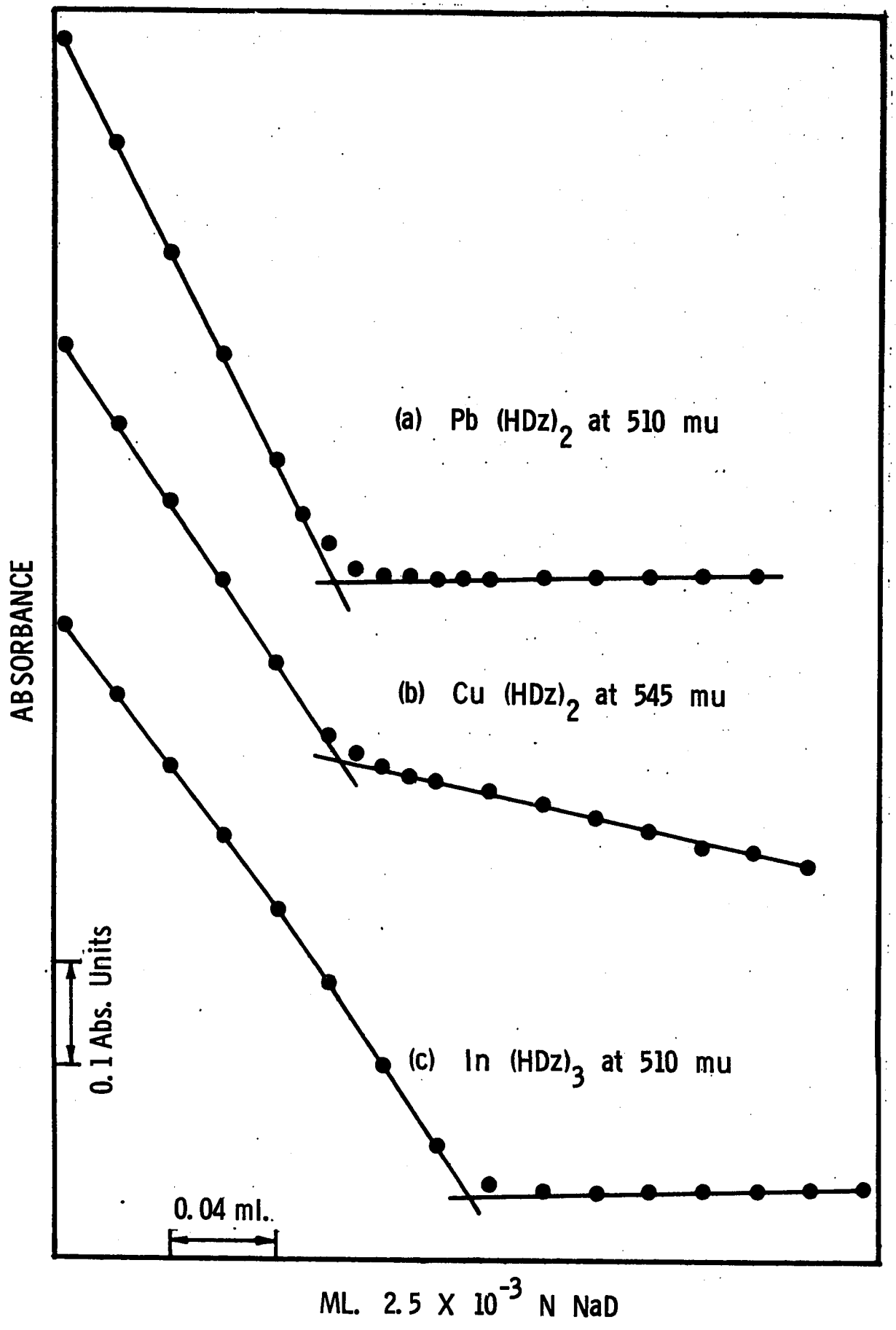
(f) $Zn(HDz)_2$ at 530 mμ

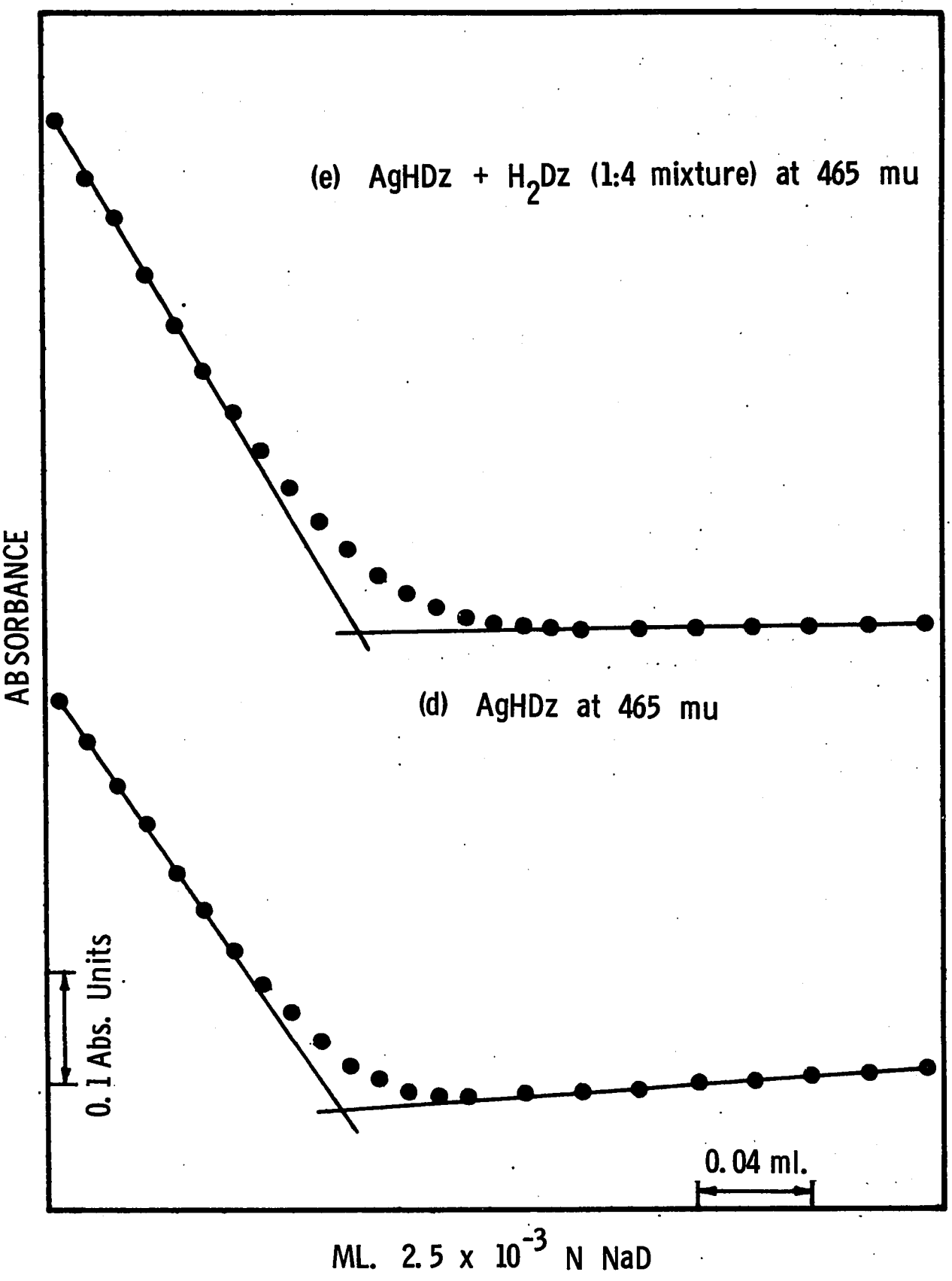
(g) $Cd(HDz)_2$ at 518 mμ

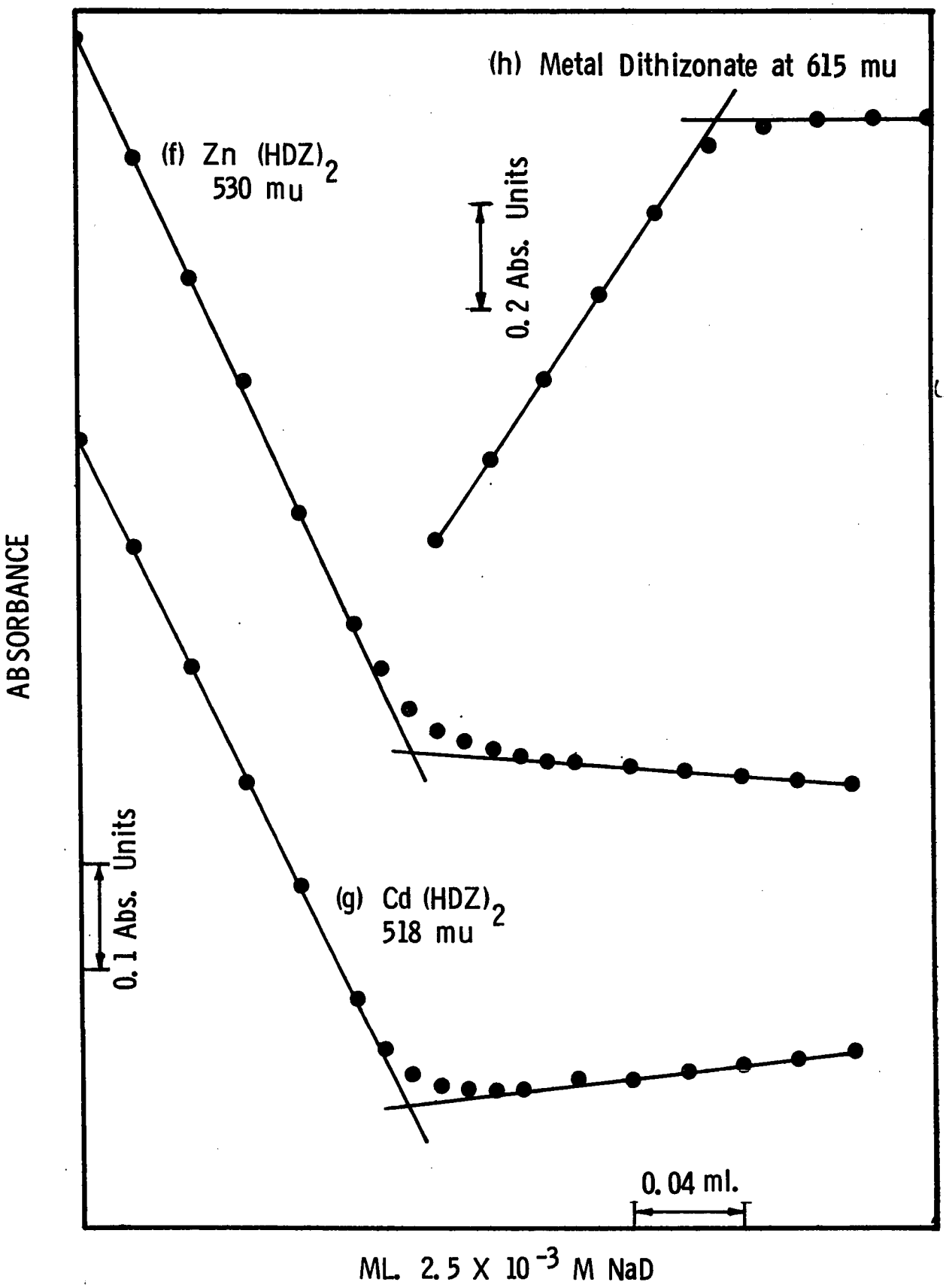
(h) Typical graph for any metal dithizonate at 615 mμ

Initial Volume of Solution: 50 ml

Note: See Tables 32-37 for concentration of metal dithizonate solutions and titrant.


(a) Pb (HDz)2 at 510 mu
(b) Cu (HDz)2 at 545 mu
(c) In (HDz)3 at 510 mu
ABSORBANCE
0.1 Abs. Units
0.04 ml.
ML. 2.5 X 10-3 N NaD


(e) AgHDz + H_2Dz (1:4 mixture) at 465 mu
(d) AgHDz at 465 mu
ABSORBANCE
0.1 Abs. Units
0.04 ml.
ML. 2.5 x 10^{-3} N NaD


(h) Metal Dithizonate at 615 mu
(f) Zn (HDZ)2
530 mu
0.2 Abs. Units
ABSORBANCE
0.1 Abs. Units
(g) Cd (HDZ)2
518 mu
0.04 ml.
ML. 2.5 X 10-3 M NaD

However, the mixtures listed in Tables 38 and 39 gave, as seen from the data there, satisfactory end points. Typical titration graphs for initial 1:1 molar ratios of metal dithizonate mixtures are shown in Figure 46 (a) to (f) (binary mixtures), and Figure 47 (a) to (c) (ternary mixtures). Only 1:1 molar-ratio mixtures were investigated.

In general, only one wavelength gave satisfactory titration graphs for mixtures. In the binary mixtures, there was a choice of two wavelengths; one gave a much smaller angle of intersection at an end point than the other, and only the latter is reported here. For the titration of ternary mixtures, the best wavelength was that of the absorption peak of the second metal that was titrated.

A discussion of the data is given in Section V C subsection 3, where a qualitative interpretation of the titration graph is suggested.

(c) Titration of Metal Oxinates with Dithizone

The oxinates of lead, copper, zinc, cadmium and indium were titrated with a 10^{-3} N standard dithizone solution in benzene.

The concentrations of the stock metal oxinate solutions* were 5×10^{-5} N. Five and 0.5-ml aliquots were diluted to

*It proved impossible to prepare sufficiently concentrated solutions of zinc oxinate and cadmium oxinates in spectrophotometric-grade benzene due to its water content. Therefore stock solutions of these metal oxinates were prepared in dried benzene, in a dry box; and dried benzene was used for diluting the aliquots of these solutions in the titration cell.

TABLE 38

SPECTROPHOTOMETRIC TITRATIONS OF BINARY MIXTURES OF METAL DITHIZONATES IN CHLOROFORM, WITH STANDARD SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL AT 25°C

Normality of standard solution of NaD in ethanol: 2.808×10^{-3} N
Initial volume of solution in titration cell : 50.0 ± 0.2 ml
Path length of titration cell : 5.0 cm

Binary Mixtures	Taken μeq.	Found* μeq.	Per Cent** Difference	Variance $S^2 \times 10^6$	Std. Deviation $S \times 10^2$
WAVELENGTH: 510 mμ					
$Pb(HDz)_2$	0.3070	0.3002	- 2.21	245	1.56
$AgHDz + Pb(HDz)_2$	0.5922	0.6031	+ 1.84	205	1.43
WAVELENGTH: 510 mμ					
$In(HDz)_3$	0.3736	0.3632	- 2.78	134	1.16
$In(HDz)_3 + Pb(HDz)_2$	0.6806	0.6759	- 0.69	25.5	0.50
WAVELENGTH: 530 mμ					
$Cu(HDz)_2$	0.2618	0.2691	+ 2.79	101	1.00
$Cu(HDz)_2 + Zn(HDz)_2$	0.5412	0.5523	+ 2.05	129	1.14
WAVELENGTH: 510 mμ					
$Cu(HDz)_2$	0.2618	0.2621	+ 0.11	52.8	0.73
$Cu(HDz)_2 + Pb(HDz)_2$	0.5688	0.5674	- 0.25	75.0	0.87
WAVELENGTH: 518 mμ					
$Cu(HDz)_2$	0.2618	0.2340	-10.62	190	1.38
$Cu(HDz)_2 + Cd(HDz)_2$	0.5458	0.5443	- 0.27	63.2	0.80
WAVELENGTH: 465 mμ					
$Cu(HDz)_2$	0.2618	0.2598	- 0.80	93.1	0.96
$Cu(HDz)_2 + Ag(HDz)$	0.5200	0.5304	+ 2.02	38.7	0.62

*Average of 3 samples.
**Calculated from μeq. found and μeq. taken.

TABLE 39

SPECTROPHOTOMETRIC TITRATIONS OF TERNARY MIXTURES OF METAL DITHIZONATES IN CHLOROFORM, WITH STANDARD SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL AT 25 ± 0.1°C

Normality of standard solution of NaD in ethanol: 2.536×10^{-3} N
Initial volume of solution in titration cell : 50.0 ± 0.2 ml
Path length of titration cell : 5.0 cm

Ternary Mixtures	Taken µeq.	Found* µeq.	Per Cent** Difference	Variance $S^2 \times 10^6$	Std. Deviation $S \times 10^2$
WAVELENGTH: 530 mµ					
$Cu(HDz)_2$	0.2618	0.2652	+ 1.30	231	1.52
$Cu(HDz)_2 + Zn(HDz)_2$	0.5564	0.5955	+ 7.03	302	1.74
$Cu(HDz)_2 + Zn(HDz)_2 + Cd(HDz)_2$	0.8404	0.8607	+ 2.42	57.0	0.76
WAVELENGTH: 510 mµ					
$Cu(HDz)_2$	0.2618	0.2602	- 0.61	131	1.15
$Cu(HDz)_2 + Pb(HDz)_2$	0.5688	0.6005	+ 5.57	226	1.50
$Cu(HDz)_2 + Pb(HDz)_2 + Zn(HDz)_2$	0.8634	0.8502	- 1.55	39.8	0.63
WAVELENGTH: 510 mµ					
$Cu(HDz)_2$	0.2618	0.2667	+ 1.87	107	1.03
$Cu(HDz)_2 + Pb(HDz)_2$	0.5688	0.5646	- 0.74	158	1.26
$Cu(HDz)_2 + Pb(HDz)_2 + AgHDz$	0.8540	0.9062	+ 6.11	44.3	0.66

*Average of 3 samples.
**Calculated from µeq. found and µeq. taken.

FIGURE 46

TYPICAL TITRATION GRAPHS OF THE SPECTROPHOTOMETRIC TITRATION OF BINARY MIXTURES OF METAL DITHIZONATES IN CHLOROFORM AT 25°C, WITH SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL

(a) $Cu(HDz)_2$ + $Zn(HDz)_2$ at 530 mμ

(b) $Cu(HDz)_2$ + $Cd(HDz)_2$ at 518 mμ

(c) $Cu(HDz)_2$ + $Pb(HDz)_2$ at 510 mμ

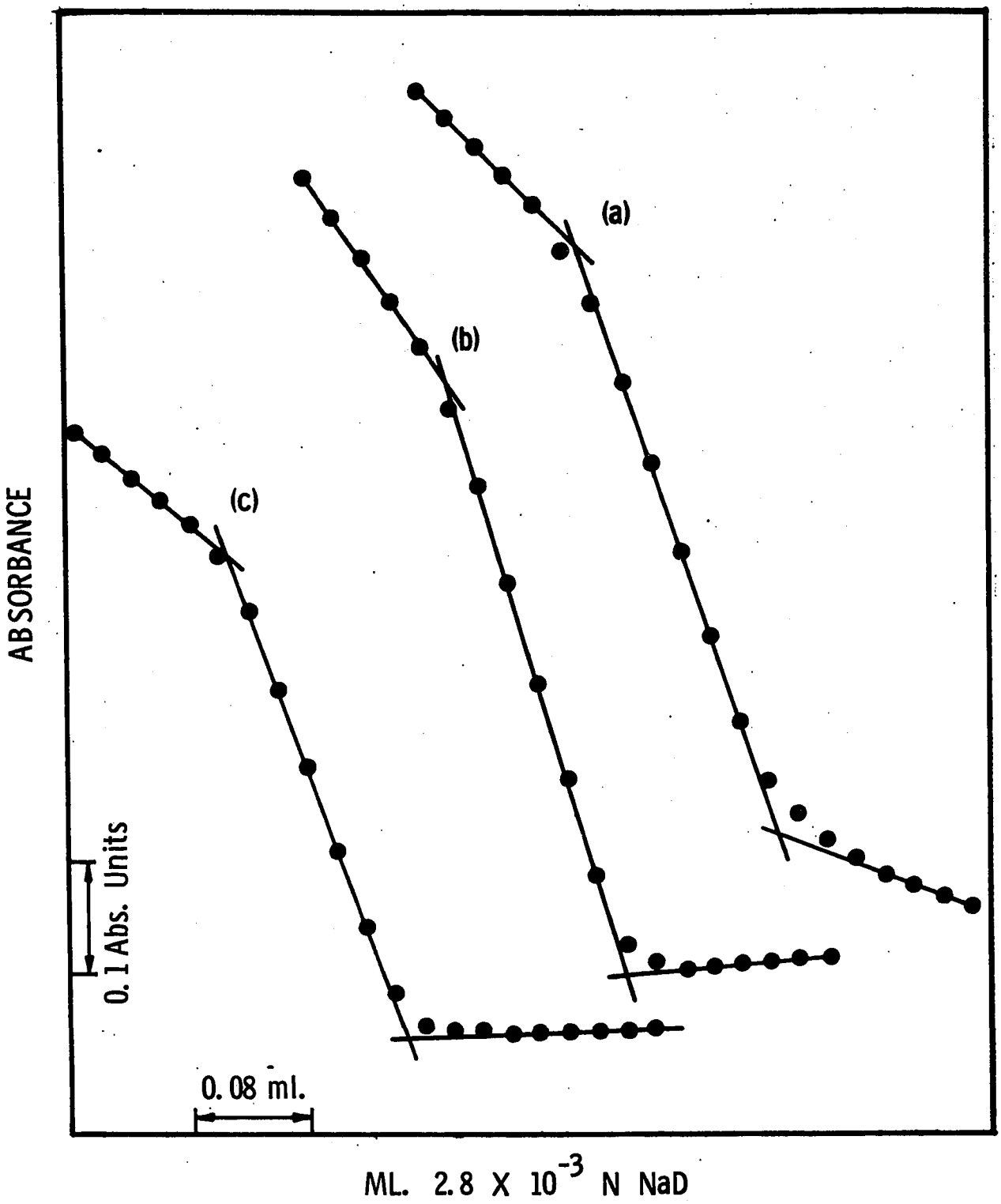
(d) $Pb(HDz)_2$ + AgHDz at 510 mμ

(e) $In(HDz)_3$ + $Pb(HDz)_2$ at 510 mμ

(f) $Cu(HDz)_2$ + AgHDz at 465 mμ

Initial Volume of solution: 50 ml

Note: The first metal dithizonate listed corresponds to the first titrated, and therefore the first end point in the graphs; in the graphs only alternate points have been plotted for clarity. See Table 38 for the concentration of the metal dithizonate solutions and titrant.


(a)
(b)
(c)
ABSORBANCE
0.1 Abs. Units
0.08 ml.
ML. 2.8 X 10^{-3} N NaD

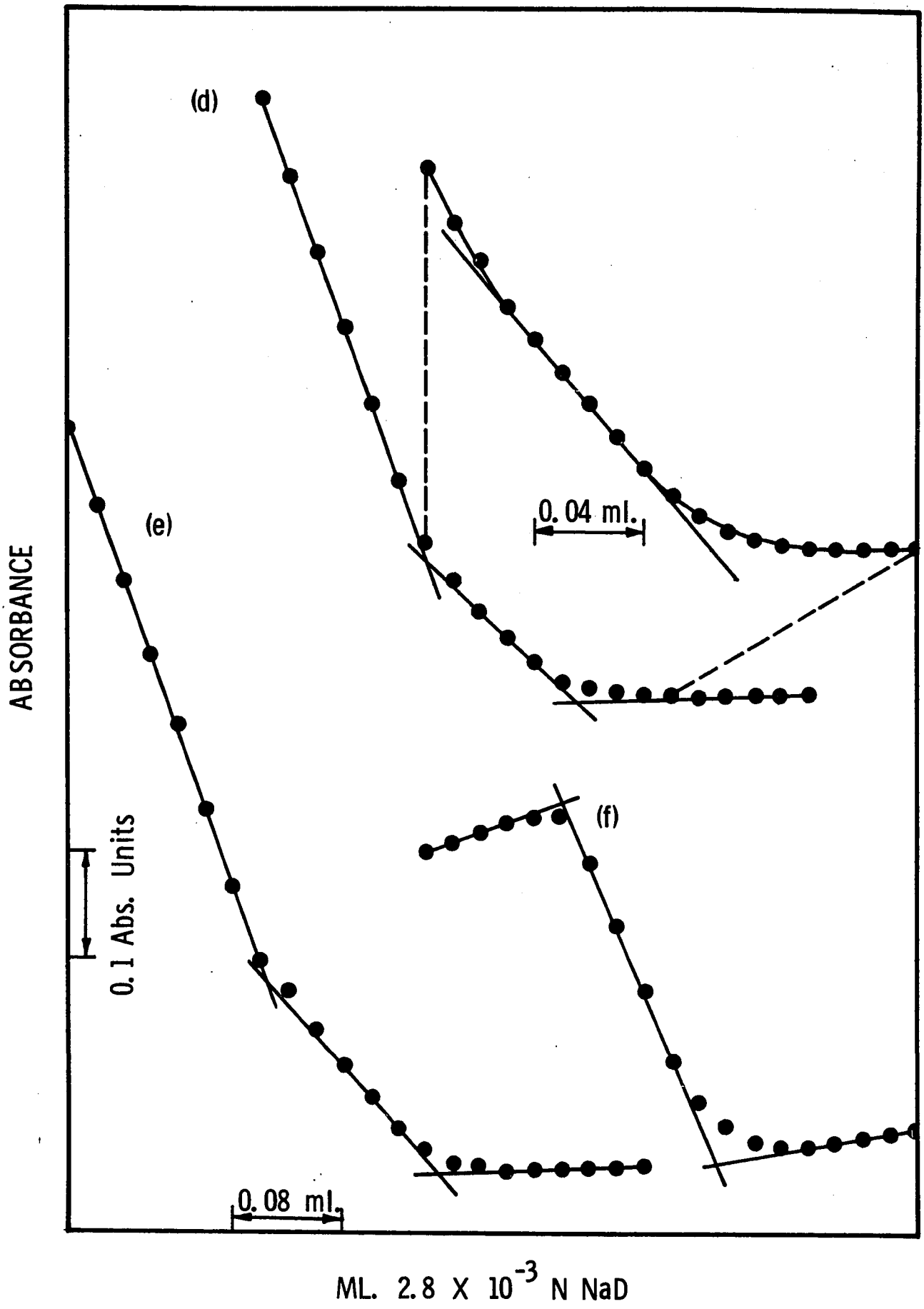

(d)
(e)
(f)
0.04 ml.
0.1 Abs. Units
0.08 ml.
ABSORBANCE
ML. 2.8 X 10^-3 N NaD

FIGURE 47

TYPICAL TITRATION GRAPHS OF THE SPECTROPHOTOMETRIC TITRATION OF TERNARY MIXTURES OF METAL DITHIZONATES IN CHLOROFORM AT 25°C, WITH SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL

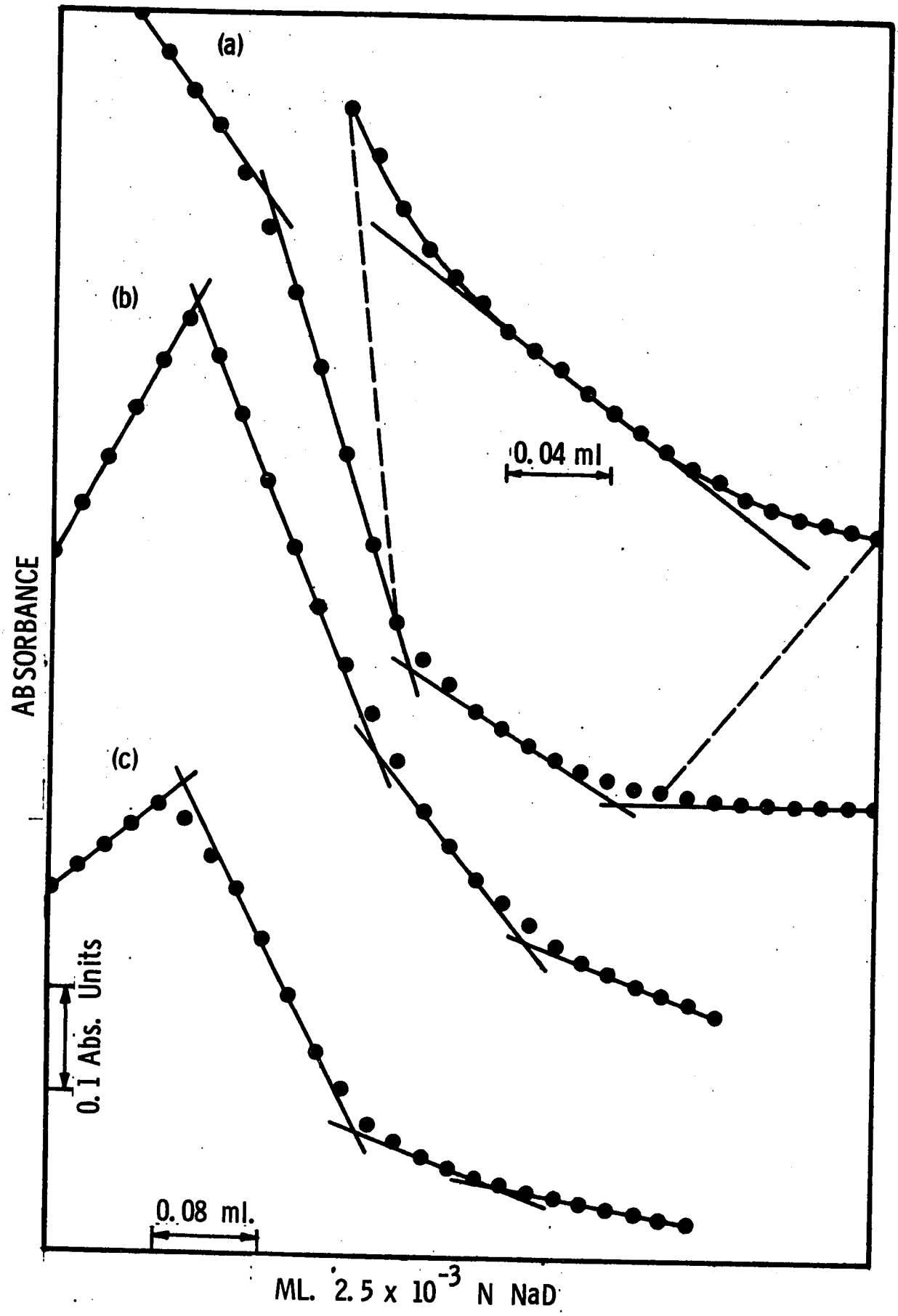
(a) $Cu(HDz)_2 + Pb(HDz)_2 + AgHDz$ at 510 mμ

(b) $Cu(HDz)_2 + Zn(HDz)_2 + Cd(HDz)_2$ at 530 mμ

(c) $Cu(HDz)_2 + Pb(HDz)_2 + Zn(HDz)_2$ at 510 mμ

Initial Volume of solution: 50 ml

Note: The metal dithizonates are listed in the order in which they are titrated; in the graphs only alternate points have been plotted for clarity. See Table 39 for concentrations of metal dithizonates and titrant.


(a)
(b)
(c)
0.04 ml
ABSORBANCE
0.1 Abs. Units
0.08 ml.
ML. 2.5 x 10^-3 N NaD

50 ± 0.2 ml and 2.50 ± 0.01 ml respectively, for the titrations. Each determination was done in replicate (n = 5).

The reactions of dithiozne with silver and nickel (11) oxinates were found to be much too slow to be practicable. Therefore their study was not pursued. Dithizone did not react with cobalt (11) oxinate; an explanation is proposed in Section V C subsection 6.

Equilibrium was found to be reached rapidly for the reactions of dithizone with lead, copper and indium oxinates, at all ratios of MOx_2:H_2Dz; no change of absorbance was observed over a period of two hours.

For copper, a constant absorbance was reached almost immediately, and it remained constant for 3½ hours. It then began to change rapidly, reaching an equilibrium value after an additional 2 hours. The rate curve is shown in Figure 48. Advantage was taken of the constancy of absorbance over the initial period, to perform titrations which proved to be entirely reproducible.

The reactions of dithizone with zinc and cadmium oxinates were slow. The rate curves are shown in Figures 49 and 50. These curves illustrate the effect of two factors: (i) the initial amount of free oxine in excess, and (ii) temperature. In the case of cadmium, the rate decreased on increasing temperature; with zinc, the rate increased. Unexpectedly, no significant increase in rate was observed

FIGURE 48

RATE OF ATTAINMENT OF EQUILIBRIUM OF THE REACTION OF COPPER OXINATE WITH DITHIZONE IN BENZENE AT 25°C

Initial Composition of Solution

Molarity of $CuOx_2$ = 2.531×10^{-6} M
Molarity of H_2Dz = 2.042×10^{-6} M
Volume of solution = 50 ml

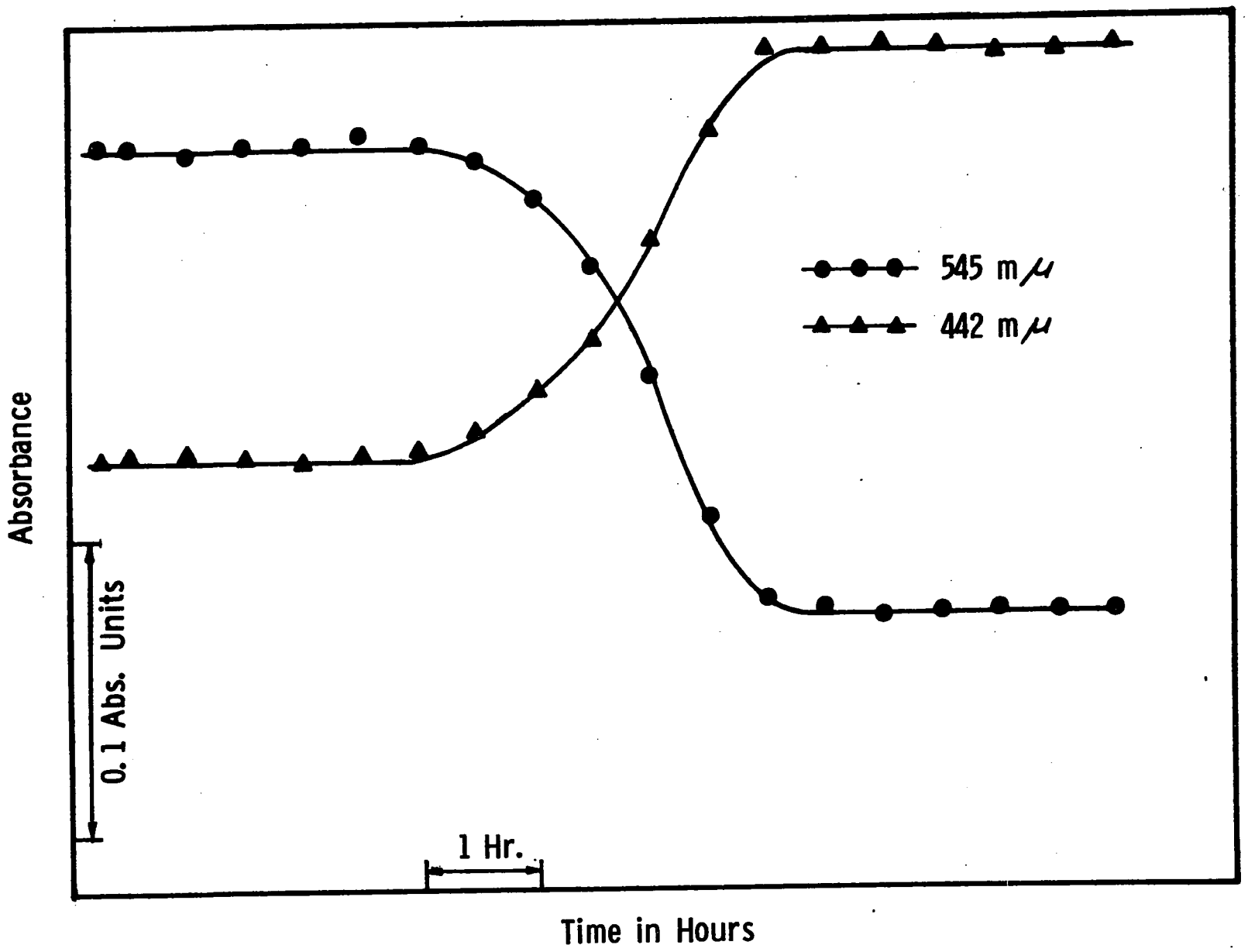

545 mμ
442 mμ
Absorbance
0.1 Abs. Units
1 Hr.
Time in Hours

FIGURE 49

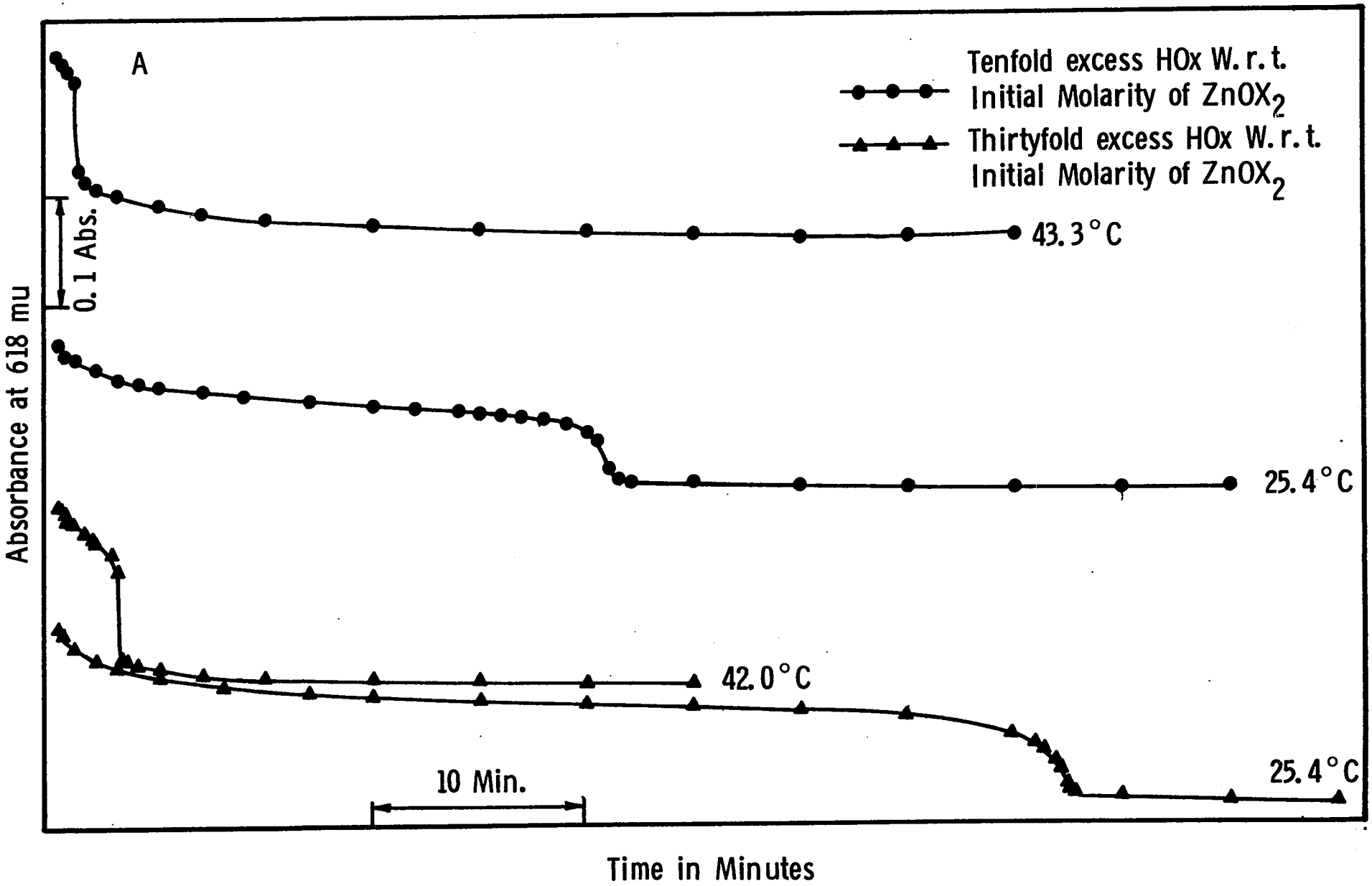
RATE OF ATTAINMENT OF EQUILIBRIUM OF THE REACTION OF ZINC OXINATE WITH DITHIZONE IN BENZENE, AS A FUNCTION OF TEMPERATURE AND INITIAL CONCENTRATION OF FREE OXINE

Initial Composition of Solution

Molarity of $ZnOx_2$ == 1.592×10^{-6} M
Molarity of H_2Dz = 5.464×10^{-6} M
Volume of solution = 50 ml

(a) λ = 618 mμ

(b) λ = 530 mμ


A
Tenfold excess HOx W. r. t.
Initial Molarity of $ZnOX_2$
Thirtyfold excess HOx W. r. t.
Initial Molarity of $ZnOX_2$
0.1 Abs.
43.3°C
25.4°C
42.0°C
25.4°C
10 Min.
Absorbance at 618 mu
Time in Minutes

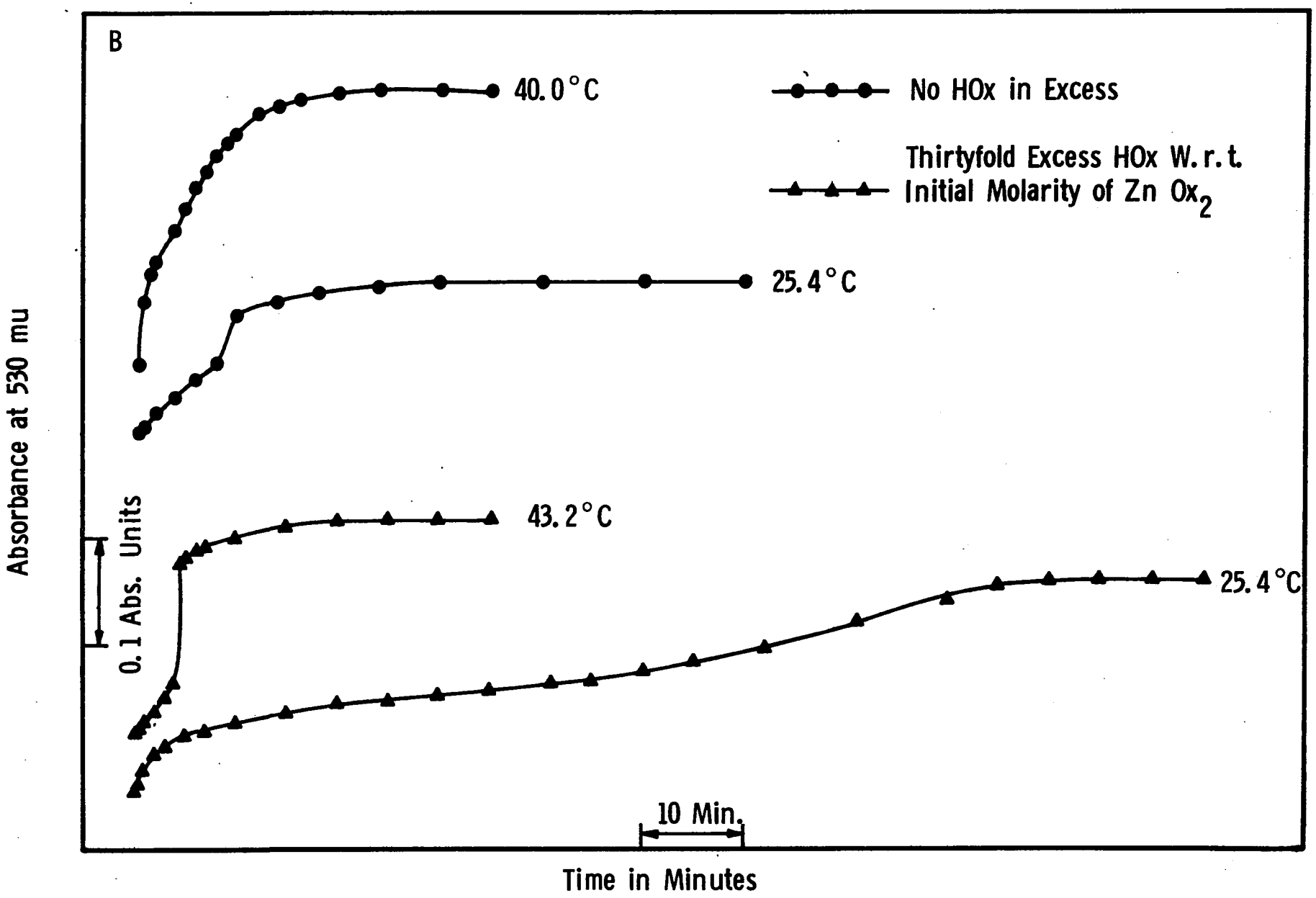

B
40.0 °C
No HOx in Excess
Thirtyfold Excess HOx W.r.t.
Initial Molarity of Zn Ox2
25.4 °C
43.2 °C
25.4 °C
0.1 Abs. Units
10 Min.
Absorbance at 530 mu
Time in Minutes

FIGURE 50

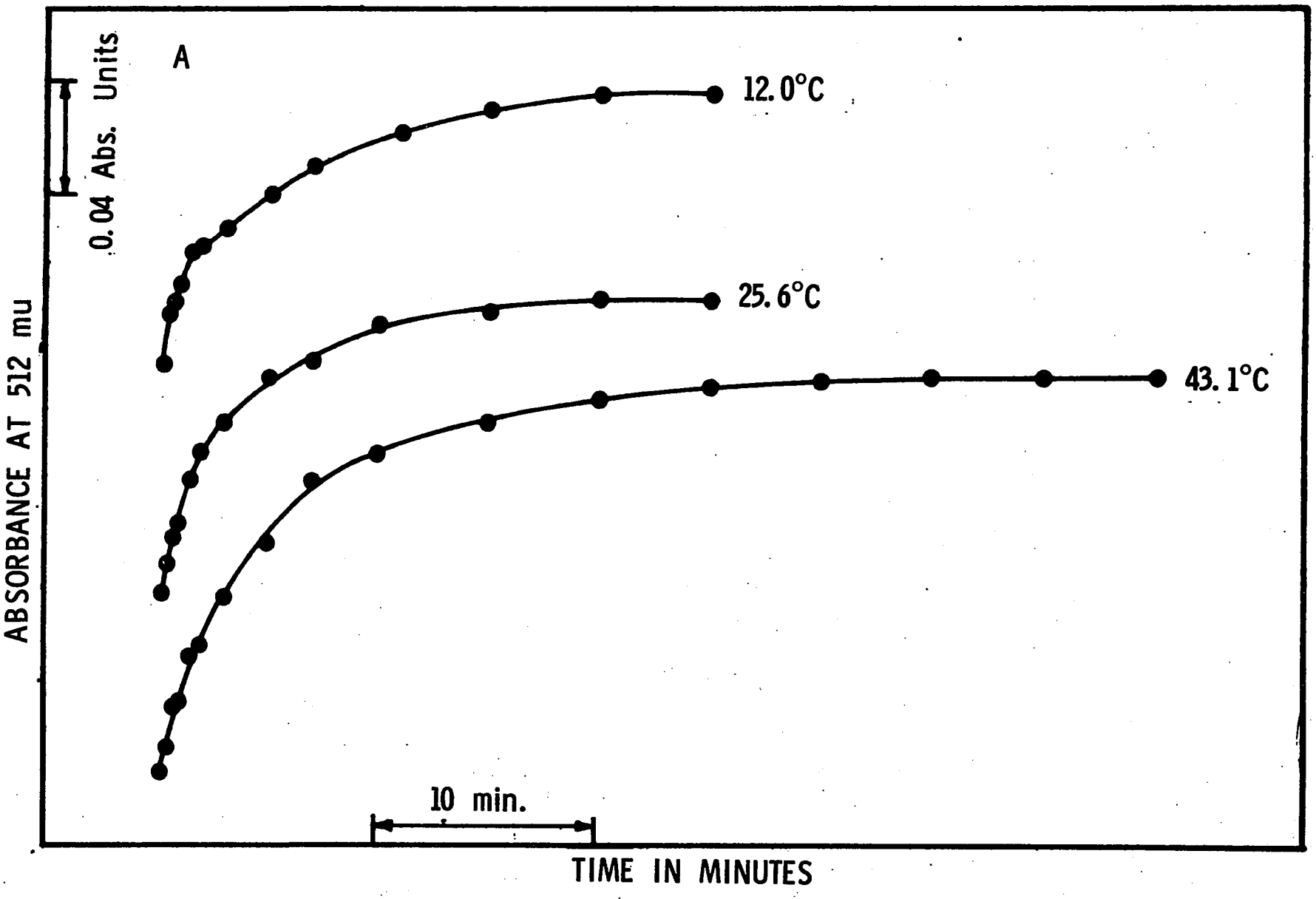
RATE OF ATTAINMENT OF EQUILIBRIUM OF THE REACTION OF CADMIUM OXINATE WITH DITHIZONE IN BENZENE

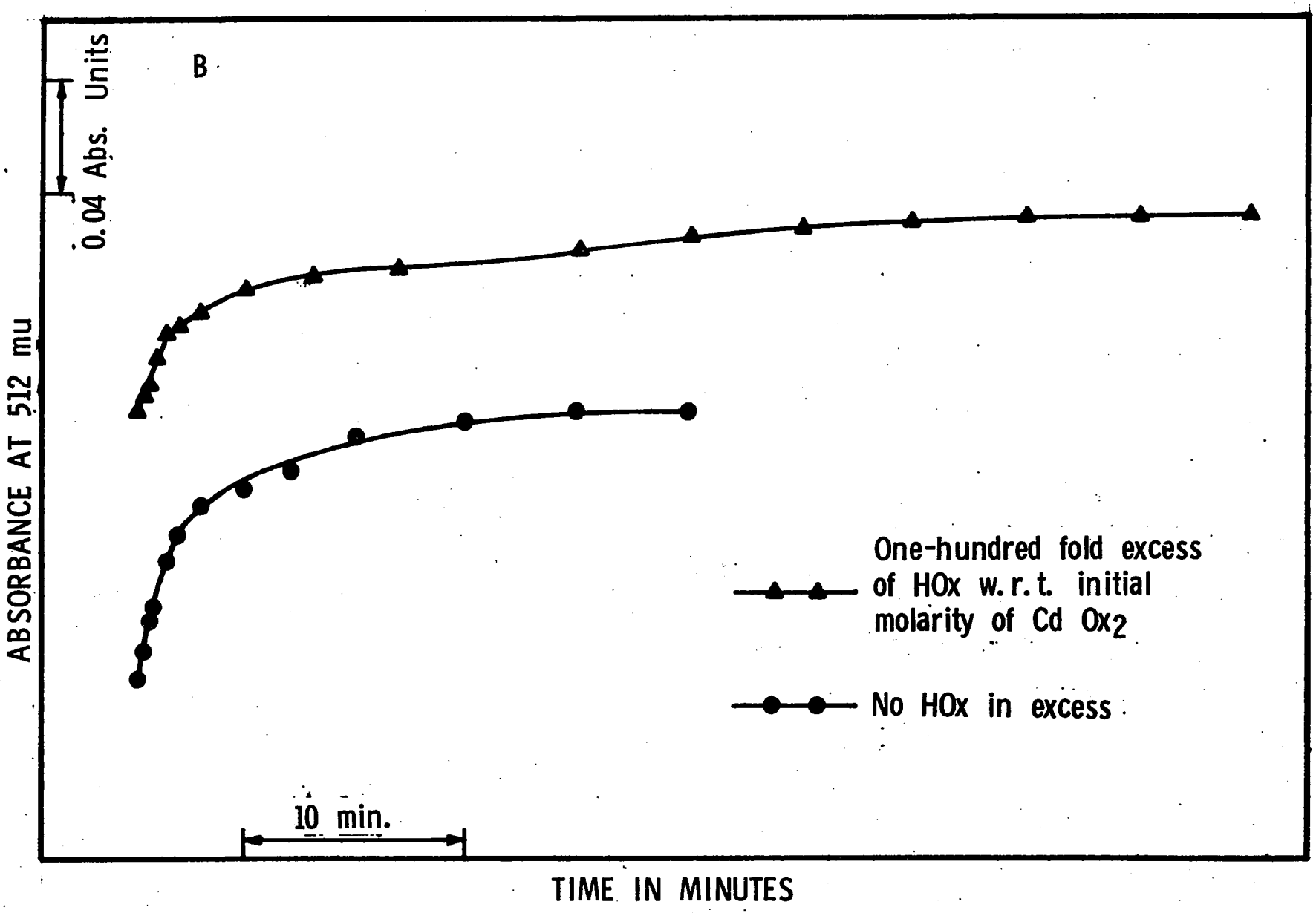
Initial Composition of Solution

Molarity of $CdOx_2$ = 2.204×10^{-6} M
Molarity of H_2Dz = 5.654×10^{-6} M
Volume of solution = 50 ml

(a) As a function of temperature, no initial free oxine.

(b) As a function of initial concentration of free oxine, at 25°C.


A
0.04 Abs. Units
12.0°C
25.6°C
43.1°C
ABSORBANCE AT 512 mu
10 min.
TIME IN MINUTES


B
0.04 Abs. Units
ABSORBANCE AT 512 mu
One-hundred fold excess of HOx w.r.t. initial molarity of Cd Ox2
No HOx in excess
10 min.
TIME IN MINUTES

for cadmium when the temperature of the initial solution was lowered from 25°C to 15°C.

In order to overcome the problem of the slow reaction of zinc and cadmium oxinates with dithizone, a different procedure was used in their titration. For titrations at 618 mμ, an accurately measured excess of dithizone solution, with respect to the estimated end point, was added to the solution of zinc or cadmium oxinate in the titration cell; the amount of dithizone added usually corresponded to about 1.5 equivalents. The solution was then allowed to equilibrate; at 25°C for cadmium and at 40°C for zinc; this required 10-20 minutes. Points for the second branch of the titration graph were obtained by adding several measured increments of dithizone solution to these solutions. It was found that the slope of the first linear branch of the titration graphs for these metal oxinates was zero. Therefore the end point was located by extrapolating the second branch of the graph to intersect with the abscissa. At the wavelength of maximum absorption of $Zn(HDz)_2$ and $Cd(HDz)_2$, the slope of the first branch of the titration graph was not zero. Therefore at this wavelength, several increments (3 to 4) of dithizone solution were added to the solution in the titration cell at the beginning of the titration in order to obtain enough points to draw the straight line. This took about 10 minutes since equilibrium was reached fairly rapidly in the early stages of the titration. Then

an accurately measured excess of dithizone was added as before and the solution allowed to equilibrate (10-20 minutes). Points for the second branch of the titration graph were obtained by adding several increments of dithizone solution to the equilibrated solution. The end point was located by extrapolating the two linear branchs of the graph.

Figure 51 illustrates the titration graphs obtained for the titration of cupric oxinate at 618 mμ and 545 mμ. The shapes of the graphs are typical of those obtained for all metal oxinates studied. At 618 mμ there was some vairation in the slope of the first branch of the curve; copper gave the most positive slope (cupric dithizonate absorbs at this wavelength), lead gave a very slight positive slope; the slopes for zinc and cadmium were zero. It was not possible to use the titration graphs obtained at 618 mμ in the titration of indium oxinate. There was curvature in the first branch of the graph, which led to uncertainty in locating the end point. Titration graphs obtained at 505 mμ for the titration of indium oxinate are shown in Figure 52. The curves illustrate the sensitivity of the reaction of indium oxinate with dithizone to initial concentrations of free oxine.

The titration of mixtures of metal oxinates were not studied.

FIGURE 51

TYPICAL TITRATION GRAPHS FOR THE TITRATION OF CUPRIC OXINATE WITH DITHIZONE IN BENZENE AT 25°C

(a) At 618 mμ

(b) At 545 mμ

Conc. standard H_2Dz solution	:	1.441×10^{-3} N
Conc. $CuOx_2$ solution in titration cell	:	6.926×10^{-6} N
Initial conc. of free oxine solution in titration cell	:	NIL
Initial volume of solution in titration cell	:	50 ml

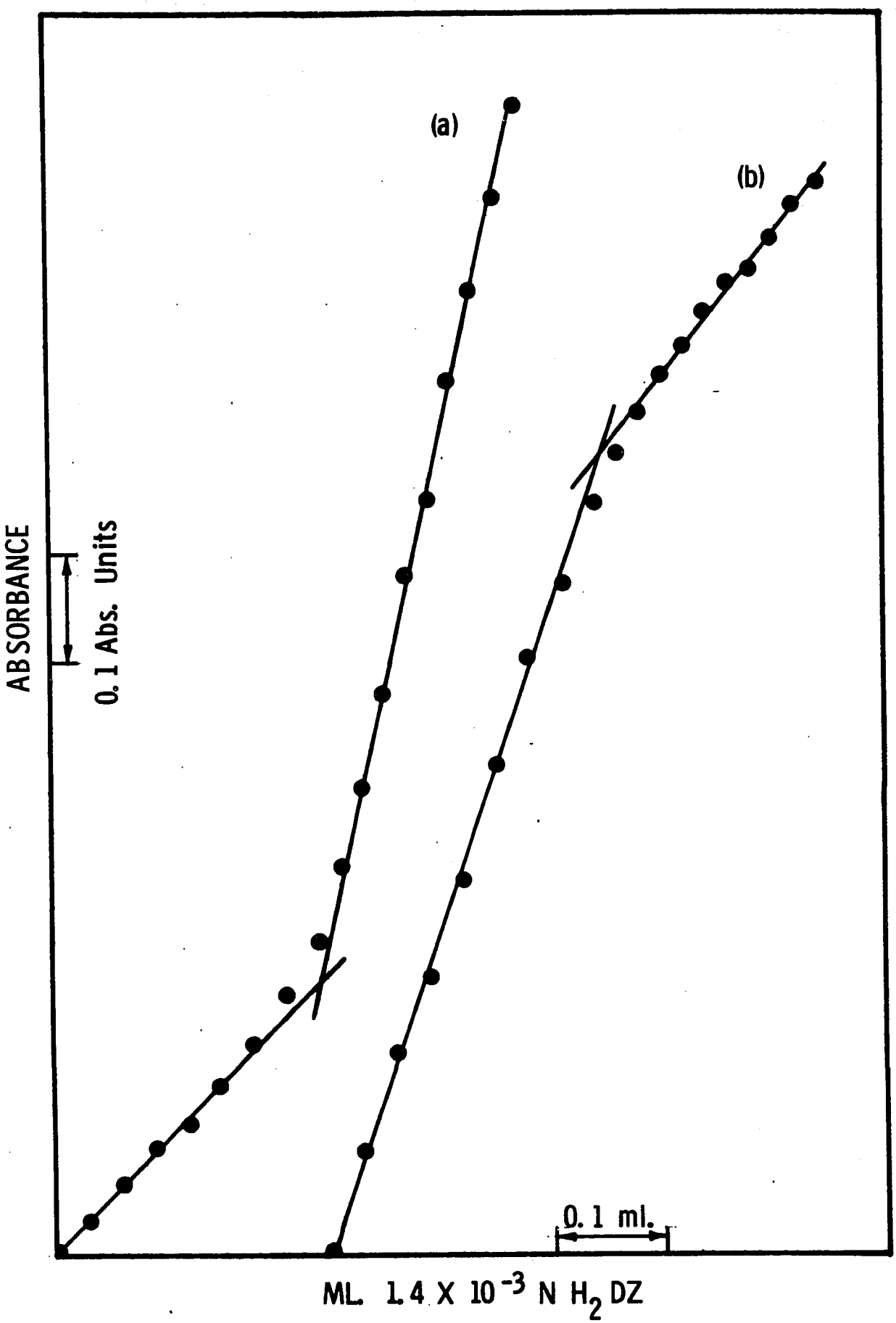

(a)
(b)
ABSORBANCE
0.1 Abs. Units
0.1 ml.
ML. 1.4 X 10⁻³ N H₂ DZ

FIGURE 52

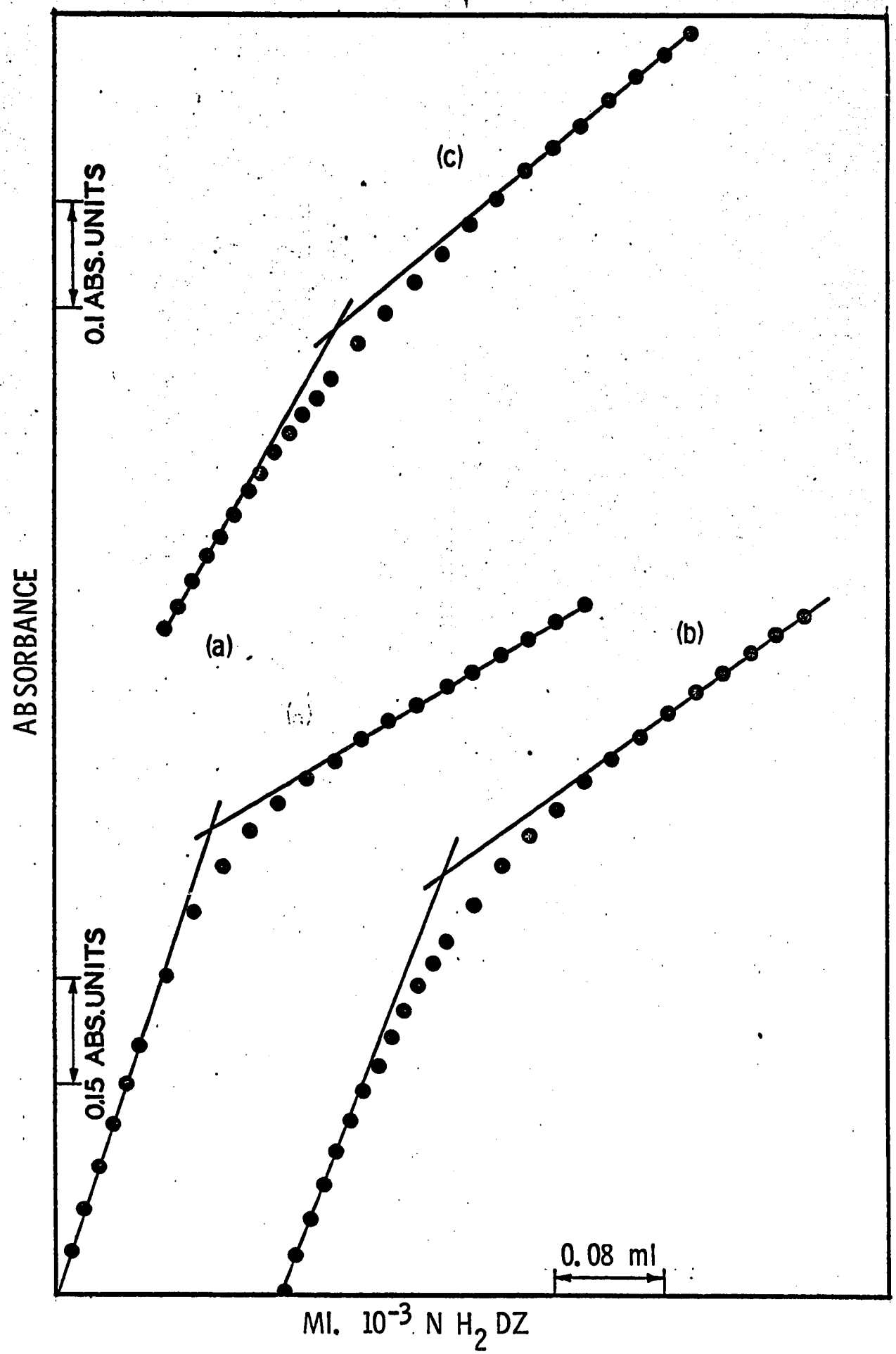
TITRATION GRAPHS ILLUSTRATING THE EFFECT OF INITIAL FREE OXINE IN THE SOLUTION FOR TITRATION WHEN INDIUM OXINATE WAS TITRATED SPECTROPHOTOMETRICALLY WITH DITHIZONE IN BENZENE AT 25°C and 505 mμ

(a) No initial concentration of free oxine

(b) Initial molar ratio $(InOx_3)_i:(HOx)_i$:1:10

(c) Initial molar ratio $(InOx_3)_i:(HOx)_i$:1:50

Initial conc. of $InOx_3$ in titration cell	:	5.312×10^{-6} N
Initial conc. of free HOx in titration cell for (b)	:	1.783×10^{-5} M
Initial conc. of free HOx in titration cell for (c)	:	8.915×10^{-5} M
Conc. of standard H_2Dz solution	:	1.042×10^{-3} N
Initial volume of solution	:	50 ml


(c)
0.1 ABS. UNITS
ABSORBANCE
(a)
(b)
0.15 ABS. UNITS
0.08 ml
Ml. 10^{-3} N H_2 DZ

The results of the titrations of single metal oxinates with dithizone in benzene are given in Tables 40-50. A statistical treatment of these data is given in Section IV D subsection 2. A theoretical interpretation of the titration graphs and of the reactions of lead, copper and indium oxinates with dithizone is given in Section IV D subsection 3. A discussion of the results is given in Section V C subsection 1(b).

2. Statistical Treatment of the Titration Data

(a) Introduction

The effect of the following factors on the accuracy and precision of the titration procedure which was developed in the present work was evaluated by statistical analyses of the data:

(1) The wavelength at which a titration was performed.

(2) Free oxine or dithizone, if initially present in the solution for titration.

(3) The method of locating the end point, namely by visual inspection, or by a least-squares method.

(4) The temperature of the solution for titration where applicable.

(b) Statistical Operations

The following statistical operations were performed on the data in Tables 32-50 in Section IV D, subsection 1. These Tables summarize the analytical data obtained from the chelate-exchange titrations. The "mean μeq MX_n found"

TABLE 40

SPECTROPHOTOMETRIC TITRATIONS OF LEAD OXINATE
WITH STANDARD DITHIZONE IN BENZENE AT 25°C

Normality of standard H_2Dz solution in benzene: 2.500×10^{-3} N at 618 mμ, 2.694×10^{-3} N at 517 mμ
Normality of lead oxinate solution in benzene : 6040×10^{-5} N
Initial volume of solution in titration cell : 50 ± 0.2 ml
Path length of titration cell : 5.0 cm

Initial Molar Ratio[1]	0		10		25		50		100	
Initial Conc. of HOx in Solution	-		3.012×10^{-5} M		7.530×10^{-5} M		1.506×10^{-4} M		3.012×10^{-4} M	
Wavelength mμ	618	517	618	517	618	517	618	517	618	517
μeq. $PbOx_2$ taken	0.3020	0.3020	0.3020	0.3020	0.3020	0.3020	0.3020	0.3020	0.3020	0.3020
μeq. $PbOx_2$ found[2]	0.2953	0.3040	0.2975	0.3045	0.2990	0.3075	0.2985	0.3035	0.2974	0.3090
% Error in μeq. found[3]	- 2.22	+ 0.66	- 1.52	+ 0.82	- 0.99	+ 1.82	- 1.16	+ 0.50	- 1.52	+ 2.32
Variance $S^2 \times 10^6$	32.12	17.50	21.05	16.88	46.98	21.88	21.43	11.25	38.13	14.38
Std. Deviation $S \times 10^3$	5.67	4.18	4.59	4.10	6.85	4.68	4.63	3.35	6.18	3.79

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $PbOx_2$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

TABLE 41

MICRO SPECTROPHOTOMETRIC TITRATIONS OF LEAD OXINATE WITH STANDARD DITHIZONE IN BENZENE AT 25°C

Normality of standard H_2Dz solution in benzene: 2.500×10^{-4} N
Normality of lead oxinate solution in benzene : 6.040×10^{-5} N
Initial volume of solution in titration cell : 2.50 ± 0.05 ml
Path length of titration cell : 1.0 cm

Initial Molar Ratio[1]	0		25		100	
Initial Conc. of HOx in Solution	-		1.51×10^{-4} M		6.024×10^{-4} M	
Wavelength mμ	618	517	618	517	618	517
μeq. $PbOx_2$ taken	0.03020	0.03020	0.03020	0.03020	0.03020	0.03020
μeq. $PbOx_2$ found[2]	0.03000	0.03025	0.03050	0.03075	0.03070	0.03035
% Error in μeq. found[3]	- 0.67	+ 0.17	+ 1.00	+ 1.82	+ 1.67	+ 0.5
Variance $S^2 \times 10^8$	116.0	153.0	281.0	93.8	79.3	33.1
Std. Deviation $S \times 10^4$	10.80	12.40	16.80	9.68	8.91	5.76

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $PbOx_2$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

TABLE 42

SPECTROPHOTOMETRIC TITRATIONS OF CADMIUM OXINATE WITH STANDARD DITHIZONE IN BENZENE AT 25°C

Normality of standard H_2Dz solution in benzene : 8.963×10^{-4} N
Normality of cadmium oxinate solution in benzene: 1.102×10^{-4} N
Initial volume of solution in titration cell : 50 ± 0.2 ml
Path length of titration cell : 5.0 cm

Initial Molar Ratio[1]	0		10		25		50		75		100	
Initial Conc. of HOx in Solution	-		2.126×10^{-5}M		6.378×10^{-5}M		1.063×10^{-4}M		1.701×10^{-4}M		2.126×10^{-4}M	
Wavelength mμ	618	512	618	512	618	512	618	512	618	512	618	512
μeq. $CdOx_2$ taken	0.2204	0.2204	0.2204	0.2204	0.2204	0.2204	0.2204	0.2204	0.2204	0.2204	0.2204	0.2204
μeq. $CdOx_2$ found[2]	0.2229	0.2216	0.2232	0.2207	0.2241	0.2217	0.2243	0.2239	0.2259	0.2256	0.2267	0.2264
% Error in μeq. found[3]	+1.13	+0.55	+1.30	+0.14	+1.68	+0.59	+1.77	+1.56	+2.50	+2.36	+2.84	+2.72
Variance $S^2 \times 10^6$	49.06	3.14	10.34	18.81	26.72	20.45	27.44	4.28	12.42	9.66	9.87	3.25
Std. Deviation $S \times 10^3$	7.00	1.78	3.22	4.34	5.17	4.52	5.24	2.07	3.52	3.11	3.14	1.80

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $CdOx_2$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

TABLE 43

MICRO SPECTROPHOTOMETRIC TITRATIONS OF CADMIUM OXINATE WITH STANDARD DITHIZONE IN BENZENE AT 25°C

Normality of standard H_2Dz solution in benzene : 1.063×10^{-4} N
Normality of cadmium oxinate solution in benzene: 1.102×10^{-4} N
Initial volume of solution in titration cell : 2.50 ± 0.05 ml
Path length of titration cell : 5.0 cm

Initial Molar Ratio[1]	0		20		100	
Initial Conc. of HOx in Solution	-		4.252×10^{-5} M		2.116×10^{-4} M	
Wavelength mμ	618	512	618	512	618	512
μeq. $CdOx_2$ Taken	0.01102	0.01102	0.01102	0.01102	0.01102	0.01102
μeq. $CdOx_2$ found[2]	0.01117	0.01109	0.01117	0.01117	0.01134	0.01126
% Error in μeq. found[3]	+1.36	+0.63	+1.36	+1.36	+2.90	+2.18
Variance $S^2 \times 10^8$	15.23	12.74	3.93	20.80	11.05	24.25
Std. Deviation $S \times 10^4$	3.90	3.57	1.98	4.56	3.32	4.92

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $CdOx_2$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

TABLE 44

SPECTROPHOTOMETRIC TITRATIONS OF COPPER OXINATE WITH STANDARD DITHIZONE IN BENZENE AT 25°C

Normality of standard H_2Dz solution in benzene : 1.365×10^{-3} N
Normality of copper oxinate solution in benzene: 6.926×10^{-5} N
Initial volume of solution in titration cell : 50 ± 0.2 ml
Path length of titration cell : 5.0 cm

Initial Molar Ratio[1]	0		10		20		40		80		100	
Initial Conc. of HOx in Solution	-		3.670×10^{-5}M		7.340×10^{-5}M		1.468×10^{-4}M		2.936×10^{-4}M		3.670×10^{-4}M	
Wavelength mμ	618	545	618	545	618	545	618	545	618	545	618	545
μeq. $CuOx_2$ taken	0.3463	0.3463	0.3463	0.3463	0.3463	0.3463	0.3463	0.3463	0.3463	0.3463	0.3463	0.3463
μeq. $CuOx_2$ found[2]	0.3442	0.3482	0.3471	0.3503	0.3493	0.3537	0.3506	0.3602	0.3572	0.3712	0.3659	0.3754
% Error in μeq. found[3]	-0.61	+0.55	+0.23	+1.18	+0.87	+2.14	+1.24	+4.00	+3.14	+7.06	+5.66	+8.40
Variance $S^2 \times 10^6$	29.02	16.99	8.20	2.46	19.25	14.08	8.71	29.02	12.39	25.90	16.07	41.63
Std. Deviation $S \times 10^3$	5.39	4.12	2.86	1.57	4.39	3.75	2.95	5.39	3.52	5.09	4.01	6.45

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $CuOx_2$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

TABLE 45

MICRO SPECTROPHOTOMETRIC TITRATIONS OF COPPER OXINATE WITH STANDARD DITHIZONE IN BENZENE AT 25°C

Normality of standard H_2Dz solution in benzene : 2.512×10^{-4} N
Normality of copper oxinate solution in benzene: 6.926×10^{-5} N
Initial volume of solution in titration cell : 2.50 ± 0.05 ml
Path length of titration cell : 1.0 cm

Initial Molar Ratio[1]	0		40		100	
Initial Conc. of HOx in Solution	-		2.936×10^{-4} M		7.34×10^{-4} M	
Wavelength mμ	618	545	618	545	618	545
μeq. $CuOx_2$ taken	0.03463	0.03463	0.03463	0.03463	0.03463	0.03463
μeq. $CuOx_2$ found[2]	0.03471	0.03491	0.03507	0.03617	0.03643	0.03758
% Error in μeq. found[3]	+0.23	+0.81	+1.27	+4.44	+5.20	+8.50
Variance $S^2 \times 10^8$	88.98	44.38	97.21	151.0	96.25	92.30
Std. Deviation $S \times 10^4$	9.43	6.66	9.86	12.29	9.81	9.61

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $CuOx_2$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

TABLE 46

SPECTROPHOTOMETRIC TITRATIONS OF ZINC OXINATE WITH STANDARD DITHIZONE IN BENZENE AT 25°C

Normality of standard H_2Dz solution in benzene: 1.033×10^{-3} N
Normality of zinc oxinate solution in benzene : 3.184×10^{-5} N
Initial volume of solution in titration cell : 50 ± 0.2 ml
Path length of titration cell : 5.0 cm

Initial Molar Ratio[1]	0		10		30	
Initial Conc. of HOx in Solution	-		1.783×10^{-5}M		5.349×10^{-5}M	
Wavelength mμ	618	528	618	528	618	528
μeq. $ZnOx_2$ taken	0.1592	0.1592	0.1592	0.1592	0.1592	0.1592
μeq. $ZnOx_2$ found[2]	0.1580	0.1619	0.1624	0.1655	0.1634	0.1655
% Error in μeq. found[3]	-0.75	+1.70	+2.00	+3.96	+2.64	+3.96
Variance $S^2 \times 10^6$	18.32	1.20	9.17	5.42	29.07	12.58
Std. Deviation $S \times 10^3$	4.28	1.10	3.03	2.33	5.39	3.53

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $ZnOx_2$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

TABLE 47

SPECTROPHOTOMETRIC TITRATIONS OF ZINC OXINATE WITH STANDARD DITHIZONE IN BENZENE AT 42.4 ± 0.4°C

Normality of standard H_2Dz solution in benzene: 1.040×10^{-3} N
Normality of zinc oxinate solution in benzene : 3.184×10^{-5} N
Initial volume of solution in titration cell : 50 ± 0.2 ml
Path length of titration cell : 5.0 cm

Initial Molar Ratio[1]	0		10		30		50	
Initial Conc. of HOx in Solution	-		1.783×10^{-5} M		5.349×10^{-5} M		8.915×10^{-5} M	
Wavelength mμ	618	528	618	528	618	528	618	528
μeq. $ZnOx_2$ taken	0.1592	0.1592	0.1592	0.1592	0.1592	0.1592	0.1592	0.1592
μeq. $ZnOx_2$ found[2]	0.1609	0.1636	0.1622	0.1671	0.1592	0.1634	0.1613	0.1675
% Error in μeq. found[3]	+1.07	+2.76	+1.88	+4.96	0.0	+2.64	+1.32	+5.20
Variance $S^2 \times 10^6$	10.19	16.1	10.53	8.26	27.66	2.99	3.62	2.50
Std. Deviation $S \times 10^3$	3.19	4.01	3.24	2.87	5.26	1.73	1.90	1.58

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $ZnOx_2$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

TABLE 48

MICRO SPECTROPHOTOMETRIC TITRATIONS OF ZINC OXINATE WITH STANDARD DITHIZONE IN BENZENE AT 42.4 ± 0.4°C

Normality of standard H_2Dz solution in benzene: 1.044×10^{-4} M for 618 mμ, 1.038×10^{-4} M for 528 mμ

Normality of zinc oxinate solution in benzene : 3.184×10^{-5} N
Initial volume of solution in titration cell : 2.50 ± 0.05 ml
Path length of titration cell : 1.0 cm

Initial Molar Ratio[1]	0		10		50	
Initial Conc. of HOx in Solution	-		3.566×10^{-5} M		1.783×10^{-4} M	
Wavelength mμ	618	528	618	528	618	528
μeq. $ZnOx_2$ taken	0.01592	0.01592	0.01592	0.01592	0.01592	0.01592
μeq. $ZnOx_2$ found[2]	0.01628	0.01640	0.01608	0.01650	0.01618	0.01640
% Error in μeq. found[3]	+2.26	+3.00	+1.00	+3.64	+1.63	+3.00
Variance $S^2 \times 10^8$	41.27	12.00	27.00	16.78	26.80	25.96
Std. Deviation $S \times 10^4$	6.42	3.46	5.20	4.10	5.18	5.10

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $ZnOx_2$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

TABLE 49

SPECTROPHOTOMETRIC TITRATIONS OF INDIUM OXINATE WITH STANDARD DITHIZONE IN BENZENE AT 25°C

Wavelength	:	505 mμ
Normality of standard H_2Dz solution in benzene	:	1.042×10^{-3} N
Normality of indium oxinate solution in benzene	:	5.312×10^{-5} N
Initial volume of solution in titration cell	:	50 ± 0.2 ml
Path length of titration cell	:	5.0 cm

Initial Molar Ratio[1]	0	5	10	20	30	50
Initial Conc. of HOx in Solution M	-	8.915×10^{-6}	1.783×10^{-5}	3.566×10^{-5}	5.349×10^{-5}	8.915×10^{-5}
μeq. $InOx_3$ Taken	0.2656	0.2656	0.2656	0.2656	0.2656	0.2656
μeq. $InOx_3$ found[2]	0.1178	0.1313	0.1375	0.1416	0.1459	0.1492
% Error in μeq. found[3]	-55.5	-50.6	-48.3	-46.7	-45.0	-43.9
Variance $S^2 \times 10^6$	15.38	10.82	3.76	18.43	8.86	26.58
Std. Deviation $S \times 10^3$	3.92	3.29	1.94	4.29	2.98	5.15

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $InOx_3$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

TABLE 50

MICRO SPECTROPHOTOMETRIC TITRATIONS OF INDIUM OXINATE WITH STANDARD DITHIZONE IN BENZENE AT 25°C

Wavelength	:	505 mμ
Normality of standard H_2Dz solution in benzene	:	1.089×10^{-4} N
Normality of indium oxinate solution in benzene	:	5.312×10^{-5} N
Initial volume of solution in titration cell	:	2.50 ± 0.05 ml
Path length of titration cell	:	5.0 cm

Initial Molar Ratio[1]	0	10	20	50
Initial Conc. of HOx in Solution	-	3.566×10^{-5}	7.132×10^{-5}	1.783×10^{-4}
μeq. $InOx_3$ taken	0.02656	0.02656	0.02656	0.02656
μeq. $InOx_3$ found[2]	0.01187	0.01394	0.01437	0.01514
% Error in μeq. found[3]	-54.8	-47.6	-45.8	-43.1
Variance $S^2 \times 10^8$	10.01	37.00	36.86	10.56
Std. Deviation $S \times 10^4$	3.16	6.08	6.07	3.25

[1]Approximate molar ratio of the initial concentration of oxine with respect to the initial concentration of $InOx_3$ present in the titration solution.
[2]Average of 5 samples.
[3]Calculated as the per cent difference between the μeq. found and μeq. taken.

is the mean of five, replicate titrations. Titrations were performed on solutions with given initial concentrations of free chelating agent (HX) at two wavelengths. The relevant formulae and methods of calculation are in references (103) and (119) respectively.

(1) Variances were computed.

(2) These variances were tested for homogeneity by using Bartlett's Criterion.

(3) The variances associated with two different methods of end-point determination were compared for the titration of copper (II) oxinate. These methods are described in Section IV C, subsection 1(a).

(4) The variances for the amount of a metal oxinate found in the presence of initial amounts of free oxine and wavelength were calculated. Then by a two-sided classification Analysis-of-Variance calculation, the effect of free oxine and wavelength and their interaction on the accuracy of a titration was estimated.

(5) In cases where free oxine initially present affected accuracy (as deduced from (4) above), a correction curve was plotted, and the regression line calculated by least squares. Then the assumption of linearity was confirmed.

(6) The means and variances for the end points of the titration of copper (II) oxinate obtained by visual inspection and least squares, were compared by using the conventional F-test and t-test, respectively.

In these statistical operations, the 5% level of significance was used. Hypotheses were rejected with a 5% risk of making an error. The level of significance will be denoted as a subscript to the symbol of the statistic calculated. The degrees of freedom will be indicated in brackets after the symbol for the statistic. When a statistic is calculated from a ratio, the degrees of freedom for the numerator are given first. For example

$$F_{0.05}\ (5,24) = 2.62$$

indicates that the value of F from the F Tables is 2.62 at the 5% level of significance, when the degrees of freedom for the numerator are 5 and those of the denominator, 24.

(c) Statistical Treatment of the Data for the Titration of Copper Oxinate with Dithizone

(i) Method for estimating the end point of titrations

The visual, and the least-squares methods for estimating the end point of a titration were compared; the data are in Table 51. The variances obtained from the least-squares method were found to be homogeneous, but those obtained from the visual-inspection method were not (see Table 1(a) and (b) of Appendix XXV for the parameter and a sample calculation). The inhomogeneity of the variances obtained from the visual-inspection method may have resulted

TABLE 51

MEANS AND VARIANCES FOR END POINTS (i) ESTIMATED BY VISUAL INSPECTION AND (ii) CALCULATED BY THE LEAST-SQUARES METHOD, IN THE TITRATION OF COPPER OXINATE WITH DITHIZONE, IN BENZENE

$CuOx_2$ taken: 0.3463 μeq.

Initial Molar Ratio $(HOx)_i : (CuOx_2)_i$	$CuOx_2$ Found[1], μeq.				Variance[2], $S^2 \times 10^6$			
	Visual Inspection		Least Squares		Visual Inspection		Least Squares	
	618 mμ	545 mμ	618 mμ	545 mμ	618 mμ	545 mμ	618 mμ	545 mμ
0	0.3431	0.3496	0.3442	0.3482	31.30	57.80	29.02	16.99
10.7	0.3463	0.3509	0.3471	0.3503	0.75	11.05	8.20	2.46
21.3	0.3490	0.3524	0.3493	0.3537	6.24	43.40	19.25	14.08
42.6	0.3528	0.3624	0.3506	0.3602	2.25	24.60	8.71	29.02
85.3	0.3586	0.3700	0.3572	0.3712	54.40	1.56	12.39	25.90
106.6	0.3667	0.3740	0.3659	0.3754	5.08	35.34	16.07	41.63

[1]Average of 5 replicate determinations.

[2]Calculated for 4 degrees of freedom.

from pre-knowledge of the amount of copper oxinate taken. Thus, there may have been a tendency to draw the "best" straight lines in favour of the expected end point. This situation would not arise in a practical titration when the amount of copper oxinate present would be unknown.

The means of the amounts of copper oxinate found by the two methods of end-point determination, were shown by the t-test not to differ significantly. Nevertheless, in the present work the end point was in all cases found by the least-squares method, because that method gave homogeneous variances.

(ii) Analysis of variance

From the experimental data (see Tables 44 and 45 of Section IV D subsection 1(c) and Tables 2(a) and (b) in Appendix XXV) the initial presence of free oxine was found to affect the accuracy of the titration of copper oxinate with dithizone. The accuracy was also different when titrations were performed at two wavelengths, 618 mμ and 545 mμ. A two-sided classification analysis of variance gave the following information:

(1) Whether to accept or reject the null hypothesis $\sigma^2_{HOx} = 0$*.

*σ^2_{HOx}, σ^2_{λ}, σ^2_{I} and σ^2_{R} represent estimates of the component of the population variance due to the effect of; (i) initial presence of free oxine in the solution; (ii) titrating at 618 mμ or 545 mμ; (iii) interaction of (i) and (ii), and (iv) reproducibility.

(2) An estimate of σ^2_{HOx} if $\sigma^2_{HOx} \neq 0$.

(3) Whether to accept or reject the null hypothesis σ^2_λ and an estimate of σ^2_λ if $\sigma^2_\lambda \neq 0$.

(4) Whether the effects of the initial presence of free oxine in the titration solution and titrating at 618 mμ and 545 mμ are additive, that is, to accept or reject the null hypothesis $\sigma^2_I = 0$.

(5) An estimate of σ^2_I if $\sigma^2_I \neq 0$.

(6) An estimate of σ^2_R.

The analysis-of-variance calculations on the data of the titration of copper oxinate with dithizone in benzene are shown in Table 3 of Appendix XXV. The null hypothesis $\sigma^2_I = 0$ was rejected because the interaction variance was significantly greater than that expected from the reproducibility variance. This indicates that the two wavelengths have different effects depending on the initial concentration of free oxine in the titration solution. The variance component was calculated as shown in Appendix XXV, Table 3.

The null hypothesis $\sigma^2_{HOx} = 0$ was also rejected. Therefore, the initial presence of free oxine in the solution for titration was significant; the variance component σ^2_{HOx} could then be calculated with the use of the equations given in Appendix XXV, Table 3. The results are summarized in Table 52.

The means at 618 mμ and 545 mμ were also compared by the conventional t-test. These comparisons were made at each

TABLE 52

SUMMARY OF RESULTS OBTAINED FROM ANALYSIS OF VARIANCE ON THE DATA OF THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE AT 618 mμ AND 545 mμ

CuOx Taken μeq.	No. of $(HOx)_i : (CuOx_2)_i$ Ratios	σ_R^2 [1] x 10^6	σ_I^2 [2] x 10^6	σ_{HOx}^2 [3] x 10^6	σ_λ^2 [4] x 10^6	σ_R x 10^3
0.3463	6	18.79	5.33	85.9	26.06	4.3
0.03463	3	0.937	0	2.268	0.827	0.97

Degrees of freedom

	0.3463 μeq. $CuOx_2$	0.03463 μeq. $CuOx_2$
(1)	48	24
(2)	5	-
(3)	5	2
(4)	1	1

of the different molar ratios $(HOx)_i:(CuOx_2)_i$. The results are in Table 53. The means are significantly different for the three cases where the ratio was 42.6:1, 85.3:1, and 106.6:1. These findings confirm those from the analysis of variance that wavelength has an effect depending on the initial concentration of free oxine in the titration solution. That the means are significantly different is not of practical importance because correction curves can be constructed for each of these wavelengths, which erase the errors (see below).

(iii) Correction for initial presence of free oxine

In subsection (ii) above it was shown that free oxine initially present in the solution for titration affected the accuracy of the titration. The per cent error E* in the titration is shown in Figure 53(a) and (b) as a function of the initial molar ratio of free oxine to copper oxinate, for two different amounts of copper oxinate, and two different wavelengths. The solid lines are the regression lines calculated by least squares from the data in Tables 2(a) and (b), Appendix XXV, the broken lines are the 95% confidence limits. The equations for these regression lines were found to be

$$E = 7.51 \times 10^{-2} R + 0.55 \text{ at } 545 \text{ m}\mu$$

$$E = 5.19 \times 10^{-2} R - 0.55 \text{ at } 618 \text{ m}\mu$$

*Calculated as the percentage difference between μeq of $CuOx_2$ taken and μeq of $CuOx_2$ found.

TABLE 53

VALUES OF t FOR THE TEST OF SIGNIFICANCE BETWEEN THE MEANS OF THE AMOUNT OF COPPER OXINATE FOUND IN TITRATIONS WITH DITHIZONE AT 618 mμ AND 545 mμ

Molar Ratio $(HOx)_i : (CuOx_2)_i$	Mean[1] $CuOx_2$ Found at 618 mμ μeq.	Mean[1] $CuOx_2$ Found at 545 mμ μeq.	Value[2] of t	Significance at 5% Level
0	0.3442	0.3482	1.32	Not Significant
10.7	0.3471	0.3503	2.19	Not Significant
21.3	0.3493	0.3537	1.70	Not Significant
42.6	0.3506	0.3602	3.34	Significant
85.3	0.3572	0.3712	5.06	Significant
106.6	0.3659	0.3754	2.80	Significant
0	0.03471	0.03491	0.39	Not Significant
42.6	0.03507	0.03617	1.56	Not Significant
106.6	0.03643	0.03758	1.87	Not Significant

The value of t at the 5% level of significance is

$t_{0.05}\ (8) = 2.31$
$t_{0.01}\ (8) = 3.36$

[1]Mean of 5 determinations.
[2]See Tables 2(a) and (b) of Appendix XXV for the variances.

FIGURE 53

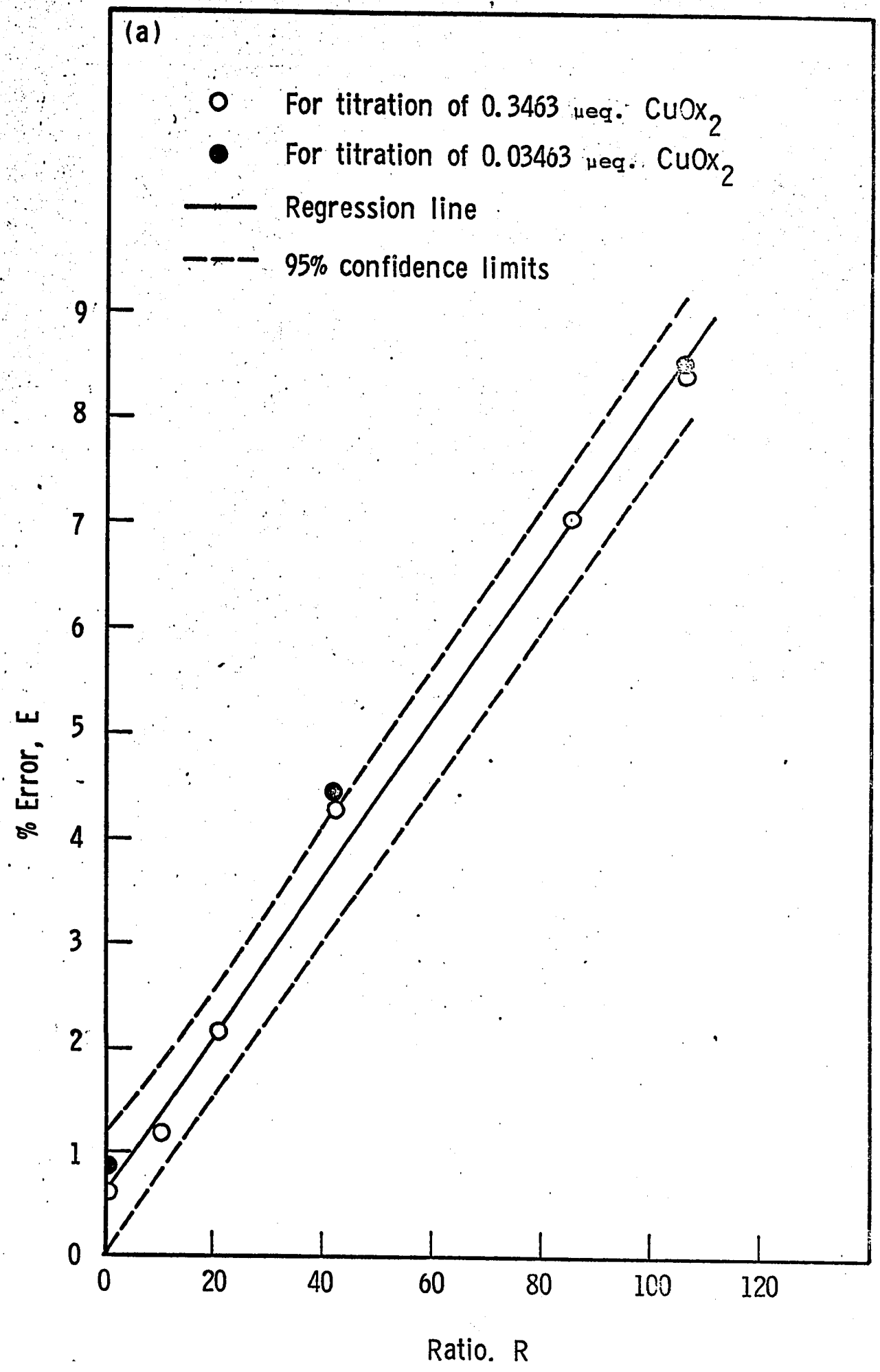
CORRECTION CURVES FOR THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE

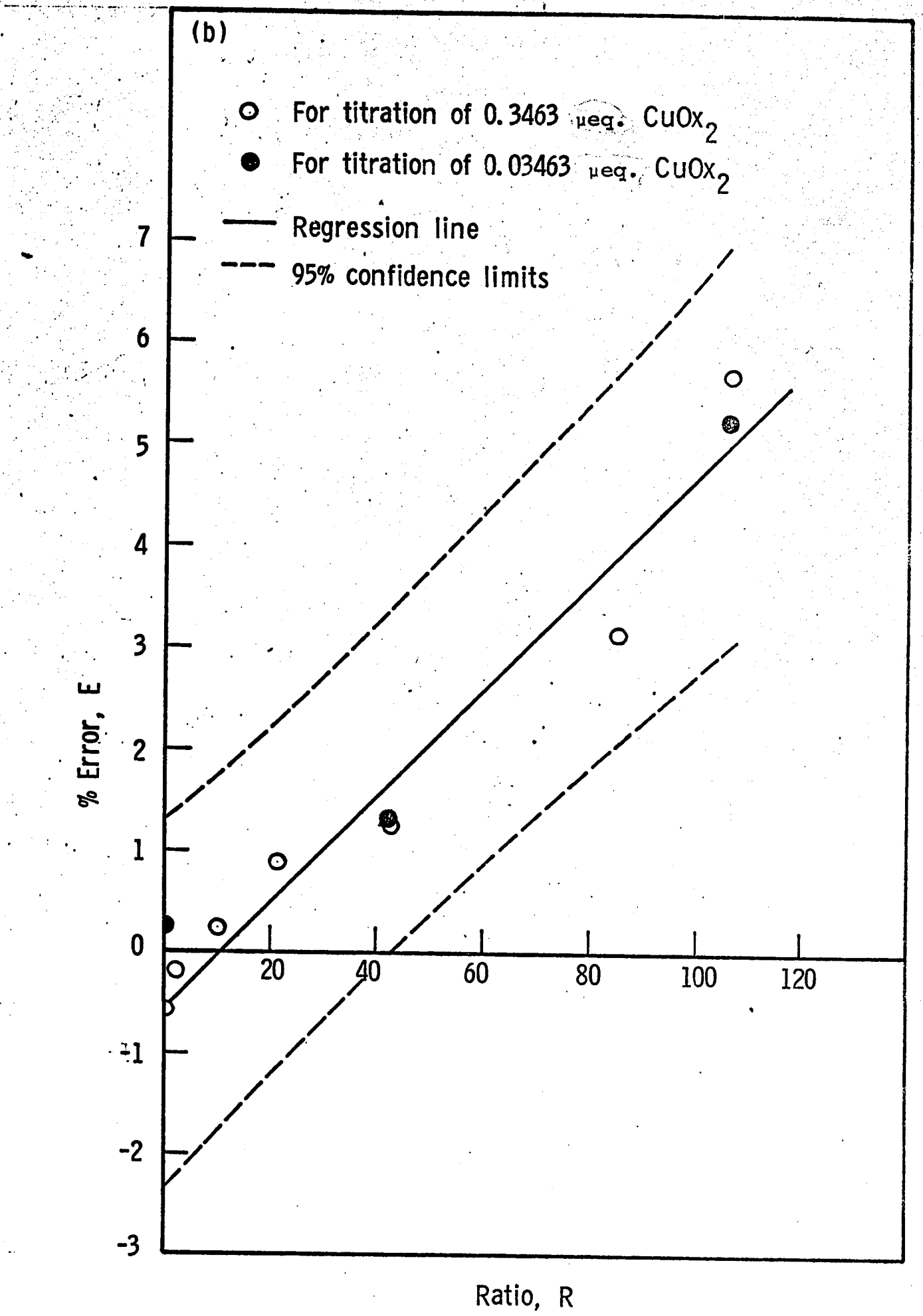
(a) For titrations at 545 mμ

(b) For titrations at 618 mμ

E is the per cent error calculated as the difference between the μeq $CuOx_2$ taken and μeq $CuOx_2$ found.

R is the initial molar ratio of free oxine with respect to the initial concentration of copper oxinate in the titration solution, $(HOx)_i/(CuOx_2)_i$.


(a)
For titration of 0.3463 μeq. $CuOx_2$
For titration of 0.03463 μeq. $CuOx_2$
Regression line
95% confidence limits
% Error, E
0
1
2
3
4
5
6
7
8
9
0
20
40
60
80
100
120
Ratio. R


(b)
For titration of 0.3463 μeq. $CuOx_2$
For titration of 0.03463 μeq. $CuOx_2$
Regression line
95% confidence limits
% Error, E
7
6
5
4
3
2
1
0
-1
-2
-3
20
40
60
80
100
120
Ratio, R

where E = per cent error calculated as the difference between μeq $CuOx_2$ taken and μeq $CuOx_2$ found

R = initial molar ratio of free oxine with respect to the initial concentration of copper oxinate in the titration solution

Since a ratio was plotted versus per cent error, these correction curves should be valid for any concentration of copper oxinate within the limits specified in Section V B. The points for the titration of 0.03463 μeq of copper oxinate were close to those obtained for the titration of 0.3463 μeq (plotted on black dots in Figures 53(a) and (b)) which confirmed this. The curve is known to be valid only for concentrations of initial free oxine up to onehundredfold in excess relative to the initial concentration of copper oxinate; data for higher ratios were not obtained in the present work.

It was verified by a regression analysis that the regression lines were linear. The difference between the angular coefficients of the regression-line equations for 618 mμ and 545 mμ was found to be significant. The calculations are in Tables 4 and 5 of Appendix XXV. This was to be expected from the results already obtained from the analysis of variance (subsection (ii) of this Section).

To obtain the correct concentration of a copper oxinate solution after it has been titrated in the presence

of an initial amount of free oxine, an iterative procedure can be used. Figure 53 is employed and it is assumed that the amount of free oxine has been determined by an independent measurement*. A sample calculation follows:

Let concentration of free oxine present initially in the titration solution be 24.24 μ mole in 50 ml
Let apparent μ mole of $CuOx_2$ found by titration with dithizone at 545 mμ be 0.374 μ mole
Apparent molar ratio $(HOx)_i/(CuOx_2)_i = 64.9$
From Figure 53(a) (545 mμ curve) the per cent error (% E) at 64.9 = 5.4%
Apply the correction 0.946 x 0.374 = 0.354 μ mole
New apparent molar ratio = $\frac{24.24}{0.354} = 68.5$
From Figure 53(a) the per cent error at 68.5 = 5.7%
Apply the correction 0.943 x 0.374 = 0.352 μ mole
New apparent ratio = $\frac{24.24}{0.352} = 69.0$
From Figure 53(a) the per cent error at 69.0 = 5.74%
Apply the correction $0.9426 \times 0.374 = 0.352_5$
Therefore true μ mole $CuOx_2$ present = 0.352 μ mole (to three significant figures)

The initial amount of free oxine need be only approximately known. In the above example, if the true free oxine concentration had been 20% higher, the μ mole of copper oxinate found after iterations would have been 0.349 μ mole, a difference of less than 1% from the previous value.

Figure 53(a) and (b) indicates that corrections for the presence of initial free oxine need not be applied if an

*Several methods are suggested under "Discussion of Results".

error of 5% in the copper result can be tolerated, provided that the titration is carried out at 618 mμ. The titration will not be as precise as at 545 mμ as shown by wide range of the 95% confidence limits. At 545 mμ, the increase in the per cent error was greater but the variance about the regression line of the correction curve was less (the 95% confidence limits are narrower). Thus if greater precision is required, 545 mμ would be the preferred wavelength for the titration.

(d) Statistical Treatment of the Data for the Titration of Indium Oxinate with Dithizone, in Benzene

Calculations similar to those for copper oxinate were also performed on the data obtained from the titration on indium oxinate with dithizone in benzene at 505 mμ. These data are in Tables 49 and 50 of Section IV D subsection 1(c). A more complete set of data is given in Table 1 of Appendix XXVI.

The variances there were found to be homogeneous according to Bartlett's criterion. A one-stage analysis of variance showed that the presence of initial free oxine had a significant effect on the titration. The calculations are given in Table 2 of Appendix XXVI. The results are summarized in Table 54.

To correct for the effect of the initial presence of free oxine, a curve similar to that described for the titration of copper oxinate was plotted. However, unlike the

TABLE 54

SUMMARY OF RESULTS OBTAINED FROM ANALYSIS OF VARIANCE ON THE DATA OF THE TITRATION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 505 mμ

$InOx_3$ Taken μeq.	No. of $(HOx)_i : (InOx_3)_i$ Ratios	σ_R^2 [1] x 10^6	σ_{HOx}^2 [2] x 10^6	σ_R x 10^6
0.2656	6	14.0	128.0	3.7
0.02656	4	0.24	1.91	0.48

[1]Degrees of freedom = 24 for 0.2656 μeq. $InOx_3$
Degrees of freedom = 16 for 0.02656 μeq. $InOx_3$

[2]Degrees of freedom = 5 for 0.2656 μeq. $InOx_3$
Degrees of freedom = 3 for 0.02656 μeq. $InOx_3$

copper oxinate curve, the per cent error when plotted as a function of the initial molar ratio $(HOx)_i:(InOx_3)_i$ was not linear. However a plot of E, the per cent error, as a function of the logarithm of the initial molar ratio was found to be linear. This is an empirical relationship and has no theoretical significance. The regression line was calculated by least squares from the data in Table 1, Appendix XXVI, and the equation* found to be

$$E = 6.86 \log R - 55.4$$

where E = per cent error calculated as the difference between μeq $InOx_3$ taken and μeq $InOx_3$ found

R = initial molar ratio $(HOx)_i:(InOx_3)_i$.

The per cent error as a function of the logarithm of the initial molar ratio $(HOx)_i:(InOx_3)_i$ is shown graphically in Figure 54. The solid line is the regression line, the broken lines, the 95% confidence limits. It was verified that this line was linear, and the relevant calculations are shown in Table 3 of Appendix XXVI.

It was found that the points obtained when 0.02656 μeq of $InOx_3$ was titrated (black circles in Figure 54) were close to those obtained when 0.2656 μeq was titrated. This confirms the validity of the curve for any concentration of indium oxinate within the limits specified in Section V B.

---

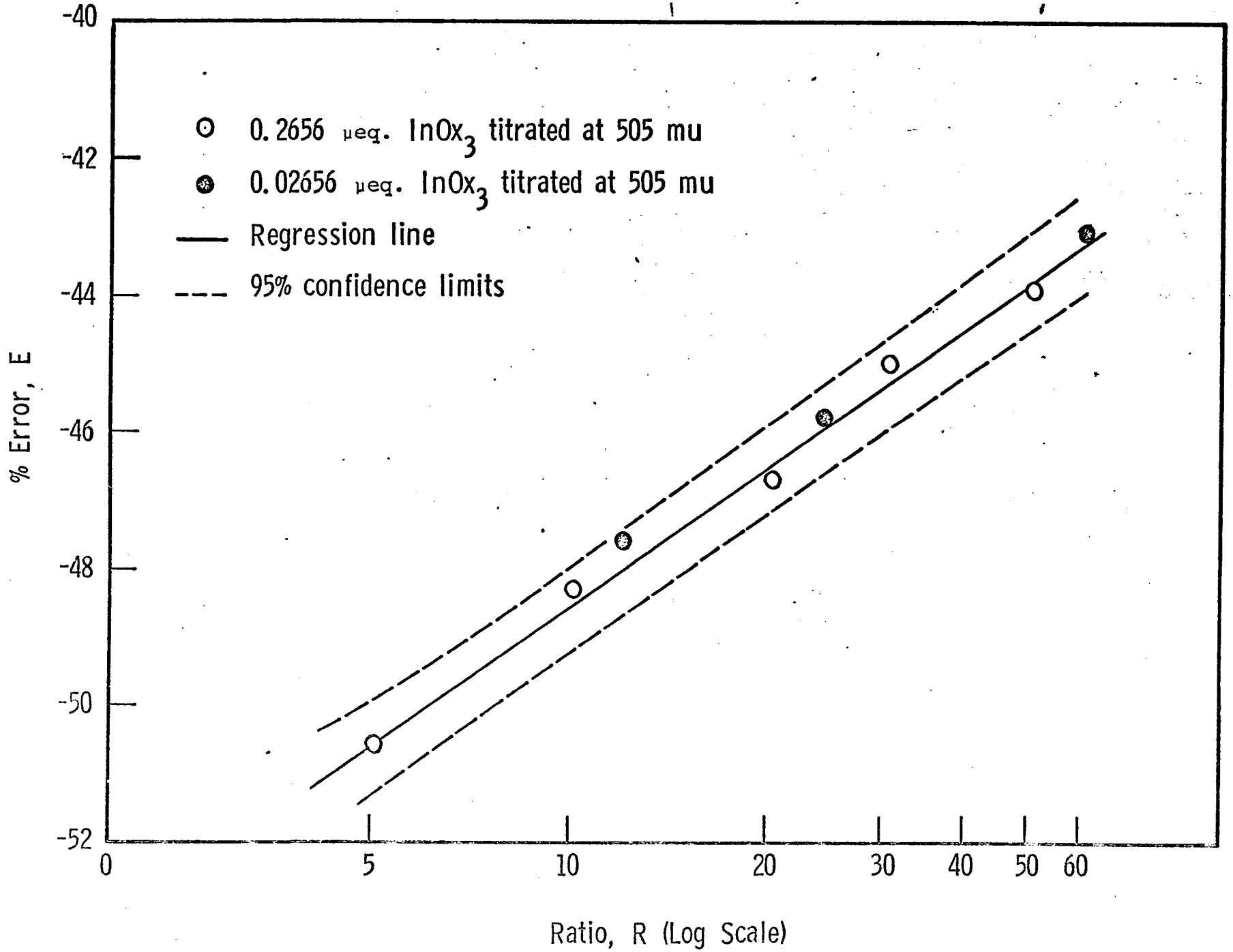
*This equation is only valid for initial molar ratios of $(HOx)_i:(InOx_3)_i$ up to 50:1. At higher ratios, the titration graph had everywhere so much curvature that the end point could not be determined.

FIGURE 54

CORRECTION CURVE FOR THE TITRATION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 505 mμ

E is the per cent error calculated as the difference between the μeq $InOx_3$ taken and μeq $InOx_3$ found

R is the initial molar ratio of free oxine with respect to the initial concentration of indium oxinate in the titration solution, $(HOx)_i/(InOx_3)_i$


-40
-42
-44
-46
-48
-50
-52
% Error, E
0.2656 µeq. InOx3 titrated at 505 mu
0.02656 µeq. InOx3 titrated at 505 mu
Regression line
95% confidence limits
0
5
10
20
30
40
50
60
Ratio, R (Log Scale)

The iteration procedure for correcting the apparent amount of indium oxinate found by titration is similar to that described for copper oxinate.

(e) Statistical Treatment of the Data for the Titration of Lead, Zinc and Cadmium Oxinates with Dithizone in Benzene

It was found in the titration of lead, zinc and cadmium oxinates, that the variances for the end points were homogeneous. It was further found, by an analysis of variance, that the presence of initial free oxine in the titration solution did not contribute to the total variance. Therefore, for each of the oxinates, the null hypothesis $\sigma^2_{HOx} = 0$ was accepted and an estimate of the population variance due to random fluctuations, σ^2_R, was obtained. It was further found that the variances for the end points when the metal oxinates were titrated at 618 mμ and the wavelength of maximum absorption of the metal dithizonate were not significantly different, at the 5% level of significance. Therefore a pooled estimate of the population variance was calculated. The results are summarized in Table 55.

The grand means were calculated from the data of Tables 40-43 and 46-47 in Section IV D subsection 1(c) for each of the given wavelengths. These means were compared, by the conventional t-test. The values of t are given in Table 55. It was found that some means were significantly different even at the 1% level of significance and they are indicated in Table 55.

TABLE 55

COMPARISON OF POOLED VARIANCES AND GRAND MEANS WHEN LEAD, ZINC AND CADMIUM OXINATES WERE TITRATED WITH DITHIZONE IN BENZENE AT 618 mμ AND THE WAVELENGTH OF MAXIMUM ABSORPTION OF THE METAL DITHIZONATE

Metal Oxinate Titrated	λ mμ	MOx_2 Taken μeq.	Grand Mean of MOx_2 Found μeq.	Value of t	Degrees of Freedom for t Test	Estimate of $\sigma_R^2 \times 10^6$	Value of F	Degrees of Freedom for F Test	Pooled Estimate of $\sigma_R^2 \times 10^6$	Standard Deviation $\sigma_R \times 10^3$
$PbOx_2$	618	0.3020	0.3057	5.79	48	19.7	1.55	24	50.2	7.1
	517	0.3020	0.2975			30.5		24		
	618	0.03020	0.03045	0.13	28	0.80	1.80	14	1.12	1.05
	517	0.03020	0.03040							
$ZnOx_2$[1]	618	0.1592	0.1609	4.20	38	12.2	1.21	19	11.2	3.3
	535	0.1592	0.1654			10.1		19		
	618	0.01592	0.01618	1.48	28	0.27	1.74	14	0.22	0.47
	535	0.01592	0.01643			0.16		14		
$CdOx_2$	618	0.2204	0.2245	1.26	58	20.1	1.52	29	16.6	4.1
	520	0.2204	0.2233			13.2		29		
	618	0.01102	0.01123	0.26	28	0.42	1.17	14	0.39	0.62
	520	0.01102	0.01117			0.36		14		

$F_{0.05}$ (14,14) = 2.49
$F_{0.05}$ (19,19) = 2.19
$F_{0.05}$ (24,24) = 1.98
$F_{0.05}$ (29,29) = 1.86

$t_{0.05}$ (28) = 1.70
$t_{0.05}$ (38) = 1.68
$t_{0.05}$ (48) = 1.68
$t_{0.05}$ (58) = 1.67

$t_{0.01}$ (28) = 2.76
$t_{0.01}$ (38) = 2.72
$t_{0.01}$ (48) = 2.68
$t_{0.01}$ (58) = 2.66

[1]For $ZnOx_2$ titrated at a solution temperature of 40°C.

Zinc oxinate was titrated at two titration-solution temperatures, 25°C and 40°C. It was found that, at a given wavelength:

(1) The presence of initial free oxine in the titration solution did not have a significant effect at either temperature.

(2) The pooled variances and grand means were not significantly different at the two temperatures. Therefore zinc oxinate can be titrated at either 25°C or 40°C with equal accuracy and precision. Only the kinetic factor influences the choice of temperature.

(f) Statistical Treatment of the Data for the Titration of Metal Dithizonates in Chloroform with Sodium Diethyldithiocarbamate in Ethanol

The variances for the end points obtained from the titration of individual metal dithizonates with sodium diethyldithiocarbamate (see Tables 32-37 of Section IV D subsection 1(b)) were found to be homogeneous by Bartlett's criterion.

Analyses of variance on the data were of limited value because the concentration range of initial free dithizone was too narrow*. A qualitative inspection of Table 32 in Section IV D subsection 1(b) suggests that the presence of

*It was possible to study only up to a fourfold excess of free dithizone with respect to the initial molar concentration of metal dithizonate (see Section IV D subsection 1(b)).

initial free dithizone may significantly affect the accuracy of the titration of silver dithizonate.

The grand means were calculated from the data in Tables 32-37. These means and the pooled variances were compared by the conventional t-test and F-test, respectively, between the given wavelengths. The results are summarized in Table 56.

3. Calculation of Equilibrium Constants

(a) Introduction

The spectrophotometric titration of metal chelates in nonaqueous low-dielectric constant solvents, proposed and developed in the present work, was based on the chelate-exchange reaction:

$$MX_n + nHY \rightleftarrows MY_n + nHX \qquad I$$

where HY is an organic chelating agent and MX_n is the metal chelate of the organic chelating agent HX. In the present work MX_n was either a metal dithizonate, $M(HDz)_n$ or a metal oxinate, MOx_n; HY was dithizone (H_2Dz), or sodium diethyl-dithiocarbamate (NaD, not HD).

The reaction of a metal oxinate with dithizone in pure benzene was elucidated and, the following discussion is concerned solely with that system*.

*The sodium diethyldithiocarbamate used as a titrant was in ethanol solution. The metal dithizonates were in chloroform which contained 1% ethanol as a stabilizer. The use of this mixed solvent would have complicated the study of this reaction.

TABLE 56

COMPARISON OF POOLED VARIANCES AND GRAND MEANS WHEN METAL DITHIZONATES IN CHLOROFORM WERE TITRATED WITH SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL AT 615 mμ AND THE WAVELENGTH OF MAXIMUM ABSORPTION OF THE METAL DITHIZONATE

Metal Dithizonate Titrated	λ mμ	$M(HDz)_n$ Taken μeq.	Mean of $M(HDz)_n$ Found μeq.	Estimate of σ_R^2 x 10^6	Value of F	Degrees of Freedom for F Test	Value of t	Degrees of Freedom for t Test	Grand Mean of $M(HDz)_n$ Found μeq.	Pooled Estimate of σ_R^2 x 10^6	Standard Deviation σ_R x 10^3
AgHDz	615	0.2286	0.2339	42.8	1.13	17 17	0.36	34	0.2335	45.5	6.7
	465	0.2286	0.2331	48.2							
	615	0.02286	0.02364	1.40	1.92	11 11	-	-	-	1.06	1.03
	465	0.04572	0.04720	0.73							
$Pb(HDz)_2$	615	0.2286	0.2284	67.9	1.58	17 17	1.67	34	0.2306	55.4	7.4
	510	0.2286	0.2328	42.9							
	615	0.02286	0.02257	1.28	1.22	11 11	0.66	22	0.2243	1.16	1.08
	510	0.02286	0.02229	1.05							
$In(HDz)_3$	615	0.2811	0.2771	74.2	1.48	17 17	0	34	0.2771	62.2	7.9
	510	0.2811	0.2771	50.3							
	615	0.02811	0.02682	1.47	1.62	11 11	0.16	22	0.02685	1.19	1.09
	510	0.02811	0.02689	0.91							
$Zn(HDz)_2$	615	0.2946	0.2880	60.3	1.80	11 11	1.65	22	0.2852	84.5	9.2
	580	0.2946	0.2818	108.7							
$Cd(HDz)_2$	615	0.2840	0.2824	42.6	1.61	11 11	1.41	22	0.2803	55.5	7.4
	518	0.2840	0.2782	68.4							

(Continued on next page)

TABLE 56 CONTINUED

COMPARISON OF POOLED VARIANCES AND GRAND MEANS WHEN METAL DITHIZONATES IN CHLOROFORM WERE TITRATED WITH SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL AT 615 mμ AND THE WAVELENGTH OF MAXIMUM ABSORPTION OF THE METAL DITHIZONATE

Metal Dithizonate Titrated	λ mμ	$M(HDz)_n$ Taken μeq.	Mean of $M(HDz)_n$ Found μeq.	Estimate of σ_R^2 x 10^6	Value of F	Degrees of Freedom for F Test	Value of t	Degrees of Freedom for t Test	Grand Mean of $M(HDz)_n$ Found μeq.	Pooled Estimate of σ_R^2 x 10^6	Standard Deviation σ_R x 10^3
$Cu(HDz)_2$	615	0.2618	0.2635	61.2	1.01	11	1.07	22	0.2652	60.8	7.8
	545	0.2618	0.2669	60.4		11					

$F_{0.05}$ (17,17) = 2.28
$F_{0.05}$ (11,11) = 2.82

$t_{0.05}$ (34) = 1.69
$t_{0.05}$ (22) = 1.72

$t_{0.01}$ (34) = 2.45
$t_{0.01}$ (22) = 2.51

In order to interpret the titration data presented in Section IV D subsection 1 for the metal oxinate-dithizone system, and also to predict the course of a titration when two or more metal oxinates are titrated simultaneously with dithizone, it was necessary to determine the equilibrium constant for the overall Reaction I.

In the course of that determination, the metal oxinate-dithizone system in benzene was found to consist of several species in equilibrium - adducts, intermediates, and reactants and products of Reaction I. It was necessary to study each of these equilibria independently, in order to find the equilibrium constant for Reaction I.

A conventional spectrophotometric technique provided the data for these reactions, from which equilibrium concentrations, and therefrom equilibrium constants were calculated. Use of a range of concentrations of reactants and a range of wavelengths, examination of forward and reverse reactions or comparison of calculated and experimental data, confirmed the validity of the equilibrium constants found.

(i) Methods Used to Calculated The Equilibrium Constants

The equilibrium concentrations of the species participating in the reactions, and their absorptivities were taken as the independent variables. Activity coefficients were assumed to be unity, and only monomers were assumed to be present.

For an initial calculation, it was assumed that only the four species specified in the titration equation (a)-I were present:

$$MOx_n + nH_2Dz \rightleftarrows M(HDz)_n + nHOx \qquad (a)\text{-}I$$

However, in general the value of its equilibrium constant, calculated from the spectrophotometric data, was then found to vary over a range of reactant concentrations. In that case, additional species were postulated (adducts and/or intermediates) - and hence additional equilibria. These additional equilibrium constants were then evaluated; and if necessary further species and equilibria were postulated, until finally the values of the equilibrium constants of all participating equilibria did remain constant, within experimental error, over the range of reactant concentrations.

Evaluation of the equilibrium constants required the solution of a set of linear equations. The following equations were available:

(1) Three mass-balance equations, namely those for total metal, total oxinate, and total dithizonate (e.g. (a)-1, (a)-2 and (a)-3 below).

(2) As many Beer's law equations as were necessary, each for a different wavelength (e.g. (a)-4 ----- (a)-n below).

(3) As many mass-law equations as there were reactions.

Let $(M)_T$, $(Ox)_T$, $(HDz)_T$ denote the stoichiometric concentrations of metal, oxinate radical and dithizonate radical,

respectively*; and let $[MOx_m(HDz)_n \cdot rHOx \cdot sH_2Dz]$ be a general formula to represent the equilibrium concentration in moles litre^{-1} of any possible species, including mixed chelates and adducts, but where m and n may not both be zero;

a_{λ_i} denote the absorptivity of a species q at wavelength λ_i;

A_{P,λ_i} denote the absorbance of a chemical solution #P at wavelength λ_i; calculated for a path length of 1 cm, unless otherwise specified.

Then the mass-balance, and Beer's law equations may be written in the following general forms:

$$(M)_T = \sum_{mnrs}\sum\sum\sum [MOx_m(HDz)_n \cdot rHOx \cdot sH_2Dz] \qquad (a)\text{-}1$$

$$(Ox)_T = \sum_{mnrs}\sum\sum\sum (m + r)[MOx_m(HDz)_n \cdot rHOx \cdot sH_2Dz] + [HOx] \qquad (a)\text{-}2$$

$$(HDz)_T = \sum_{mnrs}\sum\sum\sum (n + s)[MOx_m(HDz)_n \cdot rHOx \cdot sH_2Dz] + [H_2Dz]^{**} \qquad (a)\text{-}3$$

$$A_{P,\lambda_1} = \sum_{mnrs}\sum\sum\sum a_{\lambda_1,m,n,r,s}[MOx_m(HDz)_n \cdot rHOx \cdot sH_2Dz] + a_{\lambda_1,H_2Dz}[H_2Dz] \qquad (a)\text{-}4$$

$$\vdots$$

$$A_{P,\lambda_n} = \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \qquad (a)\text{-}n$$

The absorbance of free oxine was zero over the wavelength range for which data were used. Therefore the term for its absorbance does not appear in equations (a)-4 to (a)-n.

---

*Charges on the oxinate and dithizonate radicals are omitted for convenience, here and henceforth.

**An adduct of the form $H_2Dz \cdot HOx$ was known, from experiment, not to be present.

1) The Copper System

The copper system was the simplest to treat, because the absorptivities of each species could be independently evaluated. Evaluation of the unknown equilibrium concentrations of the various species therefore required in principle as many equations (a)-1 to (a)-n as there were unknown concentrations, However, there were finite variances associated with the experimentally evaluated quantities $(M)_T$, $(Ox)_T$ and $(HDz)_T$. Moreover, variances of the absorbance readings and of the measured absorptivities (see Appendices XVIII, XX and XXII) were a function of wavelength, and were not necessarily homogeneous. Therefore in practice the total number of equations (a)-1 to (a)-n taken was arbitrarily twice the number of independent variables (concentrations).

This set of equations was then normalized by the Gauss Method of Least Squares and the resulting normalized set was solved by the Gauss-Seidell iterative method (120).

The above-described method was also used for some calculations on the lead system.

2) The Lead System

In general, the absorptivities of the participating species were unknown. In these cases, equations (a)-1 to (a)-n were supplemented by the relevant mass-law equations. However, these mass-law equations were used in the following way:

(1) Equations (a)-1 to (a)-n were solved for the sought-for equilibrium concentrations, which were then expressed as algebraic equations in terms of the symbols for the unknown absorptivities.

(2) The equilibrium concentrations, so expressed, could then be substituted into the relevant mass-law equations, to give each equilibrium constant, K_ℓ, as a function of molar absorptivities. Thus,

$$K_\ell = f_i(a_1,....,a_j);\ i = 1,2,....k$$
$$\ell = 1,2,....$$

where f_i indicates that data for the ith chemical solution (corresponding to a specific set of values for $(M)_T$, $(Ox)_T$, and $(HDz)_T$) were used in equations (a)-1 to (a)-n, in order to obtain the various equilibrium concentrations expressed in terms of the j unknown absorptivities ($a_1,a_2....,a_j$ refer to the a_{mnrs} of equations (a)-4 to (a)-n).

The number of chemical solutions used, i.e. the value of k, had to be equal to the number of absorptivities to be evaluated, namely j (i.e. j = k). Since there were more chemical solutions than the minimum necessary, all binary combinations of the k expressions of $f_i(a_1,....,a_j)$ were equated i.e.

$$f_i(a_1,....,a_j) = f_2(a_1,....a_j)$$
$$f_1 = f_3$$
$$f_2 = f_3$$

The absorptivities could then be evaluated from these equations.

In practice, this method for the evaluation of the absorptivities would be very time-consuming for $j > 1$. Therefore, when there was more than one absorptivity to be evaluated, separate experiments were devised to study different stages of the overall reaction so that there would only be one absorptivity. For example let Reaction (a)-I take place in two stages

$$MOx_n + H_2Dz \rightleftarrows MOx_{n-1}(HDz) + HOx$$

$$MOx_{n-1}(HDz) + H_2Dz \rightleftarrows MOx_{n-2}(HDz)_2 + HOx$$

and let the absorptivities of $MOx_{n-1}(HDz)$ and $MOx_{n-2}(HDz)_2$ be unknown. Then experiments would be devised so that first, species other than $MOx_{n-1}(HDz)$ would be negligible. Its absorptivity would be evaluated by the method described above. This absorptivity and the data for the overall reaction would then be used in the equations to evaluate the absorptivity of $MOx_{n-2}(HDz)_2$, again by the method described above.

The above-described method was also used to evaluate the absorptivities of the adducts of dithizone with primary copper dithizonate.

3) The Indium System

The equilibrium constants for the indium chelate reactions were evaluated by successive approximations. Thus, equations (a)-1 to (a)-n were used in order to obtain pre-

liminary values of the equilibrium constants. Therefrom, absorbances were calculated and compared with the experimental values. The values of the equilibrium constants were then adjusted successively until the best fit of the calculated absorbances to the experimental absorbances was obtained.

(b) Copper System

(i) Introduction

1) Experimental Observations

Qualitative experimental observations made in the present work on the reactions of the copper chelates are summarized in Table 57.

The continuous-variations plot (see Figure 55) for the reaction of copper oxinate with dithizone showed, approximately, that two moles of dithizone reacted with one mole of copper oxinate. The continuous-variations plot for the reaction of secondary copper dithizonate with oxine showed that one mole of oxine reacted with one mole of CuDz (see Figure 56).

2) Comment on the continuous-variations plots for the reaction of CuDz with H_2Dz

The experimental data for the continuous-variations plots for the reaction of CuDz with dithizone at first were confusing. Thus, sets of solutions were prepared in the usual "wet" benzene (i.e. spectrophotometric-grade, undried*)

*Hereinafter this benzene will be referred to as undried benzene or benzene to distinguish it from "dry" benzene which had been dried intensively with calcium hydride.

TABLE 57

	Reaction A + B	Molar Ratio A:B	Colour of Solution	Conclusion: Principal product
1.	$CuOx_2 + H_2Dz$	50:1	Brown - Absorption spectrum matched that of CuDz solutions prepared from pure solid CuDz	CuDz
2.	$CuOx_2 + H_2Dz$	1:2	Purple - Absorption spectrum matched that of $Cu(HDz)_2$ solution prepared from pure solid $Cu(HDz)_2$	$Cu(HDz)_2$
3.	$CuOx_2 + Cu(HDz)_2$	1:1	Brown - same as 1	CuDz
4.	CuDz + HOx	1:1	Purple - same as 2	$Cu(HDz)_2$
5.	$CuDz + H_2Dz$	1:1	Purple - same as 2	$Cu(HDz)_2$ (also found by Geiger & Sandell (93)).
6.	$Cu(HDz)_2 + H_2Dz$	1:1 - 1:10	Absorption spectrum did not correspond to the sums of the spectra of $Cu(HDz)_2$ and H_2Dz	Adducts of $Cu(HDz)_2$ with dithizone formed
7.	$Cu(HDz)_2$ + HOx	1:1 - 1:100	Absorption corresponded to the concentration of $Cu(HDz)_2$ taken	No reaction

FIGURE 55

CONTINUOUS-VARIATIONS PLOTS FOR THE REACTION OF COPPER OXINATE WITH DITHIZONE AT 25°C IN UNDRIED BENZENE SOLUTIONS

(a) At 545 mμ.

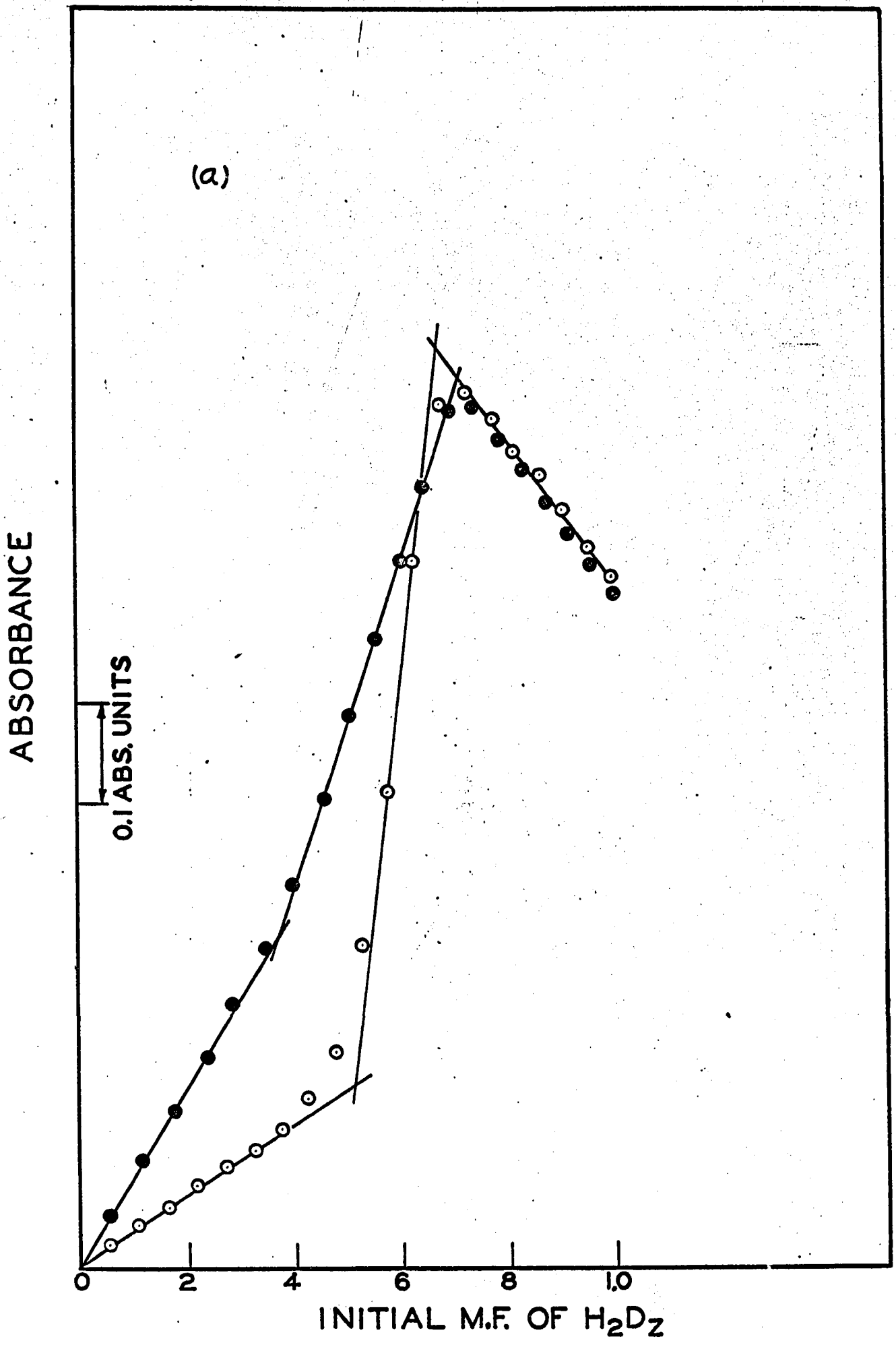
(b) At 618 mμ.

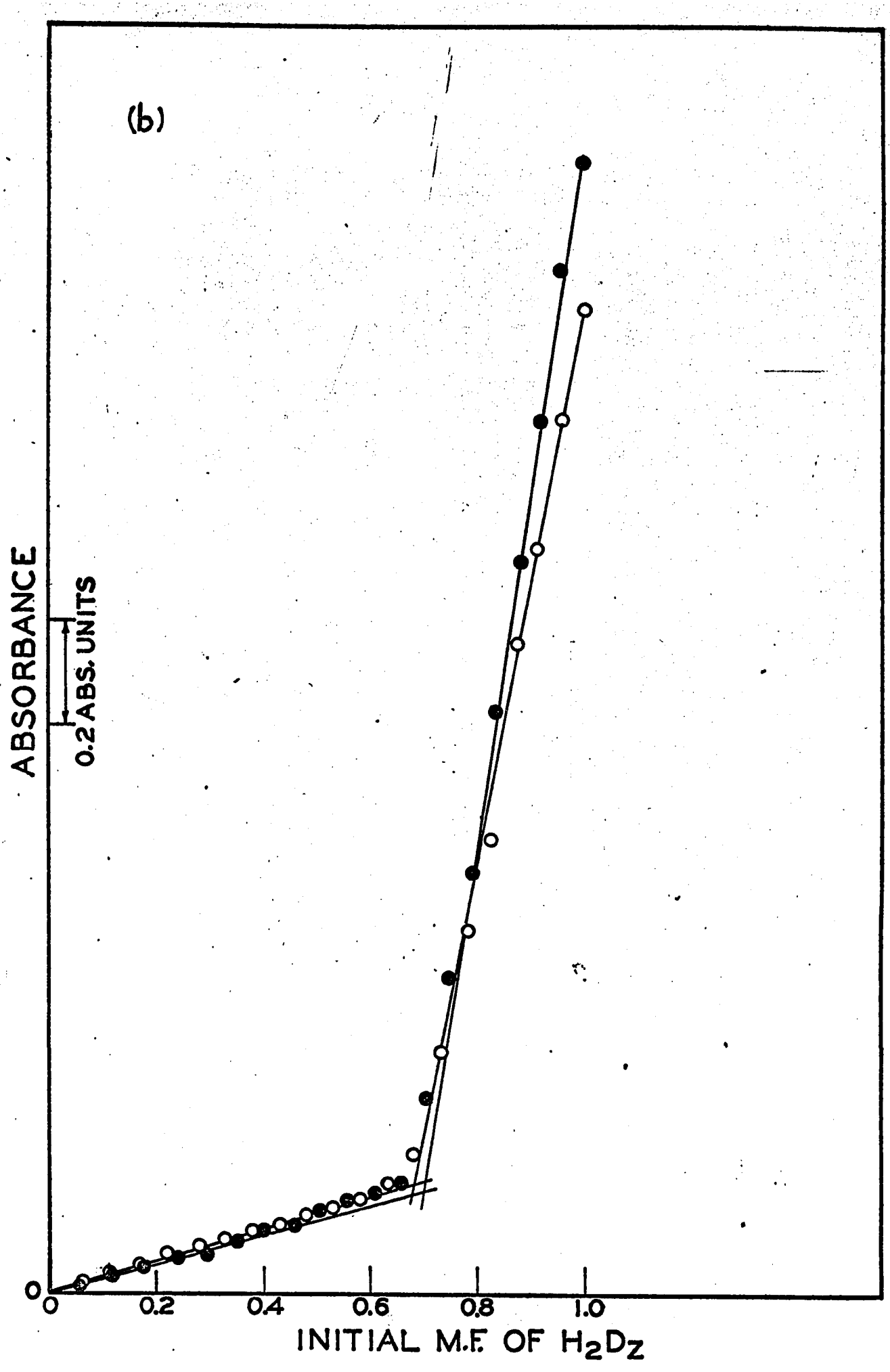
(c) At 445 mμ.

Path length = 5 cm.

⊙ Solutions contained no initial free oxine.

● Solutions contained initial free oxine, onehundredfold in excess with respect to the initial concentration of copper oxinate.


(a)
ABSORBANCE
0.1 ABS. UNITS
0
2
4
6
8
1.0
INITIAL M.F. OF H_2D_2


(b)
ABSORBANCE
0.2 ABS. UNITS
0
0
0.2
0.4
0.6
0.8
1.0
INITIAL M.F. OF H_2D_2

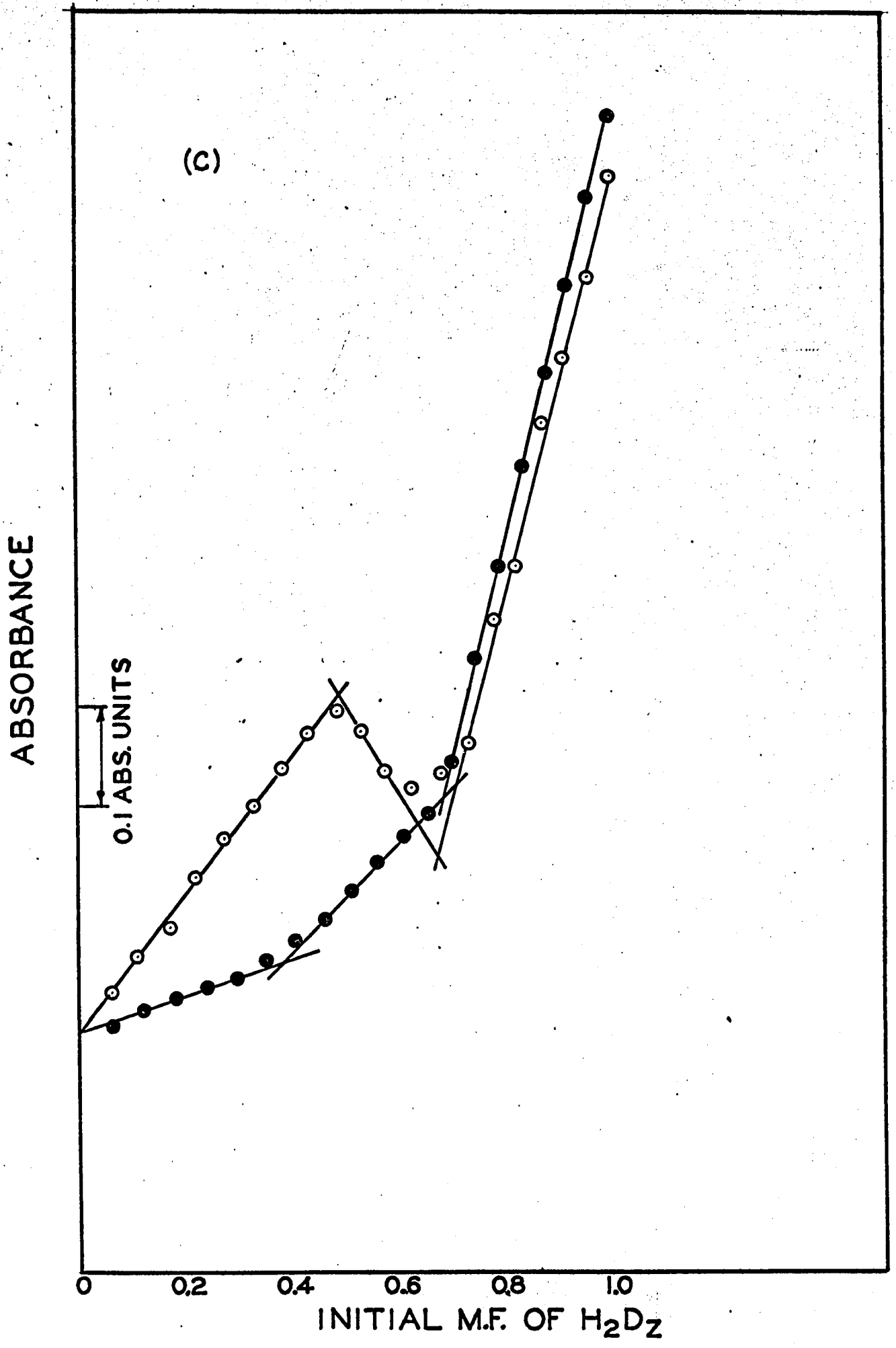
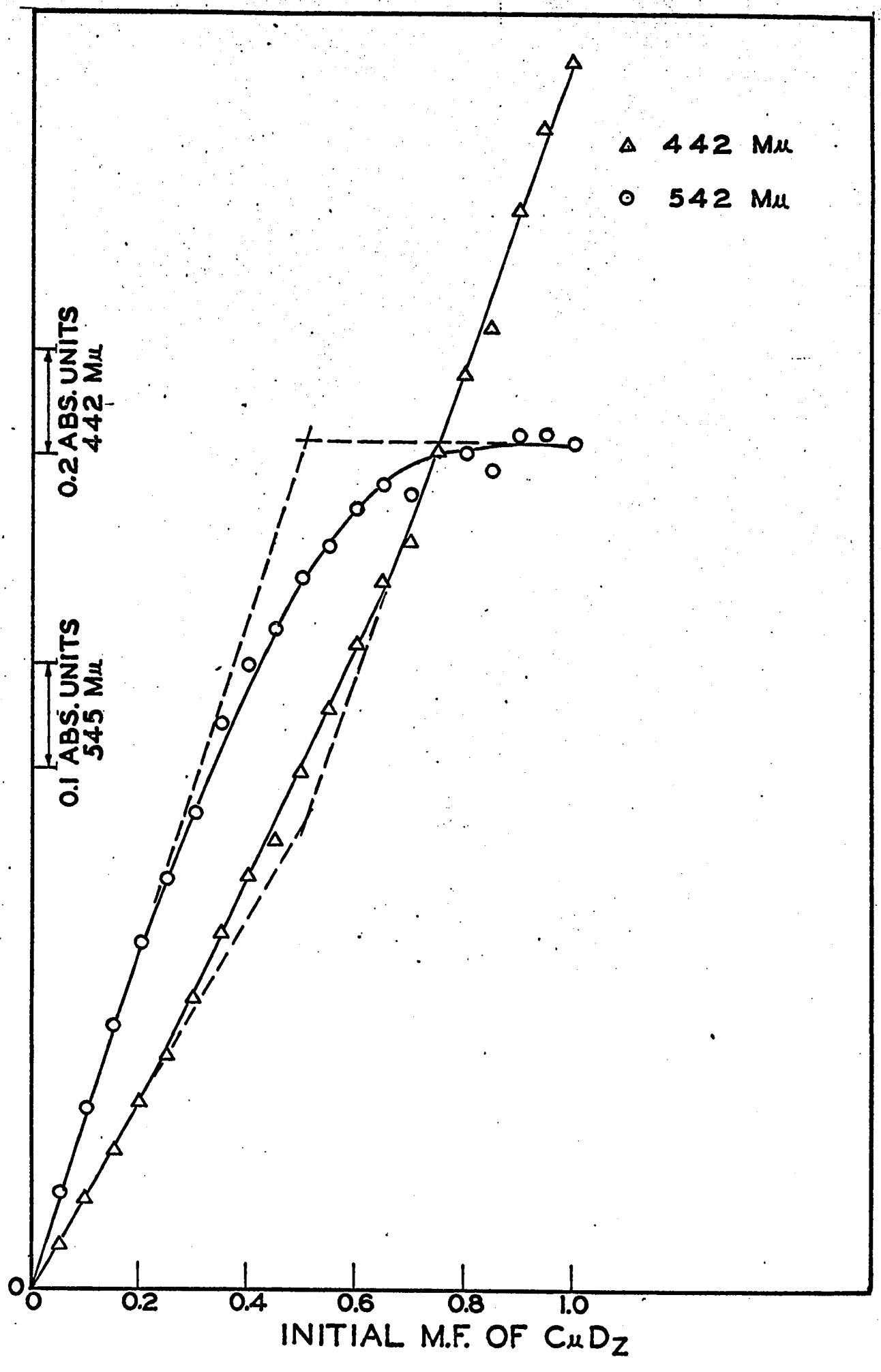

(C)
ABSORBANCE
0.1 ABS. UNITS
0
0.2
0.4
0.6
0.8
1.0
INITIAL M.F. OF H_2D_2

FIGURE 56

CONTINUOUS-VARIATIONS PLOTS FOR THE REACTION OF SECONDARY COPPER DITHIZONATE WITH OXINE IN UNDRIED BENZENE AT 25°C

Path length = 1 cm


△ 442 Mμ
○ 542 Mμ
0.2 ABS. UNITS 442 Mμ
0.1 ABS. UNITS 545 Mμ
0
0
0.2
0.4
0.6
0.8
1.0
INITIAL M.F. OF CμDz

and in the same benzene previously dried with silica gel. Above 0.5 mole fraction of H_2Dz the two plots did not agree with one another. Furthermore, in neither did the stoichiometry indicate exactly the 1:1 reaction postulated by Geiger and Sandell (93) from solvent-extraction studies. The discrepancy was resolved following experiments to confirm the existence and to measure the stabilities of adducts of $Cu(HDz)_2$ with dithizone. A continuous-variations plot was then obtained from solutions in benzene which had been intensively dried with calcium hydride, and in the preparation of which, elaborate precautions had been taken to exclude water.

The two continuous-variations plots, one with "wet" benzene solutions and the other with benzene solutions dried with calcium hydride are shown in Figure 57. The difference in the two curves can be explained as follows: water has shifted the equilibrium for the formation of the primary copper dithizonate-dithizone adducts such that the concentrations of the adducts are reduced. Confirmation of this supposition is provided later (subsection (iv)-6).

It appears that the stoichoimetry for the reaction of secondary copper dithizonate with dithizone is in fact 1:1.

3) Reactions and mass-law equations

From observation 2 in Table 1 and the data of the continuous-variations plot, the overall reaction of copper oxinate with dithizone is postulated to be:

FIGURE 57

COMPARISON OF CONTINUOUS-VARIATIONS PLOTS AT 618, 545 AND 445 mμ FOR THE REACTION OF SECONDARY COPPER DITHIZONATE WITH DITHIZONE AT 25°C IN (i) UNDRIED BENZENE SOLUTIONS AND (ii) BENZENE SOLUTIONS DRIED WITH CALCIUM HYDRIDE

(a) 618 mμ.

(b) 545 mμ.

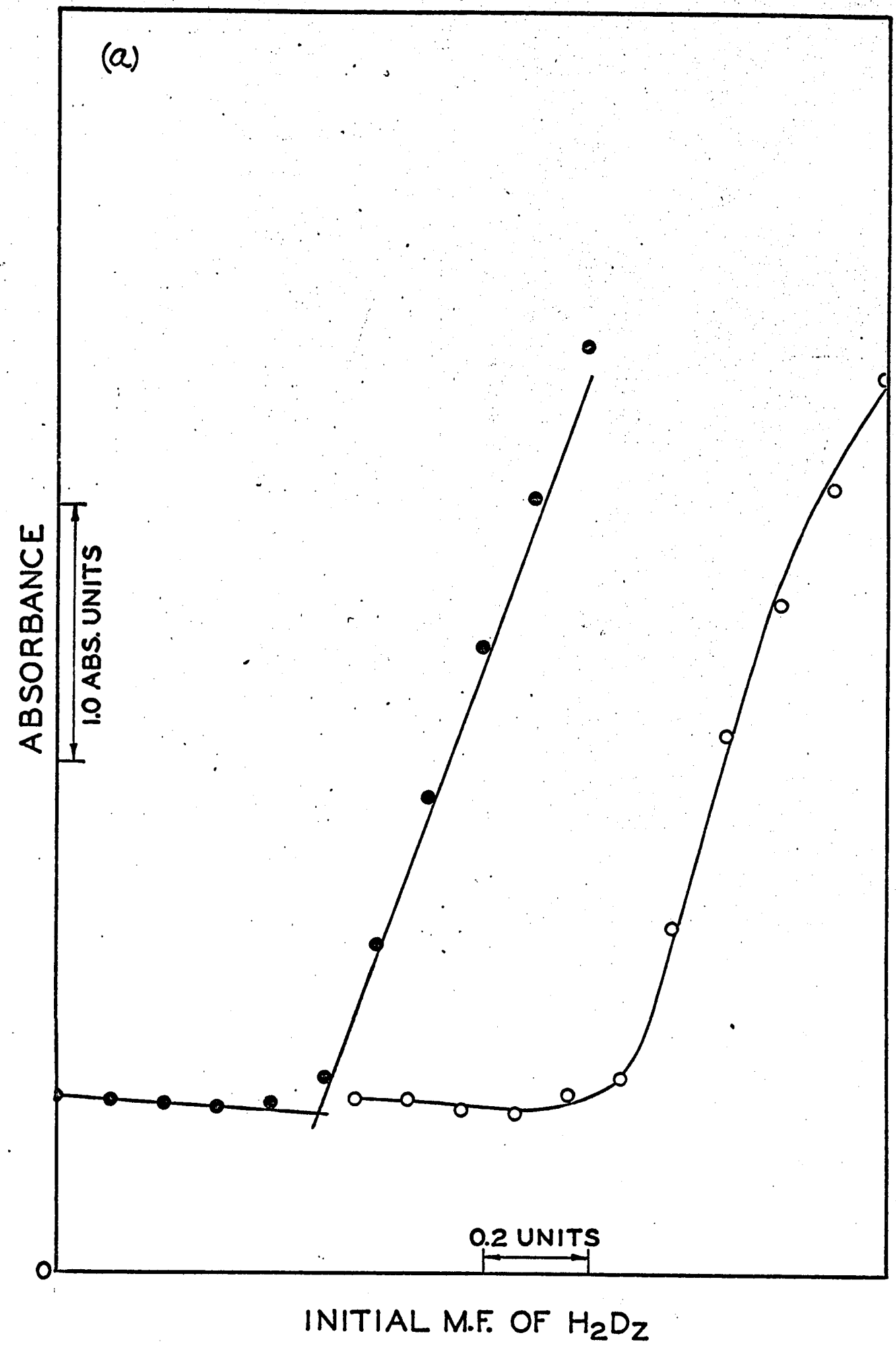
(c) 445 mμ.

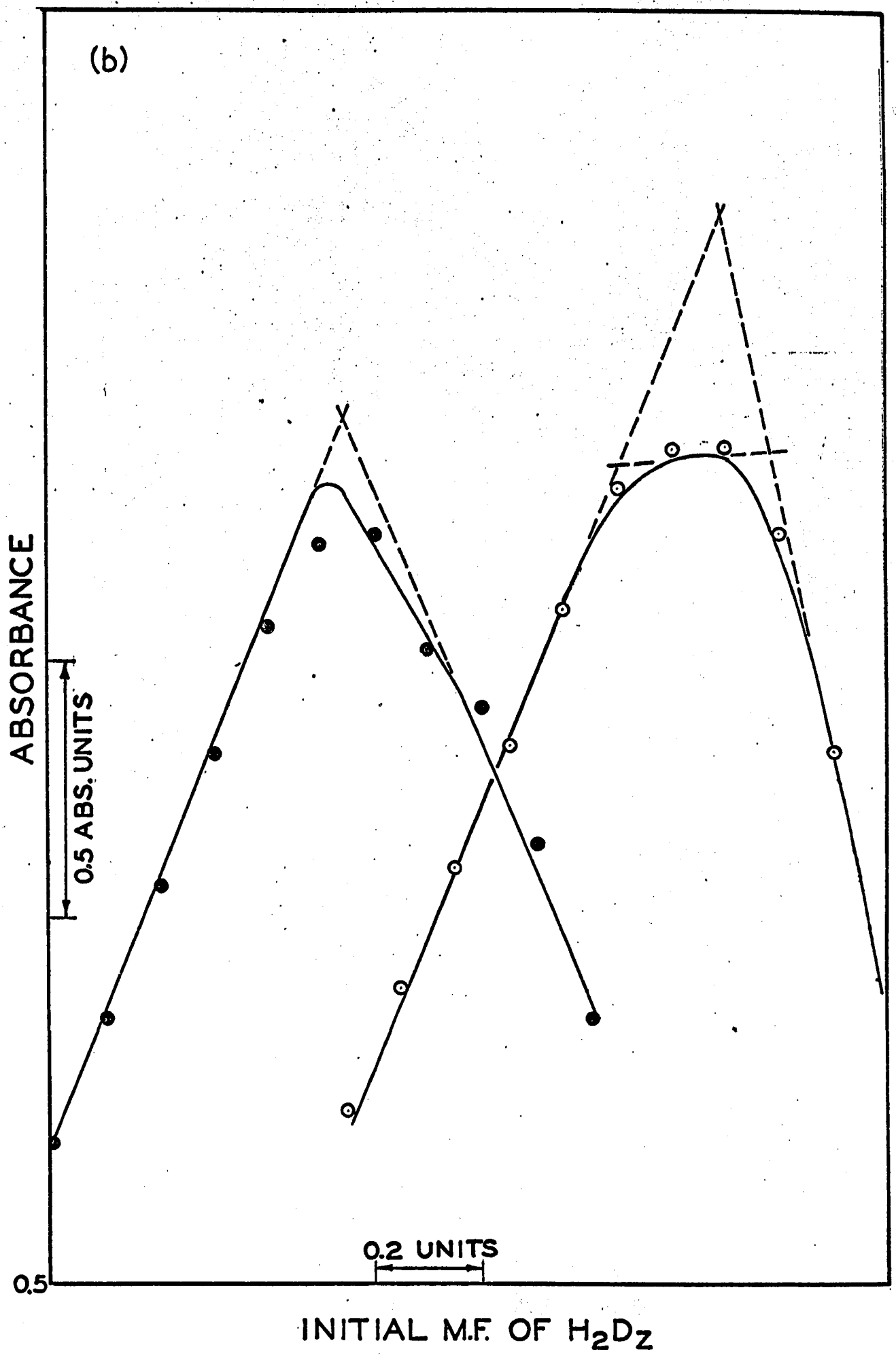
Path length = 1 cm.

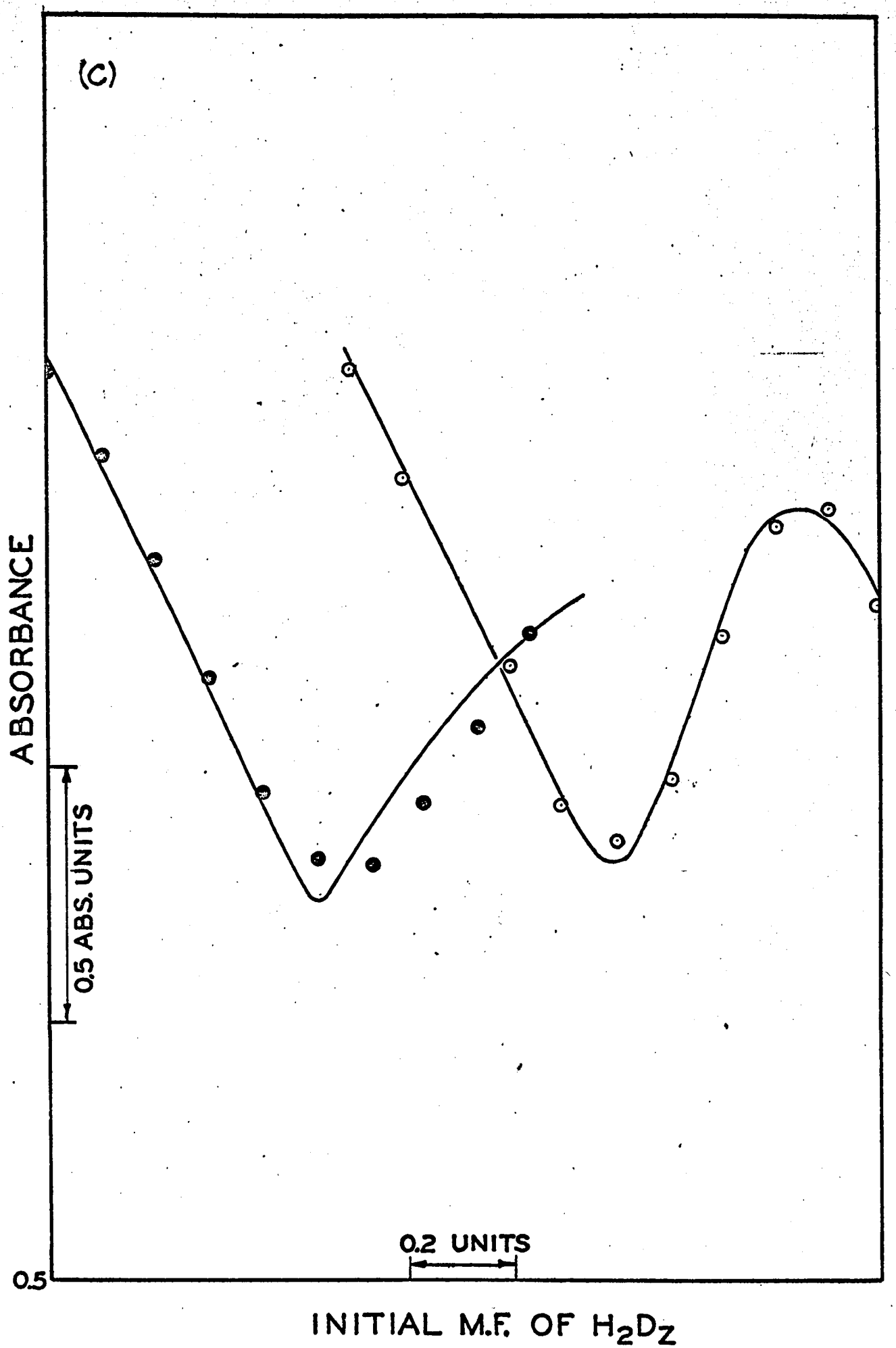
● Experimental points for undried benzene solutions (SET H - see Tables 11 and 12, Appendix XXVII, page 114a for basic data).

⊙ Experimental points for benzene solutions dried with calcium hydride (SET I - see Tables 13 and 14, Appendix XXVII, page 116a, for basic data).

The solid lines represent the calculated curves (Tables 67, subsection (iv), 6) of this Section, page 318).


(a)
ABSORBANCE
1.0 ABS. UNITS
0
0.2 UNITS
INITIAL M.F. OF H_2D_Z


(b)
ABSORBANCE
0.5 ABS. UNITS
0.5
0.2 UNITS
INITIAL M.F. OF H_2D_2


(c)
ABSORBANCE
0.5 ABS. UNITS
0.2 UNITS
0.5
INITIAL M.F. OF H_2D_2

$$CuOx_2 + 2H_2Dz \rightleftarrows Cu(HDz)_2 + 2HOx \qquad (b)\text{-I}$$

The equilibrium constant is given by

$$K_o = \frac{[Cu(HDz)_2][HOx]^2}{[CuOx_2][H_2Dz]^2} \qquad (b)\text{-1}$$

From observation 3 in Table 57 and the data of the continuous-variations plot (Figure 56), the reaction of primary copper dithizonate with copper oxinate is postulated to be:

$$CuOx_2 + Cu(HDz)_2 \rightleftarrows 2CuDz + 2HOx \qquad (b)\text{-II}$$

The equilibrium constant is given by

$$K_1 = \frac{[CuDz]^2[HOx]^2}{[CuOx_2][Cu(HDz)_2]} \qquad (b)\text{-2}$$

The reverse of reaction II also accounts for observation 4 and the continuous-variations plot (Figure 56). The equilibrium constant is the reciprocal of K_1 denoted by K_1^1. Reactions (b)-I and (b)-II also account for the presence of CuDz when dithizone is reacted with an excess of copper oxinate (observation 1). It is postulated that as soon as $Cu(HDz)_2$ is formed in Reaction (b)-I it reacts with the excess $CuOx_2$ to produce CuDz. The part of the curve to the first break in Figure 55 represents the formation of CuDz. As the concentration of $CuOx_2$ is decreased by adding dithizone, more and more free $Cu(HDz)_2$ remains in solution to produce the purple colour observed. The part of the curve to the second break in Figure 55 represents the formation of $Cu(HDz)_2$.

From observation 5, the reaction of secondary copper dithizonate with dithizone is postulated to be

$$CuDz + H_2Dz \rightleftarrows Cu(HDz)_2 \qquad (b)\text{-III}$$

With an equilibrium constant

$$K_2 = \frac{[Cu(HDz)_2]}{[CuDz][H_2Dz]} \qquad (b)\text{-3}$$

The continuous-variations plot with wet benzene in Figure 3, where undried benzene was the solvent suggested that one mole of CuDz reacted with one mole of dithizone. The calculations leading to the evaluation and confirmation of K_2 did in fact confirm this stoichiometry.

Observation 6 in Table 57 indicated that $Cu(HDz)_2$ reacted with dithizone. It was postulated that $Cu(HDz)_2$ formed one or more adducts with dithizone, according to the reaction:

$$Cu(HDz)_2 + nH_2Dz \rightleftarrows Cu(HDz)_2 \cdot n(H_2Dz) \qquad (b)\text{-IV}$$

Tests to be described later showed that this reaction as written was valid only in intensively dried benzene. The relevant equilibrium constants were:

$$K_{3_n} = \frac{[Cu(HDz)_2 \cdot n(H_2Dz)]}{[Cu(HDz)_2][H_2Dz]^n} \qquad (b)\text{-4}$$

where n = 1,2,....

A more detailed treatment of Reaction (b)-IV and the effect of water is given later in subsections (iv), 1) to 6).

The presence of an initial concentration of free oxine in the solutions would affect the extent of reactions (b)-I and (b)-II but not of (b)-III or (b)-IV. This was observed experimentally, and in Figure 55 it is shown for the reaction of copper oxinate with dithizone.

The relationship

$$K_0 = K_2^2 \cdot K_1 \qquad \text{(b)-5}$$

was used to calculate the value of K_0 from the data obtained from reactions (b)-II and (b)-III.

A mixed chelate of the type CuOx(HDz) was sought but not found in reactions (b)-I and (b)-II. The equilibrium constants calculated from the experimental data were found within experimental error to be constant without the inclusion of a mixed chelate.

4) Methods used to calculate the equilibrium constants

With the exception of the adducts of $Cu(HDz)_2$ with dithizone, the absorptivities of all species known to be present in solution for the reactions of the copper chelates were known at all wavelengths. Thus Beer's law equations described in subsection (a), page 278, at a given wavelength could be generated. In equation (a)-4, m = 2, n = 0, r = 0 and s = 0 represents $CuOx_2$ and let its absorptivity be represented by $a_{\lambda i,1}$; m = 0, n = 1, r = 0, s = 0 represents CuDz with absorptivity $a_{\lambda i,2}$; m = 0, n = 2, r = 0, s = 0 represents $Cu(HDz)_2$ with absorptivity $a_{\lambda i,3}$; m = 0, n = 2, r = 0, s = 1 represents $Cu(HDz)_2 \cdot H_2Dz$ with absorptivity $a_{\lambda i,5}$*; m = 0, n = 2, r = 0, s = 2 represents $Cu(HDz)_2 \cdot 2H_2Dz$ with absorptivity $a_{\lambda i,6}$*; and let $a_{\lambda i}, H_2Dz$ be represented by $a_{\lambda i,4}$.

*These absorptivities were not known until subsequent experiments (subsection (iv) of this Section).

For j unknown equilibrium concentrations, Beer's law equations for j wavelengths can be generated. The equilibrium concentrations can then be obtained by solving the system of linear equations. However, the absorbance and absorptivities are subject to error because they are experimental quantities. The system of equations will be inconsistent and not solvable. Therefore, additional Beer's law equations, were generated at selected wavelength intervals from 618 mμ to 400 mμ, and the resulting system was normalized as outlined in subsection (a), 1) of this Section. The system of equations used, together with the numerical values of the absorptivities given in Table 1, Appendix XVIII, Tables 2 and 3, Appendix XX and Table 2, Appendix XXII is shown in Table 58. The term in [HOx] has been ommitted because HOx did not absorb at the wavelengths used.

When species were known to be absent from a particular solution, the relevant terms were omitted.

Relevant mass-balance equations, given in the following subsections were added to the system of equations in Table 58, when necessary. Therefore at least nine Beer's law equations plus the mass-balance equations were available for calculation of the various equilibrium concentrations. The normalized equations were solved by the method given in subsection (a), 1) of this Section.

Having obtained the equilibrium concentrations of each of the species known to be present in the solutions, the

TABLE 58

SYSTEM OF LINEAR BEER'S LAW EQUATIONS FOR THE CALCULATION OF EQUILIBRIUM CONCENTRATIONS IN THE COPPER OXINATE-DITHIZONE SYSTEM IN BENZENE AT 25°C FROM EXPERIMENTAL ABSORBANCE DATA

p represents the number of the chemical solution

		$a_{\lambda_{i,1}} \times 10^{-3}[CuOx_2]$		$a_{\lambda_{i,2}} \times 10^{-4}[CuDz]$		$a_{\lambda_{i,3}} \times 10^{-4}[Cu(HDz)_2]$		$a_{\lambda_{i,4}} \times 10^{-4}[H_2Dz]$
$A_{p,618}$	=			0.68	+	1.24	+	3.47
$A_{p,575}$	=			0.68	+	3.33	+	2.16
$A_{p,545}$	=			0.79	+	4.11	+	1.04
$A_{p,525}$	=			1.04	+	3.79	+	0.66
$A_{p,500}$	=	0.07	+	1.48	+	3.27	+	0.61
$A_{p,475}$	=	0.35	+	2.02	+	2.75	+	1.46
$A_{p,445}$	=	4.20	+	2.30	+	2.44	+	1.84
$A_{p,425}$	=	5.88	+	2.19	+	2.21	+	1.58
$A_{p,400}$	=	4.75	+	1.71	+	2.07	+	0.91

equilibrium constants were calculated from the relevant mass-action law equations.

A different method was needed in order to calculate the equilibrium constants of Reaction (b)-IV because the absorptivities of the adducts were unknown. The molar absorptivities in the region 750 to 400 mμ of $Cu(HDz)_2 \cdot H_2Dz$ were first calculated by carefully adjusting the initial ratio of $(Cu(HDz)_2):(H_2Dz)$ so that it was practically the only adduct species present in solution. This was based on assumptions which were later confirmed. The absorptivity of $Cu(HDz)_2 \cdot 2H_2Dz$ was then calculated. With the absorptivities known, the equilibrium concentrations were calculated, and from them the equilibrium constants were evaluated. A detailed discussion of the calculations is in subsection (iv).

5) Analytical data

The equilibrium constants of reactions (b)-II and (b)-III were calculated from the data of the following sets of solutions in benzene at 25°C:

SET A. Continuous-variations solutions used in studying the reaction of secondary copper dithizonate with oxine (reverse of Reaction (b)-II), at a total initial concentration of reactants of 10^{-4} M, (hereinafter referred to as SET A).

SET B. Ratio solutions used in studying the reaction of primary copper dithizonate with copper oxinate (Reaction (b)-II) where the total copper concentration, $(Cu)_T$,

was varied from 1.5 x 10^{-4} to 5 x 10^{-6} M (hereinafter referred to as SET B).

SET C. Ratio solutions used in studying the reaction of secondary copper dithizonate with dithizone (Reaction (b)-III) (hereinafter referred to as SET C). The $(Cu)_T$ was varied from 2 x 10^{-4} M to 2 x 10^{-6} M. Thus, mixtures of CuDz, H_2Dz, and $Cu(HDz)_2$ were prepared which avoided the presence of adducts, but which ensured a measurable distribution of equilibrium concentrations of the three species.

The following sets of continuous-variations solutions in benzene at 25°C were prepared in order to establish the stoichoimetry of

SET D. The reaction of copper oxinate with dithizone (Reaction (b)-I) at a total initial concentration of reactants of 10^{-5} M, (hereinafter referred to as SET D).

SET E. The reaction of copper oxinate with dithizone when the solutions contained initial free oxine which was onehundredfold in excess with respect to the initial concentration of copper oxinate (hereinafter referred to as SET E).

The analytical data for SETS A to E inclusive are in Tables 1-10 of Appendix XXVII. In order to test the effect of water, additional SETS A, B and C were prepared in which the benzene had been dried with silica gel. The absorption spectra were identical with those of the original sets A, B and C.

The data from a set of ratio-solutions, hereinafter referred to as SET G, were used to calculate the equilibrium constants of reaction (b)-IV, the reaction of $Cu(HDz)_2$ with dithizone to form adducts. These solutions were prepared with benzene dried with calcium hydride, with elaborate precautions being taken to exclude water. These analytical data are in Tables 11 & 12 of Appendix XXVII. The ratios of the initial concentrations, $(Cu(HDz)_2)_i:(H_2Dz)_i$ were 1:1, 1:2, 1:4 and 1:10. Within these ratios the initial concentration of $Cu(HDz)_2$ was varied from 10^{-4} to 10^{-6} M.

The calculated equilibrium constants for the formation of these adducts were confirmed by calculating continuous-variations plots for the reaction of CuDz with dithizone. The plots were calculated for solutions prepared with undried benzene and with benzene that had been intensively dried with calcium hydride (hereinafter referred to as SET H and SET I respectively). The total concentration of reactants was 10^{-4} M. The analytical data are in Tables 13 & 14 of Appendix XXVII.

The absorptivity of $Cu(HDz)_2 \cdot H_2Dz$ was obtained from a set of ratio solutions prepared in benzene which had been intensively dried with calcium hydride (hereinafter referred to as SET J). Two initial ratios of $(Cu(HDz)_2)_i:(H_2Dz)_i$ were selected; 10:1 and 5:1. Within these ratios, the initial concentration of $Cu(HDz)_2$ was varied from 5×10^{-4} to 5×10^{-6} M. The analytical data are in Table 15 of Appen-

dix XXVII. Table 16 of Appendix XXVII shows some absorbances at selected wavelengths*.

(ii) Calculation of K_1 and $K_1{}^1$

For Reaction (b)-II

$$CuOx_2 + Cu(HDz)_2 \rightleftarrows 2CuDz + 2HOx \qquad (b)\text{-II}$$

and the reverse of Reaction (b)-II, the mass-balance equations were:

$$(Cu)_T = [CuOx_2] + [CuDz] + [Cu(HDz)_2] \qquad (b)\text{-7}$$

$$(HDz)_T = [CuDz] + 2[Cu(HDz)_2] \qquad (b)\text{-8}$$

$$(Ox)_T = 2[CuOx_2] + [HOx] \qquad (b)\text{-9}$$

Equation (b)-7 above, together with the system of equations in Table 58 (page 292) were solved with the $[H_2Dz]$ term omitted, by using the absorbance data of SETS A and B (Table 2 and 4 in Appendix XXVII, page 105a). The required equilibrium concentrations calculated from SET A are in Table 59 and those from SET B are in Table 60. The equilibrium concentration of oxine was then calculated from equation (b)-9. From the equilibrium concentrations, the values of K_1 (SET B) and $K_1{}^1$ (SET A) were calculated from equation (b)-2 and the reciprocal of equation (b)-2, respectively, for each solution (Tables 59 and 60). The mean value of K_1 was calculated therefrom to be $5.61 \pm 0.52 \times 10^{-9}$ moles^2 litre^{-2}, and the mean value of $K_1{}^1$ was $1.72 \pm 0.18 \times 10^8$ litre^2 moles^{-2}, which corresponds to a value of K_1 of $5.81 \pm 0.66 \times 10^{-9}$ moles^{2}litre^{-2}.

---

*The data was read from spectral absorbance curves which are not reproduced.

TABLE 59

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANT FOR THE REACTION
$2CuDz + 2HOx \rightleftarrows CuOx_2 + Cu(HDz)_2$
IN BENZENE AT 25°C

Basic data: SET A, Tables 1 and 2, Appendix XXVII

Solution Number	Equilibrium Concentrations M				Mass-Balance Check M		Equilibrium Constant
	$[CuOx_2]$ x 10^6	$[Cu(HDz_2]$ x 10^6	[CuDz] x 10^5	[HOx] x 10^5	$(Cu)_T$ Found x 10^5	$(Cu)_T$ Taken x 10^5	K_1^1 x 10^{-8} litre^2 mole^{-2}
CJA - 1	0	0	10.26	0	-	-	-
2	1.873	1.753	9.459	0.1420	9.822	9.755	1.82
3	3.420	3.515	8.546	0.3105	9.240	9.236	1.71
4	4.782	4.923	7.398	0.556	8.368	8.717	1.39
5	6.208	6.320	6.859	0.7467	8.112	8.211	1.50
6	7.804	7.924	6.032	0.9445	7.605	7.705	1.90
7	8.503	8.608	5.164	1.282	6.875	7.186	1.67
8	9.760	9.754	4.710	1.548	6.661	6.668	1.79
9	10.48	10.36	4.090	1.882	6.174	6.162	1.83
10	11.24	10.59	3.508	2.247	5.691	5.643	1.92
11	11.00	11.09	2.931	2.813	5.140	5.124	1.80
12	10.84	10.78	2.400	3.322	4.562	4.618	1.84
13	10.59	10.40	2.157	3.888	4.256	4.099	1.56
14	10.05	9.860	1.752	4.474	3.743	3.593	1.61
15	8.592	8.487	1.366	5.285	3.074	3.074	1.40
16	7.597	7.671	1.004	5.958	2.531	2.568	1.61
17	6.618	6.610	0.7355	6.672	2.058	2.050	1.81
18	5.162	5.159	0.5155	7.480	1.548	1.544	1.79
19	3.492	3.589	0.3005	8.122	1.009	1.025	2.10
20	1.843	1.883	0.1502	9.137	0.5228	0.519	1.84
21	0	0	0	9.984	-	-	-

Mean value of K_1^1 = 1.71 x 10^8 litre^2 mole^{-2}
Variance $_1$ = 3.61 x 10^{14}
Std. Deviation = 0.19 x 10^8 (for 18 degrees of freedom)

TABLE 60

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANT FOR THE REACTION
$CuOx_2 + Cu(HDz)_2 \rightleftarrows 2CuDz + 2HOx$
IN BENZENE AT 25°C

Basic data: SET B, Tables 3 and 4, Appendix XXVII

Solution Number	Equilibrium Concentration M				Mass-Balance Check M		Equilibrium Constant
	$[CuOx_2]$ x 10^6	[CuDz] x 10^5	$[Cu(HDz)_2]$ x 10^5	(HOx] x 10^5	$(Cu)_T$ Found x 10^5	$(Cu)_T$ Taken x 10^5	K_1 x 10 mole^2 litre^{-2}
CRB - 1	61.07	5.915	3.958	6.396	15.98	15.97	5.92
2	41.97	5.708	4.858	6.366	14.76	15.09	6.47
3	39.35	3.218	3.547	4.540	10.70	10.65	6.23
4	6.669	4.541	4.546	4.870	9.754	9.767	4.74
5	18.47	2.909	0.4929	2.510	5.276	5.324	5.86
6	3.490	2.380	2.694	3.024	5.423	5.193	5.51
7	3.402	2.275	2.449	3.042	5.064	"	5.75
8	3.437	2.379	2.557	3.035	5.091	"	5.63
9	0.3058	0.7538	0.1186	0.5592	0.9029	0.9767	4.90
10	0.2842	0.8734	0.1632	0.5636	1.065	"	5.22
11	0.2992	0.8062	0.1267	0.5606	0.9628	"	5.39
12	0.06339	0.4768	0.03741	0.2504	0.5206	0.5193	6.01
13	0.06512	0.4956	0.03631	0.2420	0.5384	"	6.08
14	0.06166	0.4553	0.03827	0.2489	0.4997	"	5.45

Mean value of K_1 = 5.61×10^{-9} mole^2 litre^{-2}
Variance = 2.70×10^{-19}
Std. Deviation = 0.52×10^{-9} (for 13 degrees of freedom)

The variances associated with these two mean values of K_1 were not significantly different at the 95% confidence level, nor were the means. Therefore the grand mean $K_1 = 5.71 \times 10^{-9}$, the pooled variance, 3.63×10^{-19} and the pooled standard deviation (for 31 degrees of freedom), 0.60×10^{-9}, are reported.

A sample calculation follows:

Solution #CJA-7 from SET A (Tables 1 and 2, Appendix XXVII).

Systems of equations:

$$0.7186 = 10^4[CuOx_2] + 10^4[CuDz] + 10^4[Cu(HDz)_2]$$

$$0.458 = + 0.68 \times 10^4[CuDz] + 1.24 \times 10^4[Cu(HDz)_2]$$

$$0.638 = + 0.68 \times 10^4[CuDz] + 3.34 \times 10^4[Cu(HDz)_2]$$

$$0.762 = + 0.79 \times 10^4[CuDz] + 4.11 \times 10^4[Cu(HDz)_2]$$

$$0.863 = + 1.04 \times 10^4[CuDz] + 3.79 \times 10^4[Cu(HDz)_2]$$

$$1.045 = 0.07 \times 10^3[CuOx_2] + 1.48 \times 10^4[CuDz] + 3.27 \times 10^4[Cu(HDz)_2]$$

$$1.281 = 0.35 \times 10^3[CuOx_2] + 2.02 \times 10^4[CuDz] + 2.75 \times 10^4[Cu(HDz)_2]$$

$$1.435 = 4.20 \times 10^3[CuOx_2] + 2.30 \times 10^4[CuDz] + 2.44 \times 10^4[Cu(HDz)_2]$$

$$1.371 = 5.88 \times 10^3[CuOx_2] + 2.19 \times 10^4[CuDz] + 2.21 \times 10^4[Cu(HDz)_2]$$

$$1.101 = 4.75 \times 10^3[CuOx_2] + 1.71 \times 10^4[CuDz] + 2.07 \times 10^4[Cu(HDz)_2]$$

Normal equations:

$$1.7490 \times 10^8[CuOx_2] + 4.1470 \times 10^8[CuDz] + 4.4267 \times 10^8[Cu(HDz)_2] = 2.7026 \times 10^4$$

$$4.1470 \times 10^8[CuOx_2] + 2.2912 \times 10^9[CuDz] + 3.5682 \times 10^9[Cu(HDz)_2] = 1.5283 \times 10^5$$

$$4.4267 \times 10^8[CuOx_2] + 3.5682 \times 10^9[CuDz] + 7.8261 \times 10^9[Cu(HDz)_2] = 2.5564 \times 10^5$$

These normal equations were then solved by the Gauss-Seidell method to give:

$[CuOx_2] = 8.503 \times 10^{-6}$ M

$[CuDz] = 5.164 \times 10^{-5}$ M

$[Cu(HDz)_2] = 8.608 \times 10^{-6}$ M

$[HOx] = 2.983 \times 10^{-5} - 2 \times 8.503 \times 10^{-6}$

$= 1.282 \times 10^{-5}$ M

Mass-balance check:

$(Cu)_T$ Found $= 8.503 \times 10^{-6} + 5.164 \times 10^{-5} + 8.608 \times 10^{-6}$

$= 6.875 \times 10^{-5}$ M

$(Cu)_T$ Taken $= 7.186 \times 10^{-5}$ M

Equilibrium constant:

$$K_1{}^1 = \frac{(8.503 \times 10^{-6})\ (8.608 \times 10^{-6})}{(5.164 \times 10^{-5})^2 (1.282 \times 10^{-5})^2} = 1.67 \times 10^8 \text{litre}^2\text{mole}^{-2}$$

$K_1 = 5.98 \times 10^{-9}$ mole^{2}litre^{-2}

(iii) Calculation of K_2

The mass-balance equations for Reaction (b)-III

$$CuDz + H_2Dz \rightleftarrows Cu(HDz)_2 \qquad \text{(b)-III}$$

were:

$$(Cu)_T = [CuDz] + [Cu(HDz)_2] \qquad \text{(b)-10}$$

$$(HDz)_T = [CuDz] + 2[Cu(HDz)_2] + [H_2Dz] \qquad \text{(b)-11}$$

The equilibrium concentrations for SET C were calculated from equations (b)-10, (b)-11, and the system of equations in Table 58, with the terms in $CuOx_2$ omitted, by using the experimental absorbance data (Table 6, Appendix XXVII). The results are in Table 61. The equilibrium constant K_2 for

TABLE 61

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANT FOR THE REACTION
$CuDz + H_2Dz \rightleftarrows Cu(HDz)_2$
IN BENZENE AT 25°C

Basic data: SET C, Tables 5 and 6, Appendix XXVII

Solution Number	Equilibrium Concentration M			Mass-Balance Check M		Equilibrium Constant
	$[H_2Dz]$ x 10^7	$[CuDz]$ x 10^6	$[Cu(HDz)_2]$ x 10^5	$(Cu)_T$ Found x 10^5	$(Cu)_T$ Taken x 10^5	K_2 x 10^{-7} litre mole^{-1}
CRC - 1	1.376	20.40	18.98	21.02	20.35	6.76
2	6.652	3.685	17.70	18.07	17.76	7.22
3	5.309	4.402	17.48	17.92	"	7.48
4	4.334	5.373	17.47	18.00	"	7.50
5	1.498	10.15	8.982	9.997	10.17	5.91
6	2.187	3.243	4.774	5.098	5.086	6.73
7	3.126	0.8956	1.932	2.022	2.035	6.90
8	1.264	2.143	1.886	2.100	"	6.96
9	2.950	0.9520	1.935	2.030	"	6.89
10	13.54	0.1739	1.575	1.593	1.776	6.69
11	0.3655	3.172	0.8917	1.209	1.017	7.69
12	2.354	0.3032	0.4682	0.4985	0.5086	6.56
13	1.622	0.1482	0.1852	0.2000	0.2035	7.70
14	1.216	0.2125	0.1577	0.1789	0.1776	6.10
15	1.549	0.1729	0.1607	0.1800	"	6.00
16	1.136	0.2250	0.1679	0.1904	"	6.57

Mean value of K_2 = 6.85 x 10^7 litre mole^{-1}
Variance = 3.19 x 10^{12}
Std. Deviation = 0.56 x 10^7 (for 15 degrees of freedom)

each solution was calculated from the equilibrium concentrations by using equation (b)-3. The mean value was then calculated. The results are also in Table 61. The mean value of K_2 was found to be $6.85 \pm 0.56 \times 10^7$ litre mole^{-1}.

(iv) Calculation of the Equilibrium Constants for the formation of adducts of primary copper dithizonate with dithizone

1) Experimental evidence for adduct formation

When primary copper dithizonate was mixed with dithizone in benzene solutions that had been intensively dried with calcium hydride, the resulting absorption spectrum did not correspond to the sum of the individual absorption spectra of $Cu(HDz)_2$ and dithizone. To confirm that a reaction was taking place a constant initial concentration of $Cu(HDz)_2$ was mixed with increasing concentrations of dithizone. Then from

$$A_{p,\lambda_1} = a_{\lambda_1,3}[Cu(HDz)_2] + a_{\lambda_1,4}[H_2Dz]$$

$$A_{p,\lambda_2} = a_{\lambda_2,3}[Cu(HDz)_2] + a_{\lambda_2,4}[H_2Dz]$$

the apparent equilibrium concentrations of $Cu(HDz)_2$ and H_2Dz were calculated from the experimentally measured absorbances and the known absorptivities of dithizone and of primary copper dithizonate. If no reaction takes place, then the calculated concentrations should correspond, within experimental error, to the initial concentrations of $Cu(HDz)_2$ and H_2Dz. They did not. Table 62 shows how the apparent

TABLE 62

CALCULATED APPARENT CONCENTRATION OF $Cu(HDz)_2$ AS A FUNCTION OF THE INITIAL RATIO OF $(Cu(HDz)_2)_i:(H_2Dz)_i$, IN DRY BENZENE AT 25°C

Initial Ratio $[Cu(HDz)_2]_i:(H_2Dz)_i$	Calculated Apparent Concentration of $Cu(HDz)_2 \times 10^5$
10:1	1.369
5:1	1.416
2:1	1.484
1:1	1.644
1:2	1.875
1:5	1.949
1:10	2.212
1:20	2.791
1:30	3.248
1:40	3.932
1:50	4.753

Concentration of $Cu(HDz)_2$ Taken = 1.209×10^{-5} M

equilibrium concentration of $Cu(HDz)_2$, calculated from the absorbances of mixtures, increased with increasing concentrations of dithizone.

2) Theoretical deductions

It was concluded that only two adducts of primary copper dithizonate with dithizone would be formed in the present solutions. This conclusion was reached by considering the following statements:

(1) Primary copper dithizonate was found by x-ray crystallography (149) to have a square-planar structure.

(2) According to ligand-field theory (192), a square-planar structure can be regarded as an octahedral structure with greatly extended axial orbitals.

(3) Ligands containing sulphur bonds (i.e. dithizone) are known to bond strongly (165), therefore, if the ligand field is strong enough, then it is possible for the dithizone molecule to bond axially to the square-planar $Cu(HDz)_2$ molecule to form adducts.

(4) If an octahedral structure is formed, only two sites are available on the $Cu(HDz)_2$ molecule, hence only two adducts should form.

(5) Additional adducts are possible by bonding via the sulphur atom of dithizone to the hydrogens on the dithizonate radicals bonded to the copper. However, it is reasonable to assume that these hydrogen bonds would be weak. They therefore would not form in de-

tectable concentrations until the initial ratio of $(H_2Dz)_i:(Cu(HDz)_2)_i$ was exceedingly high. These ratios could not be studied by conventional absorbance measurements.

3) Equations

Reaction (b)-IV may be written as

$$Cu(HDz)_2 + H_2Dz \rightleftarrows Cu(HDz)_2 \cdot H_2Dz \qquad (b)\text{-V}$$

$$Cu(HDz)_2 \cdot H_2Dz + H_2Dz \rightleftarrows Cu(HDz)_2 \cdot 2H_2Dz \qquad (b)\text{-VI}$$

with equilibrium constants

$$K_{31} = \frac{[Cu(HDz)_2 \cdot H_2Dz]}{[Cu(HDz)_2][H_2Dz]} \qquad (b)\text{-12}$$

$$K_{32} = \frac{[Cu(HDz)_2 \cdot 2H_2Dz]}{[Cu(HDz)_2 \cdot H_2Dz][H_2Dz]} \qquad (b)\text{-13}$$

The mass-balance equations were:

$$(Cu)_T = [Cu(HDz)_2] + [Cu(HDz)_2 \cdot H_2Dz] + [Cu(HDz)_2 \cdot 2H_2Dz] \qquad (b)\text{-14}$$

$$(HDz)_T = 2[Cu(HDz)_2] + 3[Cu(HDz)_2 \cdot H_2Dz] + 4[Cu(HDz)_2 \cdot 2H_2Dz] + [H_2Dz] \qquad (b)\text{-15}$$

and the Beer's law equations:

$$A_{p,\lambda_i} = a_{\lambda_i,3}[Cu(HDz)_2] + a_{\lambda_i,5}[Cu(HDz)_2 \cdot H_2Dz] + a_{\lambda_i,6}[Cu(HDz)_2 \cdot 2H_2Dz] + a_{\lambda_i,4}[H_2Dz] \qquad (b)\text{-16}$$

The absorptivities $a_{\lambda_i,5}$ and $a_{\lambda_i,6}$ were unknown.

4) Experiments and Results

In order to calculate K_{31} and K_{32} the absorptivities $a_{\lambda_i,5}$ and $a_{\lambda_i,6}$ had to be calculated. The following pre-

liminary calculations showed that K_{32} was considerably less than K_{31}: a series of ratio solutions was prepared (SET J, see Tables 15 & 16 of Appendix XXVII for the analytical data) in which the initial concentration of $Cu(HDz)_2$ was always greater than that of dithizone. For these solutions it was assumed that (i) the equilibrium concentration of $Cu(HDz)_2 \cdot 2H_2Dz$ in solution was negligibly small and (ii) complete reaction had taken place so that the equilibrium concentrations of H_2Dz had been reduced to negligible amounts.

With the above assumptions, equations (b)-14 and (b)-15 reduced to:

$$(Cu)_T = [Cu(HDz)_2] + [Cu(HDz)_2 \cdot H_2Dz] \qquad (b)\text{-}17$$

$$(HDz)_T = 2[Cu(HDz)_2] + 3[Cu(HDz)_2 \cdot H_2Dz] \qquad (b)\text{-}18$$

and were solved simultaneously for the equilibrium concentrations. Then from

$$a_{\lambda_{i,5}} = (A_{p,\lambda} - a_{\lambda_{i,3}}[Cu(HDz)_2])/[Cu(HDz)_2 \cdot H_2Dz]$$

(for a path length of 1 cm)

the absorptivity $a_{\lambda_{i,5}}$ was calculated for each solution at 5 mμ intervals from 700 to 400 mμ, from the spectral absorbance curves. The equilibrium concentrations used are in Table 63. A table of values at 10 mμ intervals is in Table 19 of Appendix XXVII. The absorptivity versus wavelength curve is shown in Figure 58.

These absorptivities of $Cu(HDz) \cdot H_2Dz$ were confirmed by experiments described later in this subsection.

TABLE 63

EQUILIBRIUM CONCENTRATIONS OF $Cu(HDz)_2$ AND $Cu(HDz)_2 \cdot H_2Dz$ IN DRY BENZENE AT 25°C, FROM WHICH THE ABSORPTIVITY OF $Cu(HDz)_2 \cdot H_2Dz$ WAS CALCULATED

Basic data: SET J, Tables 15 and 16, Appendix XXVII

Solution Number	Equilibrium Concentration M $[Cu(HDz)_2] \times 10^5$	Equilibrium Concentration M $[Cu(HDz)_2 \cdot H_2Dz] \times 10^6$
CRJ - 1	43.48	47.8
2	21.79	23.9
3	8.714	9.56
4	6.540	7.13
5	4.348	4.78
6	2.179	2.39
7	0.8714	0.956
8	0.6540	0.713
9	0.4348	0.488
10	1.940	4.78
11	0.7758	1.912
12	0.5819	1.434
13	0.3879	0.956
14	0.1940	0.478

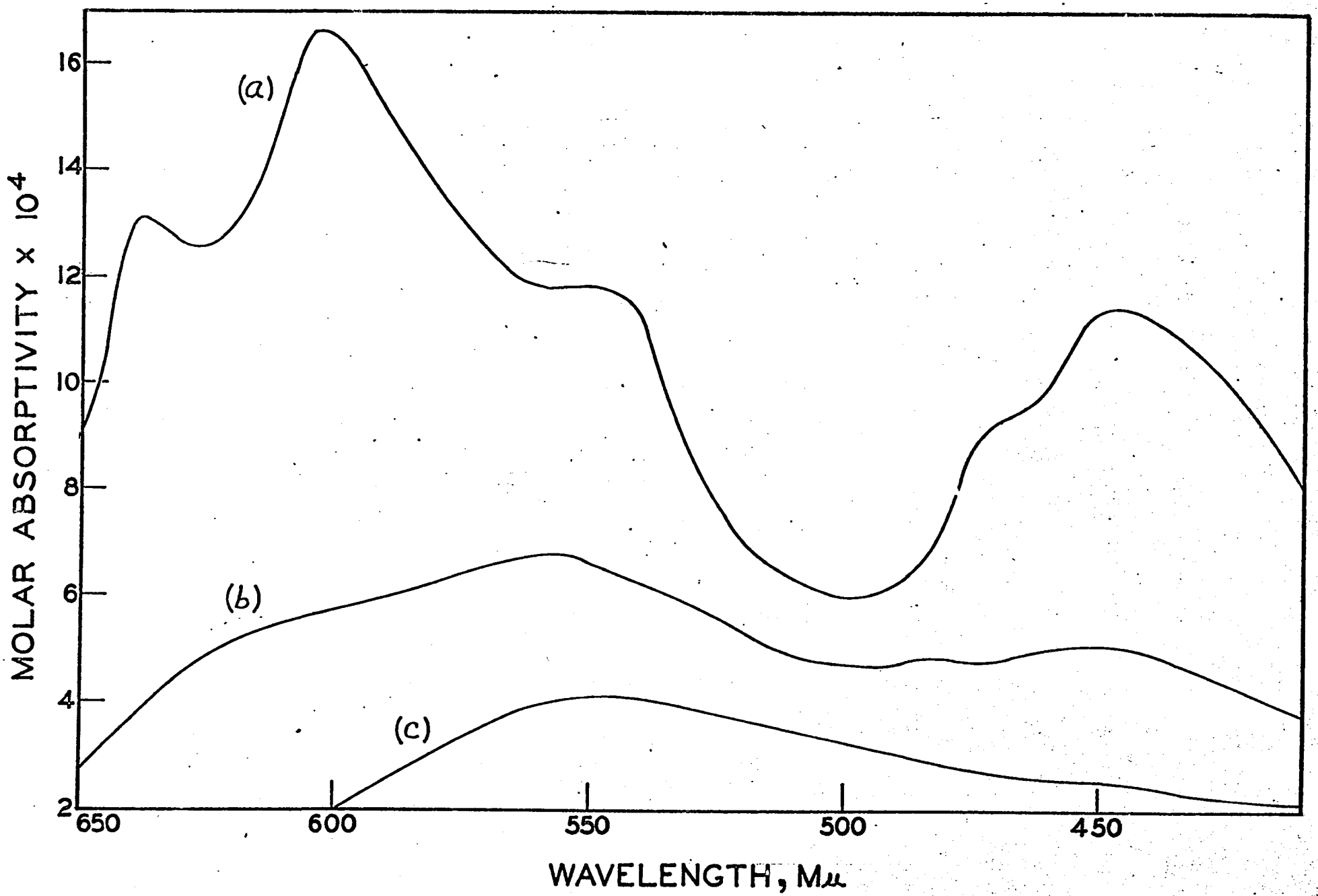
FIGURE 58

ABSORPTIVITY VERSUS WAVELENGTH FOR $Cu(HDz)_2 \cdot H_2Dz$ AND FOR $Cu(HDz)_2 \cdot 2H_2Dz$ AT 25°C IN DRY BENZENE

(a) $Cu(HDz)_2 \cdot 2H_2Dz$

(b) $Cu(HDz)_2 \cdot H_2Dz$

(c) $Cu(HDz)_2$


MOLAR ABSORPTIVITY x 10^4
16
14
12
10
8
6
4
2
(a)
(b)
(c)
650
600
550
500
450
WAVELENGTH, Mμ

A different procedure was required in order to obtain the absorptivity of $Cu(HDz)_2 \cdot 2H_2Dz$. A series of ratio solutions, SET K were used (see Table 17 & 18 of Appendix XXVII for the analytical data). It was assumed that in these solutions the equilibrium concentration of $Cu(HDz)_2$ was negligible compared to the equilibrium concentrations of the adducts and dithizone. From subsequent calculations this assumption proved to be correct.

With the above assumption equations (b)-14 and (b)-15 reduced to

$$(Cu)_T = [Cu(HDz)_2 \cdot H_2Dz] + [Cu(HDz)_2 \cdot 2H_2Dz] \qquad (b)\text{-}20$$

$$(HDz)_T = 3[Cu(HDz)_2 \cdot H_2Dz] + 4[Cu(HDz)_2 \cdot 2H_2Dz] + [H_2Dz] \qquad (b)\text{-}21$$

and the Beer's law equations were:

$$A_{p,\lambda_i} = a_{\lambda_i,5}[Cu(HDz)_2 \cdot H_2Dz] + a_{\lambda_i,6}[Cu(HDz)_2 \cdot 2H_2Dz] + a_{\lambda_i,4}[H_2Dz] \qquad (b)\text{-}22$$

Solving (b)-20 to (b)-22 by determinants

$$D[Cu(HDz)_2 \cdot H_2Dz] = a_{\lambda_i,4}[4(Cu)_T - (HDz)_T] + A_{p,\lambda_i} - a_{\lambda_i,6}(Cu)_T \qquad (b)\text{-}23$$

$$D[Cu(HDz)_2 \cdot 2H_2Dz] = a_{\lambda_i,4}[(HDz)_T - 3(Cu)_T] - A_{p,\lambda_i} + a_{\lambda_i,5}(Cu)_T \qquad (b)\text{-}24$$

$$D[H_2Dz] = a_{\lambda_i,5}[(HDz)_T - 4(Cu)_T] + a_{\lambda_i,6}[3(Cu)_T - (HDz)_T] + A_{p,\lambda_i} \qquad (b)\text{-}25$$

$$\text{Where } D = a_{\lambda_i,4} + a_{\lambda_i,5} - a_{\lambda_i,6} \qquad (b)\text{-}26$$

Let $Y = 3(Cu)_T - (HDz)_T$ $\quad X = 4(Cu)_T - (HDz)_T$ (b)-27

Substituting (b)-27 into (b)-23, (b)-24 and (b)-25 and then substituting the resulting equations into (b)-13:

$$K_{32} = \frac{[a_{\lambda_{i,5}}(Cu)_T - A_{p,\lambda_i} - a_{\lambda_{i,4}} Y]\, D}{[a_{\lambda_{i,4}} X + A - a_{\lambda_{i,6}}(Cu)_T][A_{p,\lambda_i} - a_{\lambda_{i,5}} X + a_{\lambda_{i,6}}]} \quad \text{(b)-28}$$

For each solution prepared, (b)-28 will be the same except for the values of $(Cu)_T$, X, Y and A. Thus to eliminate K_{32} all binary combinations of the ratio solutions #CRK-1 - #CRK-5 and #CRK-6 to #CRK-10, were equated to yield the systems of quadratic equations in $a_{\lambda_{i,6}}$ shown in Table 20 of Appendix XXVII.

The coefficients of each equation were calculated from the analytical data, the previously found absorptivity for $Cu(HDz)_2 \cdot H_2Dz$ and the absorbance data at 545 mμ. Each equation was solved for $a_{545,6}$ and the average of the individual values were computed. This average value was 6.40×10^4. Using this value the equilibrium concentrations of each of the species present in each of the ratio solutions #CRK-1 - #CRK-10 was calculated from equations (b)-23 to (b)-25. These are listed in Table 64. Then, using equation (b)-22, the absorptivity $a_{\lambda_{i,6}}$ was calculated at 5 mμ intervals from 700 to 400 mμ from the spectral transmission curves. A table of values at 10 mμ intervals is given in Table 21 of Appendix XXVII and the curve of absorptivity versus wavelength is illustrated in Figure 58.

TABLE 64

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANT FOR THE REACTION
$Cu(HDz)_2 + H_2Dz \rightleftarrows Cu(HDz)_2 \cdot H_2Dz$
IN DRY BENZENE AT 25°C

Basic data: SET K, Tables 17 and 18, Appendix XXVII

Solution Number	Equilibrium Concentration M $[Cu(HDz)_2 \cdot H_2Dz] \times 10^6$	$[Cu(HDz_2 \cdot 2H_2Dz] \times 10^6$	$[H_2Dz] \times 10^5$	Equilibrium Constant $K_{32} \times 10^{-4}$ litre $mole^{-1}$
CRK - 1	10.04	38.32	39.13	0.97
2	7.279	16.89	19.79	1.17
3	4.812	4.948	8.173	1.26
4	3.624	1.212	4.175	0.80
5	0.5356	0.4405	0.8143	1.01
6	5.370	42.98	86.47	0.92
7	4.600	19.58	43.42	0.98
8	3.462	6.298	17.51	1.04
9	2.651	2.184	8.825	0.93
10	0.8396	0.1364	1.801	0.90

Mean value of $K_{32} = 1.00 \times 10^4$
Variance $= 1.79 \times 10^6$
Std. Deviatiion $= 0.13 \times 10^4$ (for 9 degrees of freedom)

The equilibrium constant was calculated for each of the solutions #CRK-1 - #CRK-10, and the values are shown in Table 65.

SET G was used to obtain the value of K_{31} and to provide confirmation of K_{32} and $a_{\lambda_{i,6}}$ in the following way: a system of Beer's law equations, similar to those shown in Table 58, omitting the terms in $[CuOx_2]$ and [CuDz] but using the absorptivities for $Cu(HDz)_2$, $Cu(HDz)_2 \cdot H_2Dz$, $Cu(HDz)_2 \cdot 2H_2Dz$ and H_2Dz as coefficients were generated. With these equations and the absorbance data listed in Table 12 of Appendix XXVII, the various equilibrium concentrations were calculated by the method outlined in subsection (ii) of this Section. The equilibrium constants K_{31} and K_{32} were then calculated from equations (b)- and (b)-12 and (b)-13. The equilibrium concentrations and equilibrium constants are listed in Table 65. The average values for K_{31} and K_{32} were 6.32×10^5 and 1.16×10^4 respectively.

The fact that the values of K_{32} agreed well with those obtained from SET K confirmed the value of $a_{\lambda_{i,6}}$ and indirectly that of $a_{\lambda_{i,5}}$.

5) Confirmation of K_{31} and K_{32}

To confirm the values of K_{31} and K_{32} and the absorptivities of the adducts, the data from SET I, the continuous-variations solutions for the reaction of CuDz with dithizone in dry benzene solution were used.

TABLE 65

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANT FOR THE REACTION
$Cu(HDz)_2.H_2Dz + H_2Dz \rightleftarrows Cu(HDz)_2.2H_2Dz$
IN DRY BENZENE AT 25°C

Basic data: SET G, Tables 11 and 12 Appendix XXVII

Solution Number		Equilibrium Concentration M				Mass-Balance Check M		Equilibrium Constants litre mole^{-1}	
		$[Cu(HDz)_2]$ x 10^6	$[Cu(HDz)_2.H_2Dz]$ x 10^6	$[Cu(HDz)_2.2H_2Dz]$ x 10^6	$[H_2Dz]$ x 10^5	$(HDz)_T$ Found x 10^5	$(HDz)_T$ Taken x 10^5	K_{31} x 10^3	K_{32} x 10^4
CRG-	1	12.41	77.44	7.878	1.143	29.93	30.53	5.46	0.89
	2	7.952	38.98	3.068	0.7794	15.29	15.27	6.29	1.01
	3	4.151	20.23	0.1198	0.2047	3.003	3.053	6.50	1.06
	4	2.000	2.993	-	0.2138	1.512	1.527	7.00	-
	5	0.6624	0.3121	-	0.07373	0.2998	0.3053	6.39	-
	6	0.9879	47.58	50.50	6.717	40.88	41.10	7.17	1.58
	7	1.272	33.22	14.20	4.151	20.09	20.55	6.29	1.03
	8	1.177	8.005	0.8866	1.035	4.028	4.110	6.56	1.07
	9	0.8472	3.790	0.3077	0.6656	2.053	2.055	6.72	1.22
	10	0.5232	0.4871	-	0.1578	0.4086	0.4110	5.90	-
	11	0.1780	27.73	71.76	26.14	63.20	62.24	5.96	0.99
	12	0.2137	17.85	30.98	12.58	30.35	31.12	6.64	1.38
	13	0.3830	7.414	2.086	3.058	6.194	6.224	6.33	0.92
	14	0.4986	4.049	0.4147	1.422	2.904	3.112	5.71	0.72
	15	0.3354	0.6721	-	0.3397	0.6084	0.6224	5.90	-
	16	-	10.61	88.80	86.29	125.0	125.6	-	0.97
	17	-	11.38	37.97	43.35	61.95	62.83	-	0.77
	18	-	4.403	5.607	9.096	12.66	12.56	-	1.40
	19		3.042	1.855	6.927	6.124	6.283	-	0.88
	20	-	0.9069	0.0923	0.951	1.261	1.256	-	1.07

TABLE 65 CONTINUED

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANT FOR THE REACTION
$Cu(HDz)_2.H_2Dz + H_2Dz \rightleftarrows Cu(HDz)_2.2H_2Dz$
IN DRY BENZENE AT 25°C

Basic data: SET G, Tables 11 and 12 Appendix XXVII

Mean value of K_{31}	=	6.32×10^5
Variance	=	22.4×10^8
Std. Deviation	=	0.47×10^5 (for 14 degrees of freedom)
Mean value of K_{32}	=	1.16×10^4
Variance	=	5.79×10^6
Std. Deviation	=	0.24×10^4 (for 15 degrees of freedom)

The mass-balance equations for the reactions

$$CuDz + H_2Dz \rightleftarrows Cu(HDz)_2 \qquad (b)\text{-III}$$

$$Cu(HDz)_2 + H_2Dz \rightleftarrows Cu(HDz)_2 \cdot H_2Dz \qquad (b)\text{-V}$$

$$Cu(HDz)_2 \cdot H_2Dz + H_2Dz \rightleftarrows Cu(HDz)_2 \cdot 2H_2Dz \qquad (b)\text{-VI}$$

were:

$$(Cu)_T = [CuDz] + [Cu(HDz)_2] + [Cu(HDz)_2 \cdot H_2Dz] + [Cu(HDz)_2 \cdot 2H_2Dz] \qquad (b)\text{-29}$$

$$(HDz)_T = [CuDz] + 2[Cu(HDz)_2] + 3[Cu(HDz)_2 \cdot H_2Dz] + 4[Cu(HDz)_2 \cdot 2H_2Dz] + [H_2Dz] \qquad (b)\text{-30}$$

From equations (b)-3, (b)-12 and (b)-13 it can be shown that:

$$[Cu(HDz)_2] = K_2[CuDz][H_2Dz] \qquad (b)\text{-31}$$

$$[Cu(HDz)_2 \cdot H_2Dz] = K_2K_{31}[CuDz][H_2Dz]^2 \qquad (b)\text{-32}$$

$$[Cu(HDz)_2 \cdot 2H_2Dz] = K_2K_{31}K_{32}[CuDz][H_2Dz]^3 \qquad (b)\text{-33}$$

Substituting (b)-31, (b)-32 and (b)-33 into (b)-29 and rearranging

$$[CuDz] = \frac{(Cu)_T}{1 + K_2[H_2Dz] + K_2K_{31}[H_2Dz]^2 + K_2K_{31}K_{32}[H_2Dz]^3} \qquad (b)\text{-34}$$

Then substituting (b)-31 to (b)-33 and (b)-34 for CuDz into equation (b)-30 and rearranging, a fourth order equation in $[H_2Dz]$ was obtained:

$$[H_2Dz]^4 + [H_2Dz]^3\left\{\frac{1}{K_{32}} + [4(Cu)_T - (HDz)_T]\right\} + [H_2Dz]^2\left\{\frac{1}{K_{31}K_{32}} + \frac{[3(Cu)_T - (HDz)_T]}{K_{32}}\right\} + [H_2Dz]\left\{\frac{1}{K_2K_{31}K_{32}} + \frac{[2(Cu)_T - (HDz)_T]}{K_{31}K_{32}}\right\} + \frac{(Cu)_T - (HDz)_T}{K_2K_{31}K_{32}} = 0 \qquad (b)\text{-35}$$

The values of $K_2 = 6.85 \times 10^7$, $K_{31} = 6.32 \times 10^5$ and $K_{32} = 1.08 \times 10^4$ and the analytical data given in Table 13 of

Appendix XXVII, were inserted into the equation. This equation was then solved by the conventional computer program for solving polynomials based on a modified Downhill-Newton method.

There was only one positive, real root of equation (b)-35 for each of the solutions of SET I. This value of $[H_2Dz]$ was then substituted into equation (b)-34 to obtain [CuDz]. The equilibrium concentrations of the other species were then calculated from equations (b)-31 to (b)-33. The calculated equilibrium concentrations are listed in Table 66.

Using the Beer's law equation:

$$\frac{A_{p,\lambda_i}}{b} = a_{\lambda_{i,2}}[CuDz] + a_{\lambda_{i,3}}[Cu(HDz)_2] + a_{\lambda_{i,5}}[Cu(HDz)_2 \cdot H_2Dz] + a_{\lambda_{i,6}}[Cu(HDz)_2 \cdot 2H_2Dz] + a_{\lambda_{i,4}}[H_2Dz] \qquad (b)\text{-}36$$

the absorbance was calculated for 618, 545 and 445 mμ from the calculated equilibrium concentrations and the absorptivities. In Table 68 and in Figure 57 these calculated absorbances are compared with the experimental ones. The agreement was excellent and confirmed the values of K_{31}, K_{32} and the absorptivities of the adducts.

6) Effect of water

It was shown in subsection (i), 2) of the present Section that the continuous-variations plot for the reaction of CuDz with dithizone in solutions prepared in undried benzene (SET H) differed markedly from that obtained with

TABLE 66

CALCULATED EQUILIBRIUM CONCENTRATIONS OF THE SPECIES PRESENT IN THE SOLUTIONS FOR THE CONTINUOUS VARIATION PLOT OF THE REACTION OF CuDz WITH H_2Dz IN DRY BENZENE AT 25°C

Basic data: SET I, Tables 13 and 14, Appendix XXVII

$K_2 = 6.85 \times 10^7$* $K_{31} = 6.32 \times 10^5$ $K_{32} = 1.08 \times 10^4$

Solution Number	Equilibrium Concentration M x 10^5				
	[CuDz]	[Cu(HDz)$_2$]	[Cu(HDz)$_2$.H_2Dz]	[Cu(HDz)$_2$.$2H_2Dz$]	[H_2Dz]
CJI- 1	10.00	0	0	0	0
2	8.001	0.9976	0.0011	0	0.0002
3	6.006	1.987	0.0061	0	0.0005
4	4.021	2.959	0.0201	0	0.0011
5	2.069	3.864	0.0666	0	0.0027
6	0.4110	4.194	0.3948	0.0007	0.0149
7	0.0227	2.120	1.828	0.0289	0.1365
8	0.0005	0.3513	2.358	0.2904	1.062
9	0	0.0622	1.378	0.5598	3.502
10	0	0.0134	0.5593	0.4273	6.586
11	0	0	0	0	10.01

*See page 301.

TABLE 67

CALCULATED EQUILIBRIUM CONCENTRATIONS OF THE SPECIES PRESENT IN THE SOLUTIONS FOR THE CONTINUOUS VARIATION PLOT OF THE REACTION OF CuDz WITH H_2Dz IN "WET" BENZENE AT 25°C

Basic data: SET H, Tables 13 and 14, Appendix XXVII

$K_2 = 6.85 \times 10^7$* $K_{31}^1 = 12.64 \times 10^3$ $K_{32}^1 = 2.16 \times 10^2$

Solution Number	Equilibrium Concentration M x 10^5				
	[CuDz]	[$Cu(HDz)_2$]	[$Cu(HDz)_2.H_2Dz$]	[$Cu(HDz)_2.2H_2Dz$]	[H_2Dz]
CJH- 1	10.17	0	0	0	0
2	8.000	0.9997	0	0	0.0002
3	6.001	1.999	0	0	0.0005
4	4.001	2.998	0	0	0.0011
5	2.004	3.994	0.0015	0	0.0029
6	1.069	4.852	0.0406	0	0.0662
7	0.0036	3.397	0.5975	0.0019	1.392
8	0.0010	2.143	0.8500	0.0062	3.138
9	0.0003	1.202	0.7886	0.0095	5.193
10	0	0.5090	0.4825	0.0084	7.501
11	0	0	0	0	10.07

* See page 301.

TABLE 68

COMPARISON OF CALCULATED AND EXPERIMENTAL ABSORBANCES FOR THE CONTINUOUS VARIATION PLOTS OF THE REACTION OF CuDz WITH H_2Dz IN UNDRIED AND DRY BENZENE AT 25°C

Pathlength = 1 cm

	SET H Undried Benzene							SET I "Dry" Benzene					
Solution Number	618 mμ		545 mμ		445 mμ		Number	618 mμ		545 mμ		445 mμ	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.		Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
CJH- 1	0.69	0.68	0.79	0.74	2.30	2.27	CJI- 1	0.68	0.68	0.79	0.828	2.30	2.28
2	0.675	0.67	1.043	1.012	2.084	2.11	2	0.67	0.68	1.043	1.066	2.084	2.07
3	0.66	0.66	1.296	1.270	1.868	1.908	3	0.66	0.64	1.295	1.295	1.870	1.87
4	0.644	0.64	1.549	1.523	1.652	1.674	4	0.65	0.63	1.547	1.532	1.657	1.702
5	0.633	0.66	1.801	1.775	1.437	1.456	5	0.66	0.69	1.794	1.794	1.453	1.433
6	0.653	0.67	2.036	1.932	1.241	1.322	6	0.76	0.76	2.010	2.04	1.321	1.360
7	1.215	1.29	1.926	1.948	1.390	1.310	7	1.29	1.35	2.091	2.11	1.504	1.479
8	1.802	1.86	1.758	1.729	1.537	1.436	8	2.02	2.09	2.102	2.12	1.803	1.762
9	2.371	2.44	1.550	1.618	1.658	1.572	9	2.68	2.63	1.924	1.951	1.994	1.970
10	2.930	3.03	1.308	1.350	1.758	1.758	10	3.15	3.08	1.546	1.528	1.985	2.01
11	3.490	3.63	1.040	1.009	1.840	1.880	11	3.47	3.51	1.040	1.045	1.840	1.82

solutions prepared in benzene dried with calcium hydride. It was also found that when the ratio solutions, SET G, were prepared in undried benzene, the equilibrium concentrations of $Cu(HDz)_2 \cdot H_2Dz$ and $Cu(HDz)_2 \cdot 2H_2Dz$ were considerably reduced.

If it is assumed that in undried benzene solutions water was bound to the copper chelates, then reaction (b)-III may be written:

$$CuDz \cdot 2H_2O + H_2Dz \rightleftarrows Cu(HDz)_2 \cdot 2H_2O \qquad \text{(b)-VII}$$

Water did not affect the extent of this reaction. When adducts are formed the reactions may be written

$$Cu(HDz)_2 \cdot 2H_2O + H_2Dz \rightleftarrows Cu(HDz)_2 \cdot H_2O \cdot H_2Dz + H_2O \qquad \text{(b)-VIII}$$

$$Cu(HDz)_2 \cdot H_2O \cdot H_2Dz + H_2Dz \rightleftarrows Cu(HDz)_2 \cdot 2H_2Dz + H_2O \qquad \text{(b)-IX}$$

The presence of water would be expected to affect the extent of these reactions, and this was observed experimentally.

To confirm the above equations (b)-VIII and (b)-IX, the continuous-variations plot for SET H was calculated from equation (b)-36. The concentration of water in the benzene had been found to be 2×10^{-2} M by Karl-Fischer titration. This concentration is so large compared to the concentration of the chelate species and dithizone that it could be considered to be constant.

The mass-action law equations for reactions (b)-VIII and (b)-IX may be written as:

$$K_{31}{}^{1} = \frac{[Cu(HDz)_2 \cdot H_2O \cdot H_2Dz]}{[Cu(HDz)_2 \cdot 2H_2O]\,[H_2Dz]} \cdot [H_2O] \qquad \text{(b)-37}$$

$$K_{32}{}^{1} = \frac{[Cu(HDz)_2 \cdot 2H_2Dz]}{[Cu(HDz)_2 \cdot H_2O \cdot H_2Dz][H_2Dz]} \cdot [H_2O] \qquad (b)\text{-}39$$

where $K_{31}{}^{1}$ and $K_{32}{}^{1}$ are the apparent formation constants of the "aquo-adducts".

If now it is assumed that $K_{31}{}^{1} \approx K_{31}[H_2O]$, and $K_{32}{}^{1} \approx K_{32}[H_2O]$, then the values of

$$K_{31}{}^{1} = 6.32 \times 10^{5} \times 2 \times 10^{-2} = 12.64 \times 10^{3}$$

and

$$K_{32}{}^{1} = 1.16 \times 10^{4} \times 2 \times 10^{-2} = 2.32 \times 10^{2}$$

These values were then substituted into equation (b)-35, and the same calculations as those for SET I on page 315 were performed. The calculated equilibrium concentrations are listed in Table 67. In Table 68, and Figure 57 the calculated absorbances were compared both with the experimental absorbances of SET H, and those of SET I. The purpose of the comparison was to confirm or reject equations (b)-VIII and (b)-IX, and the assumptions that $K_{31}{}^{1} \approx K_{31}(H_2O)$ and $K_{32}{}^{1} \approx K_{32}(H_2O)$. The agreement is not especially good. The experimental data shows more curvature at the break. However, the fact that taking water into account caused the absorbances of the dry benzene solutions to shift towards the experimental undried benzene data, is consistent with the occurrence of reactions (b)-VIII and (b)-IX.

Figure 57 also shows that there was very little difference in the absorbances before the break which confirms that in reaction (b)-VII water has no effect. The

stoichiometry of reaction (b)-III was assumed to be 1:1 in the calculations. The agreement between the calculated and experimental data of SET I before the break (< 0.5 mole fraction of H_2Dz) confirms this assumption.

(v) Calculation of the Titration Graph for the Titration of Copper Oxinate with Dithizone in Benzene at 25°C

By using the equilibrium constants calculated in this Section, theoretical titration graphs were calculated for the titration of copper oxinate with dithizone. These graphs were then compared with the experimental graphs.

There were four titration graphs to compare:

(1) Titration graphs obtained at 618 mμ and 545 mμ when the titration solution did not initially contain free oxine.

(2) Titration graphs, obtained at 618 mμ and 545 mμ when the solution for titration contained free oxine, approximately onehundredfold in excess of the initial concentration of copper oxinate in the titration solution.

The titrations of copper oxinate with dithizone had been carried out in undried benzene solutions. Therefore, for the calculation, $K_{31}{}^1$ the formation constant of $Cu(HDz)_2 \cdot H_2Dz \cdot H_2O$, was used instead of K_{31}, as was done in subsection (iv) 6).

From Table 67, column 5 it is seen that the contribution of $Cu(HDz)_2 \cdot 2H_2Dz$ to the absorbance may be considered to be negligible compared to that of the other absorbing species in solution.

To derive the titration graphs, the equilibrium concentrations of each species present in solution were calculated for each point on the titration graph. The equilibrium constants obtained in the preceding subsections were used, together with the analytical data given in Table 69. The total absorbances at 618 mμ and 545 mμ were calculated from the products of the absorptivities at these wavelengths and the equilibrium concentrations.

Participating species were $CuOx_2$, CuDz, $Cu(HDz)_2$, $Cu(HDz)_2 \cdot H_2Dz$, H_2Dz and HOx in the proportions shown in Table 69.

1) Initial free oxine absent

It was not possible to derive a simple equation in one unknown to describe each point of the titration graph. Therefore the graph was calculated in stages as follows:

(1) Before the Equivalence Point ($2(Cu)_T >> (HDz)_T$)

It was assumed that when the concentration of copper oxinate was much larger than the concentration of dithizone added, the first seven points of the graph, the equilibrium concentration of free dithizone was negligible. The concentration of $Cu(HDz)_2 \cdot H_2Dz$ was, therefore, also negligible.

The mass-balance and mass-law equations were:

$$(Cu)_T = [CuOx_2] + [CuDz] + [Cu(HDz)_2] \qquad (b)\text{-}41$$

$$(Ox)_T = 2[CuOx_2] + [HOx] \qquad (b)\text{-}42$$

$$(HDz)_T = [CuDz] + 2[Cu(HDz)_2] \qquad (b)\text{-}43$$

$$K_1 = \frac{[CuDz]^2[HOx]^2}{[Cu(HDz)_2][CuOx_2]} = 5.71 \times 10^{-9} \text{ moles}^2 \text{ litre}^{-2} \qquad (b)\text{-}44$$

TABLE 69

ANALYTICAL DATA AND CALCULATED EQUILIBRIUM CONCENTRATIONS OF THE SPECIES PRESENT IN SOLUTION WHEN CuOx WAS TITRATED WITH H_2Dz IN BENZENE AT 25°C

Molarity of stock H_2Dz solution in benzene = 1.441×10^{-3} M
Molarity of stock $CuOx_2$ solution in benzene = 3.463×10^{-5} M
Aliquot $CuOx_2$ solution taken = 5 ML
Initial volume of titration solution = 50 ML

ML. H_2Dz Solution	$(HDz)_T$ Added M x 10^6	Equilibrium Concentrations M x 10^6					
		$[CuOx_2]$	$[CuDz]$	$[Cu(HDz)_2]$	$[Cu(HDz)_2 . H_2Dz]$	$[H_2Dz]$	$[HOx]$
0.0	0	3.463	0	0	0	0	0
0.03	0.8646	2.598	0.8646	0	0	0	1.729
0.06	1.729	1.767	1.729	0	0	0	3.392
0.09	2.594	0.9027	2.527	0.0557	0	0	5.121
0.12	3,458	0.2892	2.889	0.2486	0	0	6.348
0.15	4.323	0.1411	2.321	1.001	0	0	6.644
0.18	5.188	0.0130	1.478	1.855	0	0	6.900
0.21	6.052	0	0.9157	2.546	0.0013	0.0406	6.926
0.24	6.917	0	0.2261	3.228	0.0085	0.2084	"
0.27	7.814	0	0.0562	3.370	0.0372	0.8744	"
0.30	8.646	0	0.0292	3.362	0.0713	1.678	"
0.33	9.511	0	0.0195	3.338	0.1054	2.49	"
0.36	10.38	0	0.0145	3.309	0.1391	3.325	"
0.39	11.24	0	0.0115	3.279	0.1722	4.153	"
0.42	12.10	0	0.0095	3.249	0.2046	4.983	"

By rearranging equations (b)-41 to (b)-43 and since with no initial free oxine $2(Cu)_T = (Ox)_T$, the following equations were obtained:

$$[CuDz] = [HOx] - (HDz)_T \qquad (b)\text{-}45$$

$$[CuOx_2] = \frac{2(Cu)_T - [HOx]}{2} \qquad (b)\text{-}46$$

$$[Cu(HDz)_2] = \frac{2(HDz)_T - [HOx]}{2} \qquad (b)\text{-}47$$

Substitution of equations (b)-45 to (b)-47 into equation (b)-44 gives

$$[HOx]^4 - 2(HDz)_T[HOx]^3 + [HOx]^2\{\frac{4(HDz)_T^2 - K_1}{4}\}$$

$$+ K_1[HOx]\{\frac{(HDz)_T + (Cu)_T}{2}\} - K_1(HDz)_T(Cu)_T = 0 \qquad (b)\text{-}48$$

This equation was solved for the equilibrium concentration of oxine, by the conventional computer program.

The equilibrium concentrations of the other species were then calculated from equations (b)-45 to (b)-47.

(2) <u>In the Region of the Equivalence Point ($2(Cu)_T \approx (HDz)_T$); and beyond the Equivalence Point ($2(Cu)_T << (HDz)_T$)</u>

It was assumed that in these regions, the concentration of $CuOx_2$ was negligible.

The mass-balance and mass-law equations were:

$$(Cu)_T = [CuDz] + [Cu(HDz)_2] + [Cu(HDz)_2 \cdot H_2O \cdot H_2Dz] \qquad (b)\text{-}49$$

$$(HDz)_T = [CuDz] + 2[Cu(HDz)_2] + 3[Cu(HDz)_2 \cdot H_2O \cdot H_2Dz] + [H_2Dz] \qquad (b)\text{-}50$$

$$K_2 = \frac{[Cu(HDz)_2]}{[CuDz][H_2Dz]} = 6.85 \times 10^7 \text{ litre mole}^{-1} \qquad (b)\text{-}51$$

$$K_{31}^{1} = \frac{[Cu(HDz)_2 \cdot H_2O \cdot H_2Dz]}{[Cu(HDz)_2][H_2Dz]} = 12.64 \times 10^3 \text{ litre mole}^{-1} \quad \text{(b)-52}$$

From the above equations, the following cubic equation in $[H_2Dz]$ was derived:

$$[H_2Dz]^3 + [H_2Dz]^2 \{ \frac{1}{K_{31}^{1}} + (3(Cu)_T - (HDz)_T) \} + [H_2Dz] \{ \frac{1}{K_2 K_{31}^{1}} + \frac{(2(Cu)_T - (HDz)_T)}{K_{31}^{1}} \} + \frac{(Cu)_T - (HDz)_T}{K_2 K_{31}^{1}} = 0 \quad \text{(b)-53}$$

This equation was solved in order to obtain the rest of the points of the titration graph; conventional formulae for solving cubic equations were used. Having obtained the value of $[H_2Dz]$, the equilibrium concentration of each of the other species present in the solution were calculated, for each point.

c) Results

The results of the calculations are in Table 69. The calculated absorbances at 618 mμ and 545 mμ are compared with the experimental ones in Table 71 and in Figure 59.

The agreement was not good; an entirely satisfactory explanation for the disagreement, based on reaction rates, is given in the Section on Discussion of Results (page 424).

2) Initial Free Oxine, Onehundredfold in excess of the initial concentration of Copper Oxinate

To simplify calculations of the titration graph, the justifiable approximation was made that the equilibrium concentration (HOx) equaled the initial concentration $(HOx)_A$, for the entire titration.

An equation valid for each point on the titration graph was derived as follows:

TABLE 70

ANALYTICAL DATA AND CALCULATED EQUILIBRIUM CONCENTRATIONS OF THE SPECIES PRESENT IN SOLUTION WHEN $CuOx_2$ WAS TITRATED WITH H_2Dz AT 25°C IN BENZENE SOLUTIONS WHICH CONTAINED INITIAL FREE HOx, ONEHUNDREDFOLD IN EXCESS WITH RESPECT TO THE INITIAL MOLAR CONCENTRATION OF $CuOx_2$ IN THE TITRATION CELL

Molarity of stock H_2Dz solution in benzene = 1.441×10^{-3} M
Molarity of stock $CuOx_2$ solution in benzene = 3.463×10^{-5} M
Molarity of free HOx in the titration solution = 3.67×10^{-4} M
Aliquot $CuOx_2$ solution taken = 5 ML
Initial volume of solution = 50 ML

ML. H_2Dz Solution	(HDz) Added M x 10^6	Equilibrium Concentrations M x 10^6				
		[$CuOx_2$]	[CuDz]	[$Cu(HDz)_2$]	[$Cu(HDz)_2.H_2Dz$]	[H_2Dz]
0.0	0	3.463	0	0	0	0
0.03	0.8646	2.942	0.1999	0.3205	0	0.0234
0.06	1.729	2.481	0.2730	0.7086	0	0.0379
0.09	2.594	2.038	0.3103	1.114	0	0.0524
0.12	3.458	1.608	0.3230	1.531	0.0013	0.0692
0.15	4.323	1.191	0.3142	1.956	0.0022	0.0908
0.18	5.188	0.7912	0.2838	2.385	0.0037	0.1231
0.21	6.052	0.4200	0.2238	2.813	0.0065	0.1835
0.24	6.917	0.1255	0.1303	3.193	0.0144	0.3476
0.27	7.814	0.0203	0.0537	3.350	0.0386	0.9111
0.30	8.646	0.0059	0.0290	3.356	0.0717	1.689
0.33	9.511	0.0027	0.0194	3.335	0.1056	2.504
0.36	10.38	0.0015	0.0145	3.308	0.1391	3.328
0.39	11.24	0	0.0115	3.278	0.1722	4.155
0.42	12.10	0	0.0095	3.248	0.2046	4.985

TABLE 71

COMPARISON OF CALCULATED AND EXPERIMENTAL ABSORBANCES OF THE TITRATION GRAPH OF THE TITRATION OF $CuOx_2$ WITH H_2Dz IN BENZENE AT 25°C

Pathlength = 5 cm

ML. H_2Dz Solution	A*				B**			
	618 mμ		545 mμ		618 mμ		545 mμ	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
0	0	0	0	0	0	0	0	0
0.03	0.028	0.028	0.035	0.092	0.031	0.033	0.075	0.091
0.06	0.055	0.060	0.069	0.192	0.060	0.070	0.158	0.179
0.09	0.074	0.091	0.102	0.276	0.089	0.099	0.244	0.266
0.12	0.113	0.122	0.165	0.367	0.118	0.131	0.331	0.355
0.15	0.141	0.153	0.300	0.476	0.148	0.163	0.420	0.450
0.18	0.169	0.193	0.440	0.563	0.180	0.208	0.509	0.526
0.21	0.196	0.225	0.562	0.636	0.216	0.241	0.598	0.620
0.24	0.246	0.266	0.686	0.720	0.268	0.283	0.684	0.684
0.27	0.372	0.380	0.752	0.770	0.378	0.368	0.750	0.759
0.30	0.519	0.500	0.802	0.820	0.521	0.491	0.802	0.802
0.33	0.668	0.668	0.850	0.857	0.669	0.624	0.850	0.850
0.36	0.818	0.784	0.898	0.897	0.819	0.759	0.898	0.889
0.39	0.969	0.936	0.945	0.937	0.969	0.891	0.945	0.926
0.42	1.119	1.079	0.992	0.976	1.119	1.025	0.992	0.963

* Titration solution contained no initial free oxine.
** Titration solution contained free oxine, onehundredfold in excess with respect to the initial concentration of copper oxinate.

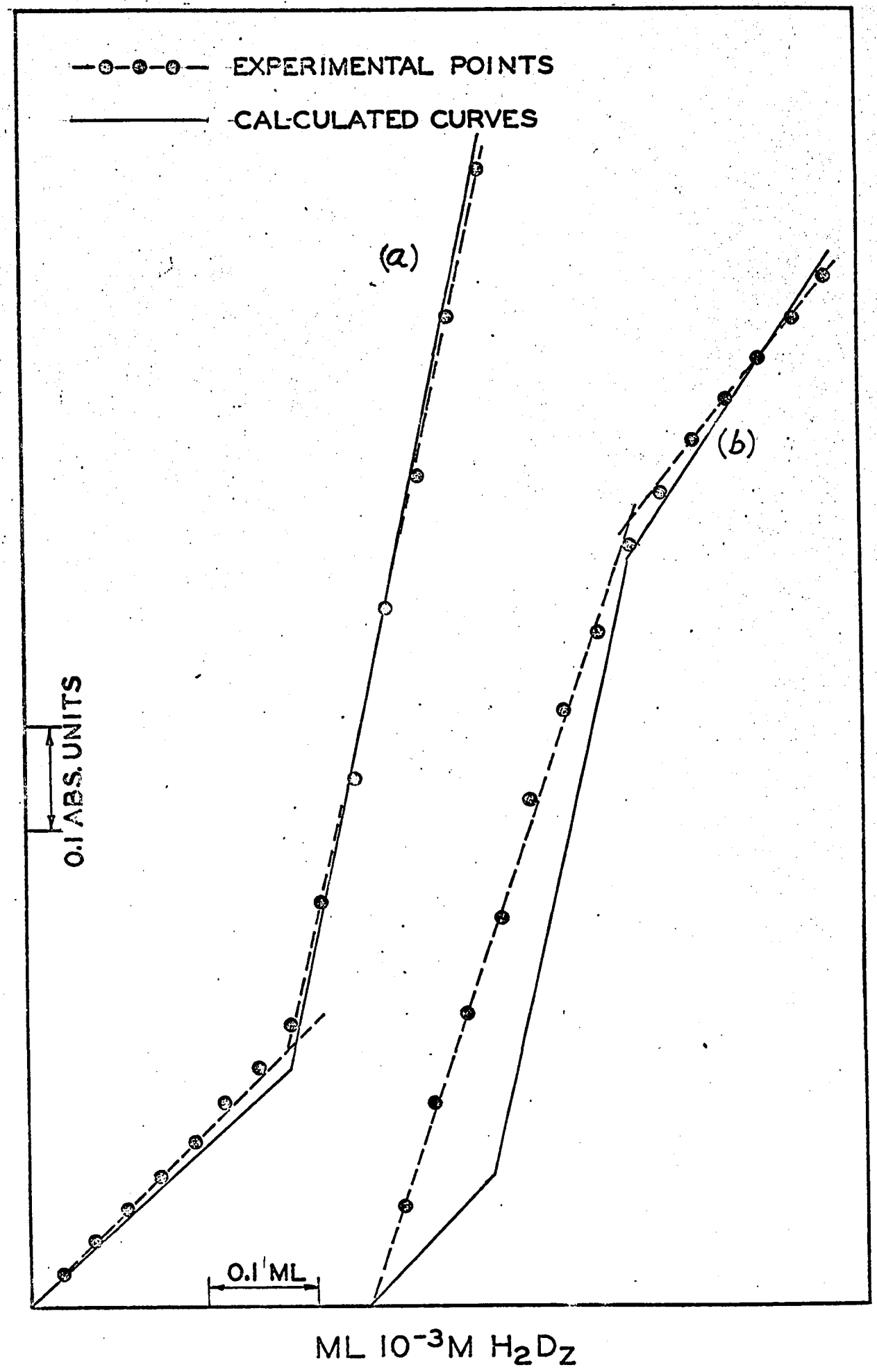
FIGURE 59

COMPARISON OF THE CALCULATED AND EXPERIMENTAL TITRATION GRAPHS OF THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE AT 25°C

(a) At 618 mμ.

(b) At 545 mμ.

Molarity of H_2Dz solution in benzene	:	1.441×10^{-3} M
Molarity of $CuOx_2$ solution in titration cell	:	3.463×10^{-6} M
Initial volume of solution	:	50 ml
Path length	:	5 cm


EXPERIMENTAL POINTS
CALCULATED CURVES
(a)
(b)
ABSORBANCE
0.1 ABS. UNITS
0.1 ML
ML 10⁻³M H₂Dz

$$(Cu)_T = [CuOx_2] + [CuDz] + [Cu(HDz)_2] + [Cu(HDz)_2 \cdot H_2O \cdot H_2Dz] \qquad (b)\text{-}54$$

$$(HDz)_T = [CuDz] + 2[Cu(HDz)_2] + 3[Cu(HDz)_2 \cdot H_2O \cdot H_2Dz] + [H_2Dz] \qquad (b)\text{-}55$$

$$[HOx]_A \doteq [HOx]$$

$$K_1 = \frac{[CuDz]^2}{[CuOx_2][Cu(HDz)_2]} \cdot (HOx)_A^2 = 5.71 \times 10^{-9} \text{ litres}^2 \text{ mole}^{-2} \qquad (b)\text{-}56$$

$$K_2 = \frac{[Cu(HDz)_2]}{[CuDz][H_2Dz]} = 6.85 \times 10^7 \text{ litre mole}^{-1} \qquad (b)\text{-}51$$

$$K_{31}{}^1 = \frac{[Cu(HDz)_2 \cdot H_2O \cdot H_2Dz]}{[Cu(HDz)_2][H_2Dz]} = 12.64 \times 10^3 \text{ litre mole}^{-1} \qquad (b)\text{-}52$$

On substituting equations (b)-51, (b)-52 and (b)-56 into equation (b)-55 for all species except [CuDz],

$$[CuDz] = \frac{(HDz)_T - [H_2Dz]}{1 + 2K_2[H_2Dz] + 3K_2K_{31}{}^1[H_2Dz]^2} \qquad (b)\text{-}57$$

where $[Cu(HDz)_2] = K_2[CuDz][H_2Dz]$ (b)-58

$[Cu(HDz)_2 \cdot H_2O \cdot H_2Dz] = K_2K_{31}{}^1[CuDz][H_2Dz]^2$ (b)-59

$$[CuOx_2] = \frac{[CuDz]}{K_1K_2[H_2Dz]} \cdot (HOx)_A^2 \qquad (b)\text{-}60$$

On substituting equations (b)-57 to (b)-60 into equation (b)-54 and rearranging, the following equation was obtained:

$$[H_2Dz]^4 + [H_2Dz]^3\left\{\frac{1}{K_{31}{}^1} + [3(Cu)_T - (HDz)_T]\right\} + [H_2Dz]^2\left\{\frac{1}{K_2K_{31}{}^1} + \frac{[2(Cu)_T - (HDz)_T]}{K_{31}{}^1}\right\} + [H_2Dz]\left\{\frac{(HOx)_A^2}{K_1K_2{}^2K_{31}{}^1} + \frac{[(Cu)_T - (HDz)_T]}{K_2K_{31}{}^1}\right\} - \frac{(HDz)_T(HOx)_A^2}{K_1K_2{}^2K_{31}{}^1} = 0 \qquad (b)\text{-}61$$

Equation (b)-61 was solved for each point of the titration graph, using the computer program described in subsection (iv), 5).

Having obtained the equilibrium concentration of $[H_2Dz]$, the equilibrium concentrations of each of the other species present in solution were calculated from equations (b)-57 to (b)-60. The absorbances were then calculated as described previously.

The results are in Table 70. The calculated absorbances at 618 mμ and 545 mμ are compared with the experimental absorbances in Table 71 and in Figure 60.

The agreement was not especially good. Again, an entirely satisfactory explanation is presented in the Section on "Discussion of Results", page 424.

(vi) Summary

The equilibrium constants of the following reactions were calculated to be

1. $2CuDz + 2HOx \rightleftarrows CuOx_2 + Cu(HDz)_2$

$K_1^1 = 1.71 \times 10^8$ litre^2 mole^{-2}

$S = 0.19 \times 10^8$ (18 deg. of free.)

2. $CuOx_2 + Cu(HDz)_2 \rightleftarrows 2CuDz + 2HOx$

$K_1 = 5.61 \times 10^{-9}$ mole^2 litre^{-2}

$S = 0.52 \times 10^{-9}$ (13 deg. of free.)

3. $CuDz + H_2Dz \rightleftarrows Cu(HDz)_2$

$K_2 = 6.85 \times 10^7$ litre mole^{-1}

$S = 0.56 \times 10^7$ (15 deg. of free.)

4. $Cu(HDz)_2 + H_2Dz \rightleftarrows Cu(HDz)_2 \cdot HDz$

$K_{31} = 6.32 \times 10^5$ litre mole^{-1}

$S = 0.47 \times 10^5$ (14 deg. of free.)

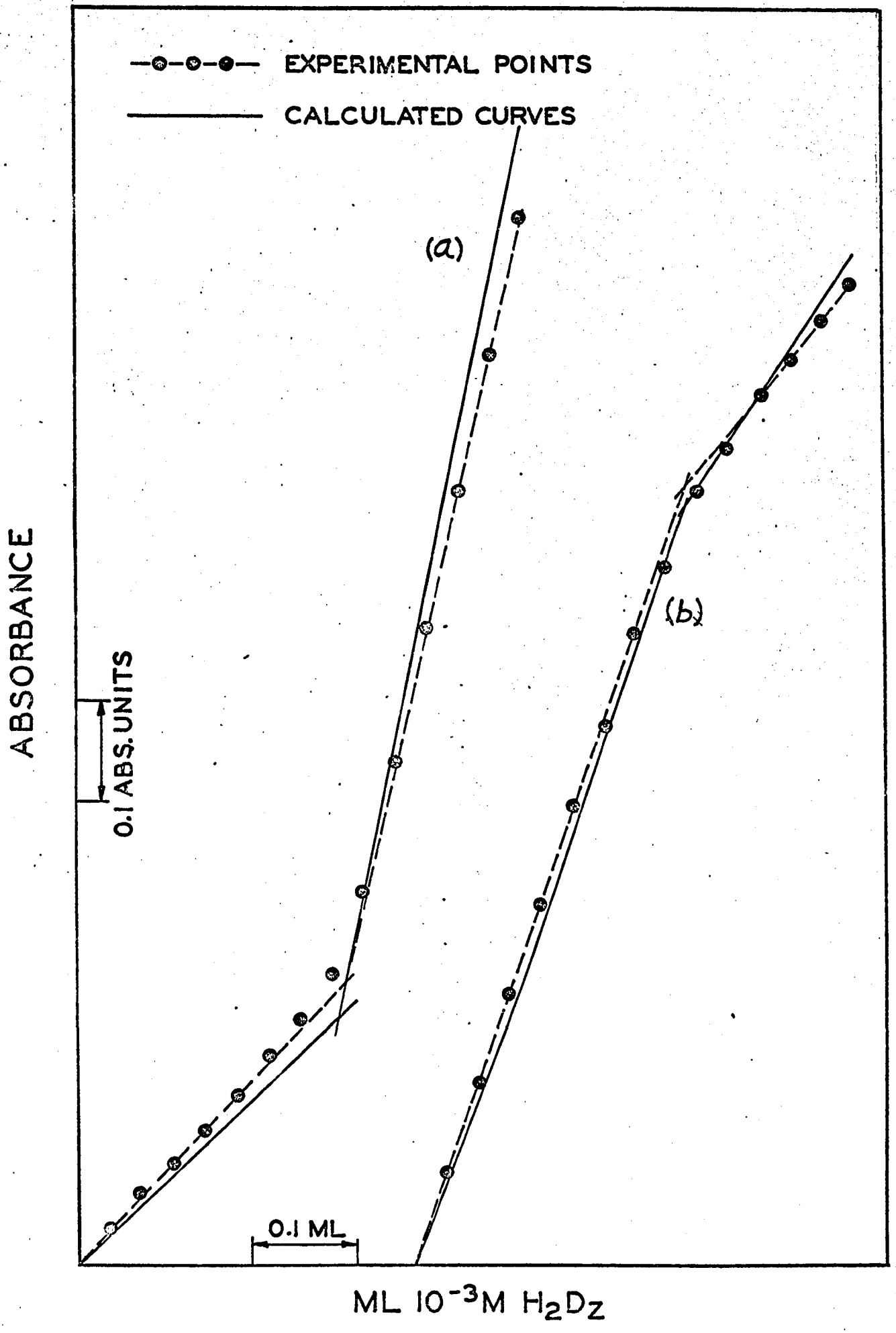
FIGURE 60

COMPARISON OF CALCULATED AND EXPERIMENTAL TITRATION GRAPHS FOR THE TITRATION OF COPPER OXINATE WITH DITHIZONE AT 25°C IN BENZENE SOLUTION WHICH CONTAINED INITIAL FREE OXINE, ONEHUNDREDFOLD IN EXCESS WITH RESPECT TO THE INITIAL MOLAR CONCENTRATION OF COPPER OXINATE IN THE TITRATION

(a) At 618 mμ.

(b) At 545 mμ.

Molarity of H_2Dz solution in benzene	:	1.441×10^{-3} M
Molarity of $CuOx_2$ solution in titration cell	:	3.463×10^{-6} M
Molarity of HOx solution in titration cell	:	3.670×10^{-4} M
Initial volume of solution	:	50 ml
Path length	:	5 cm


EXPERIMENTAL POINTS
CALCULATED CURVES
(a)
(b)
ABSORBANCE
0.1 ABS. UNITS
0.1 ML
ML 10⁻³M H₂Dz

5. $Cu(HDz)_2 \cdot H_2Dz + H_2Dz \rightleftarrows Cu(HDz)_2 \cdot 2H_2Dz$

$K_{32} = 1.08 \times 10^4$ litre $mole^{-1}$

$S = 0.22 \times 10^4$ (24 deg. of free.)

6. $CuOx_2 + 2H_2Dz \rightleftarrows Cu(HDz)_2 + 2HOx$

$K_0 = K_2^2 \cdot K_1 = 2.64 \times 10^7$

$S = 0.57 \times 10^7$

(c) The Indium System

(i) Introduction

The following reactions for the indium chelates were observed to take place in benzene solution:

(1) The reaction of indium oxinate with dithizone was very sensitive to the initial amount of free oxine in the solution. This suggested that the equilibrium constant or constants were relatively low. Furthermore, the resulting absorption spectrum did not coincide with the sum of the spectra of unreacted dithizone and the free indium dithizonate produced in the reaction. The experiment indicated that mixed chelates were produced.

(2) When indium oxinate and indium dithizonate were mixed, the resultant absorption spectrum was not quite coincident with the sum of the separate spectra. Therefore a mixed chelate was indicated.

(3) When oxine was added to indium dithizonate the absorption spectrum of the indium dithizonate was drastically changed. Furthermore, the resulting absorption spectrum did not coincide with the sum of the spectra of

unreacted indium dithizonate and the free dithizone produced in the reaction. This provided further evidence that mixed chelates existed.

(4) When indium dithizonate was mixed with dithizone, the resultant absorption spectrum was coincident with the sum of the separate spectra of indium dithizonate and dithizone. It was concluded that adducts of indium dithizonate with dithizone probably did not form.

(5) Continuous-variations plots showed that one mole of indium oxinate reacted with three moles of dithizone, and that one mole of indium dithizonate reacted with three moles of oxine.

(6) When indium oxinate was mixed with oxine, the resultant absorption spectrum was coincident with the separate spectrum of indium oxinate. It was concluded that adducts of indium oxinate with dithizone did not form.

When the equilibrium constants of the various indium reactions were calculated, it was assumed at once that mixed chelates of the type $InOx_2(HDz)$ and $InOx(HDz)_2$ existed. This assumption was based on observations (1), (2) and (3) above and experience with the lead system (subsection (d) of this Section, page 370). The equilibrium constants obtained over a range of concentrations were not constant when the presence of mixed chelates was ignored. When the presence of mixed chelates were included in the calculations, constant equilibrium constants were obtained. These facts strongly support the assumption that mixed chelates existed.

Based on observation (5), the overall reaction when indium oxinate was reacted with dithizone was postulated to be

$$InOx_3 + 3H_2Dz \rightleftarrows In(HDz)_3 + 3HOx \qquad (c)\text{-I}$$

Reaction (c)-I was further described in steps, in order to include the formation of mixed chelates. Thus,

$$InOx_3 + H_2Dz \rightleftarrows InOx_2HDz + HOx \qquad (c)\text{-II}$$

$$InOx_2HDz + H_2Dz \rightleftarrows InOx(HDz)_2 + HOx \qquad (c)\text{-III}$$

$$InOx(HDz)_2 + H_2Dz \rightleftarrows In(HDz)_3 + HOx \qquad (c)\text{-IV}$$

with

$$K_0 = \frac{[In(HDz)_3][HOx]^3}{[InOx_3][H_2Dz]^3} \qquad (c)\text{-1}$$

$$K_1 = \frac{[InOx_2HDz][HOx]}{[InOx_3][H_2Dz]} \qquad (c)\text{-2}$$

$$K_2 = \frac{[InOx(HDz)_2][HOx]}{[InOx_2HDz][H_2Dz]} \qquad (c)\text{-3}$$

$$K_3 = \frac{[In(HDz)_3][HOx]}{[InOx(HDz)_2][H_2Dz]} \qquad (c)\text{-4}$$

The reciprocals of the above equilibrium constants will be designated, K_0^1, K_1^1, K_2^1, K_3^1, respectively.

The equilibrium constants at 25°C for reactions (c)-II, (c)-III and (c)-IV were calculated from the data of two continuous-variations plots representing two sets of solutions:

SET A. Indium oxinate was reacted with dithizone in benzene solutions containing free oxine, fiftyfold in excess with respect to the total, molar concentration of reactants.

SET B. Indium dithizonate was reacted with oxine in benzene solutions.

In SET A the total concentration of reactants was 10^{-5} M and in SET B it was 10^{-4} M. The values obtained for K_1, K_2, and K_3 were confirmed by calculating continuous-variations plots for two additional sets of solutions:

SET C. The reaction of indium oxinate with dithizone in benzene solutions containing no initial free oxine.

SET D. The reaction of indium oxinate with dithizone in benzene solutions containing a tenfold initial excess of oxine with respect to the total molar concentration of reactants. These calculated continuous-variations plots were then compared with the experimental plots.

The analytical data for SETS A to D are in Tables 1-4 of Appendix XXVIII.

For reactions (c)-II - (c)-IV, the mass-balance equations used were:

$$(In)_T = [InOx_3] + [InOx_2HDz] + [InOx(HDz)_2] + [In(HDz)_3] \quad (c)\text{-}5$$

$$(Ox)_T = 3[InOx_3] + 2[InOx_2HDz] + [InOx(HDz)_2] + [HOx] \quad (c)\text{-}6$$

$$(HDz)_T = [InOx_2HDz] + 2[InOx(HDz)_2] + 3[In(HDz)_3] + [H_2Dz] \quad (c)\text{-}7$$

In equation (a)-4 of subsection (a) page 278, m = 3, n = r = s = o, represents $InOx_3$ and let its absorptivity be denoted by $a_{\lambda_{i,1}}$; m = 2, n = 1, r = s = o represent $InOx_2(HDz)$ with absorptivity $a_{\lambda_{i,2}}$; m = 1, n = 2, r = s = o represents $InOx(HDz)_2$ with absorptivity $a_{\lambda_{i,3}}$; m = o, n = 3, r = s = o

represents $In(HDz)_3$ with absorptivity $a_{\lambda_i,4}$; and let the absorptivity of dithizone be designated by $a_{\lambda_i,5}$.

Then the Beer's law equations were:

$$A_{p,\lambda_i} = a_{\lambda_i,1}[In(HDz)_3] + a_{\lambda_i,2}[InOx(HDz)_2] + a_{\lambda_i,3}[InOx_2(HDz)] + a_{\lambda_i,4}[InOx_3] + a_{\lambda_i,5}[H_2Dz] \qquad (c)\text{-}8$$

where A_{p,λ_i} is the absorbance of solution #p at wavelength λ_i at 25°C. The path length is 1 cm.

Oxine does not absorb in the visible region (see Figure 38, page 194). It was known that $a_{618,1} = a_{618,4} = 0$ (see Table 4 of Appendix XX and Table 3 of Appendix XXII) and it was assumed that $a_{618,2} = a_{618,3} = 0$*. Absorbance measurements at 618 mμ would then give an independent measure of the equilibrium concentration of dithizone, from the equation

$$[H_2Dz] = \frac{A_{p,618}}{a_{618,5}} \text{ for 1 cm path length} \qquad (c)\text{-}9$$

(see Table 1 of Appendix XVIII for the absorptivities of dithizone).

By substituting equations (c)-2 to (c)-4 for each metal chelate into equation (c)-5 and rearranging:

$$[InOx_3] = \frac{(In)_T}{1 + K_1\frac{[H_2Dz]}{[HOx]} + K_1K_2\frac{[H_2Dz]^2}{[HOx]^2} + K_1K_2K_3\frac{[H_2Dz]^3}{[HOx]^3}} \qquad (c)\text{-}10$$

---

*The mixed chelate PbOxHDz was known not to absorb at 618 mμ (subsection (a) page 382) and its absorptivity from 600 to 400 mμ was approximately one-half that of lead dithizonate.

also

$$[InOx_2(HDz)] = K_1\frac{[H_2Dz]}{[HOx]} \cdot [InOx_3] \qquad (c)\text{-}11$$

$$[InOx(HDz)_2] = K_1K_2\frac{[H_2Dz]^3}{[HOx]^2} \cdot [InOx_3] \qquad (c)\text{-}12$$

$$[In(HDz)_3] = K_1K_2K_3\frac{[H_2Dz]^3}{[HOx]^3} \cdot [InOx_3] \qquad (c)\text{-}13$$

These equations were used to calculate equilibrium concentrations after K_1, K_2 and K_3 had been evaluated.

In equations (c)-2 - (c)-4 and equations (c)-5 - (c)-7 there are eight unknowns (five equilibrium concentrations and threeequilibrium constants) and only six equations. Thus to solve for the unknowns at least two Beer's law equations were needed. However, the absorptivities of the mixed chelates were unknown.

Therefore a different approach was required, in order to evaluate the equilibrium constants.

From equations (c)-5 - (c)-7 it can be shown that

$$(HOx) = (Ox)_T - 3(In)_T + (HDz)_T - (H_2Dz) \qquad (c)\text{-}14$$

Let

$$R = (Ox)_T - 3(In)_T + (HDz)_T \qquad (c)\text{-}15$$

Substituting equations (c)-2 - (c)-4 in equations (c)-5 - (c)-7 and rearranging, the following equation was obtained:

$$(In)_T\left[K_1\frac{(H_2Dz)}{R-(H_2Dz)} + 2K_1K_2\frac{(H_2Dz)^2}{R-(H_2Dz)^2} + 3K_1K_2K_3\frac{(H_2Dz)^3}{R-(H_2Dz)^3}\right]$$

$$= [(HDz)_T - (H_2Dz)]\left[1 + K_1\frac{(H_2Dz)}{R-(H_2Dz)} + \frac{K_1K_2(H_2Dz)^2}{R-(H_2Dz)^2} + \frac{K_1K_2K_3(H_2Dz)^3}{R-(H_2Dz)^3}\right] \qquad (c)\text{-}16$$

Let

$$Az = [H_2Dz] \qquad (c)\text{-}18$$

and let

$$(In)_T = X(HDz)_T \qquad (c)\text{-}19$$

Then substituting equations (c)-18 and (c)-19 in equation (c)-16 and multiplying, the following equation was obtained:

$$Az^4[1-K_1 + K_1K_2-K_1K_2K_3]$$

$$+ Az^3[(HDz)_T(X-1)(1-K_1 + K_1K_2-K_1K_2K_3)-X(HDz)_T(2K_1K_2K_3-K_1K_2-1) + R(2K_1-K_1K_2-3)$$

$$+ Az^2R[(HDz)_T(X-1)(2K_1-K_1K_2-3)-X(HDz)_T(K_1K_2-3) + R(3-K_1)]$$

$$+ AzR^2[(HDz)_T(X-1)(3-K_1)-3X(HDz)_T-R] + R^3(HDz)_T = 0 \qquad (c)\text{-}20$$

(ii) Calculation of K_1 from the Solutions of SET A

To simplify the calculations for SET A above, the following assumptions were made:

(i) Up to 0.45 mole fraction of dithizone (Solution #JIA-2 to #JIA-10, Table 1, Appendix XXVIII), the equilibrium concentrations of $In(HDz)_3$ and $InOx(HDz)_2$ were negligible compared to the equilibrium concentrations of $InOx_3$ and $InOx_2HDz$;

(ii) From 0.5 mole fraction of dithizone to 0.85 (Solution #JIA-11 to #JIA-18, Table 1, Appendix XXVIII), the equilibrium concentration of $In(HDz)_3$ was negligible compared to the equilibrium concentrations of $InOx_3$, $InOx_2HDz$ and $InOx(HDz)_2$.

Using assumption (i), equation (c)-20 reduces to

$$Az^2[1-K_1] + Az[(HDz)_T(X-1)(1-K_1)-X(HDz)_T-R] + R(HDz)_T = 0 \qquad (c)\text{-}21$$

and using assumption (ii), equation (c)-20 reduces to

$$Az^3[K_1-K_1K_2-1] + Az^2[(HDz)_T(X-1)(K_1-K_1K_2-1)-X(HDz)_T(1 + K_1K_2) + R(2-K_1)] + AzR[(HDz)_T(X-1)(2-K_1)-2X(HDz)_T-R] + R^2(HDz)_T = 0 \qquad (c)-22$$

Since Az could be calculated from equation (c)-9, values for K were calculated from the following equation obtained by rearranging equation (c)-21

$$K_1 = \frac{[(HDz)_T-Az][R-Az]}{Az[Az + (X-1)(HDz)_T]} \qquad (c)-23$$

The average value for K_1 was found to be 88.7 ± 10.1. A sample calculation follows:

Sample Calculation on JIA-4

$(In)_T = 8.502 \times 10^{-6}$ M $(Ox)_T = 5.499 \times 10^{-4}$ M

$(HDz)_T = 1.498 \times 10^{-6}$ M $A_{618} = 0.118$ X = 5.6667

$R = 5.259 \times 10^{-4}$; b = 5 cm

$$Az = \frac{0.118}{5 \times 3.47 \times 10^4} = 6.801 \times 10^{-7}$$

Using equation (c)-23

$$K_1 = \frac{[1.498 \times 10^{-6} - 6.801 \times 10^{-7}][5.259 \times 10^{-4} - 6.801 \times 10^{-7}]}{[6.801 \times 10^{-7}][4.6667 \times 1.498 \times 10^{-6} + 6.801 \times 10^{-7}]}$$

$$= 82.4$$

Inserting K = 88.7 in equation (c)-21, a theoretical absorbance curve at 618 mμ was calculated to cover the data used to obtain K_1. The scatter in the experimental points about the calculated curve suggested that K_1 should be adjusted to minimize the scatter. Therefore, values of K_1 were tried until the best fit with the experimental data was obtained. The final value of K_1 was 92.0. This value will be confirmed later.

Having obtained a value for K_1, K_2 was calculated from equation (c)-22 for solutions JIA-11 to JIA-18 in the same way as above using the known experimental values of Az.

K_2 proved not to be constant except for solutions JIA-11 to JIA-13. Therefore assumption (ii) was considered invalid over the range of mole fractions considered. However, the average of the few constant values obtained, 9.88, provided a starting value for subsequent calculations.

(iii) Calculation of K_2 and K_3 from the data of SET B

The reaction of indium dithizonate with oxine was the reverse of equations (c)-II - (c)-IV:

$$In(HDz)_3 + HOx \overset{K_3^1}{\rightleftarrows} InOx(HDz)_2 + H_2Dz \qquad (c)\text{-V}$$

$$InOx(HDz)_2 + HOx \overset{K_2^1}{\rightleftarrows} InOx_2(HDz) + H_2Dz \qquad (c)\text{-VI}$$

$$InOx_2(HDz) + HOx \overset{K_1^1}{\rightleftarrows} InOx_3 + H_2Dz \qquad (c)\text{-VII}$$

An equation similar to equation (c)-16, using equations (c)-5 to (c)-7, (c)-14, (c)-15 and (c)-19 and the reciprocals of equations (c)-2 to (c)-4, were derived:

$$X^1\left[3K_1^1K_2^1K_3^1\frac{(R-Az)^3}{Az^3} + 2K_2^1K_3^1\frac{(R-Az)^2}{Az^2} + K_2^1\frac{(R-Az)}{Az}\right]$$

$$= \left[1-\frac{(R-Az)}{(Ox)_T}\right]\left[K_1^1K_2^1K_3^1\frac{(R-Az)^3}{Az^3} + K_2^1K_3^1\frac{(R-Az)^2}{Az^2} + K_3^1\frac{(R-Az)}{Az} + 1\right] \qquad (c)\text{-24}$$

where $X^1 = (In)_T/(Ox)_T$ and K_1^1, K_2^1 and K_3^1 are the reciprocals of K_1, K_2 and K_3 respectively.

To simplify the calculation on the data of SET B, it was assumed that for mole fractions of oxine from 0 to 0.85 (#JZB-1 to #JZB-19, Table 2, Appendix XXVIII), the equilibrium concentration of $InOx_3$ was negligible compared to the equilibrium concentrations of $In(HDz)_3$, $InOx(HDz)_2$ and $InOx_2(HDz)$.

Thereby, the $K_1{}^1K_2{}^1K_3{}^1\frac{(R-Az)^3}{Az^3}$ terms could be dropped from equation (c)-24. In multiplying out equation (c)-24 the following equation was obtained:

$$Az^3[1 + K_2{}^1K_3{}^1-K_3{}^1] + Az^2[R(2K_3{}^1-3K_2{}^1K_3{}^1-1) + (Ox)_T(1-K_2{}^1K_3{}^1(2X -1) + K_3{}^1(X^1-1)] + RK_3{}^1Az[R(3K_2{}^1-1) + (Ox)_T(2K_2{}^1(2X^1-1)-(X^1-1))]-K_2{}^1K_3{}^1R^2[(2X^1-1)(Ox)_T + R] = 0 \qquad (c)-25$$

To obtain a starting value for K_3, it was assumed that for mole fractions of oxine from 0 to 0.45 (Solution #JZB-1 to #JZB-10), the equilibrium concentrations of $InOx_3$ and $InOx_2HDz$ were negligible compared to those of $In(HDz)_3$ and $InOx(HDz)_2$. Omitting the $K_1{}^1K_2{}^1K_3{}^1\frac{(R-Az)^3}{Az^3}$ and $K_1{}^1K_2{}^1\frac{(R-Az)^2}{Az^2}$ terms in equation (c)-24 and rearranging gave

$$K_3{}^1 = \frac{[(Ox)_T-(R-Az)]}{[(X^1-1)(Ox)_T + (R-Az)]} \cdot \frac{Az}{(R-Az)} \qquad (c)-26$$

The average value of $K_3{}^1$ was found to be 0.444 ± 0.138. Then by starting with $K_2{}^1 = 0.100$ (see subsection (ii) of this Section) and $K_3{}^1 = 0.444$, equation (c)-25 was solved for Az, and from it the absorbance at 618 mμ, to cover the data used to obtain $K_3{}^1$. The uneven scatter in the experimental points about the calculated curve suggested that the values of $K_3{}^1$ and $K_2{}^1$ should be adjusted to minimize the scatter. Therefore, values of $K_3{}^1$ and $K_2{}^1$ were tried until a good fit to the experimental data was obtained. The results of a few of these many calculations for the continuous-variations plots are listed in Table 72* and

*The results given in Table 72 are for the entire curve calculated from equation (c)-24 and using $K_1{}^1 = \frac{1}{92.0} = 0.01086$.

TABLE 72

COMPARISON OF ABSORBANCES AT 618 mμ CALCULATED FOR DIFFERENT VALUES FOR K_3^1 AND K_2^1, WITH EXPERIMENTAL ABSORBANCES OF SET B

Basic data: SET B, Table 2, Appendix XXVIII

Solution Number	Initial Mole Fraction HOx	Absorbance at 618 mμ b = 1 cm K_1^1 = 0.01086					
			Calculated				
		Experimental	K_2^1 = 0.1428 K_3^1 = 0.300	K_2^1 = 0.100 K_3^1 = 0.444	K_2^1 = 0.1428 K_3^1 = 0.222	K_2^1 = 0.1428 K_3^1 = 0.3333	K_2^1 = 0.100 K_3^1 = 0.300
JZB - 1	0	0	0	0	0	0	0
2	0.050	0.082	0.082	0.103	0.070	0.091	0.082
3	0.101	0.159	0.165	0.205	0.137	0.180	0.165
4	0.149	0.216	0.246	0.308	0.205	0.267	0.246
5	0.200	0.325	0.328	0.408	0.274	0.353	0.328
6	0.250	0.400	0.407	0.511	0.340	0.437	0.407
7	0.300	0.511	0.491	0.591	0.411	0.506	0.484
8	0.350	0.524	0.543	0.660	0.461	0.558	0.533
9	0.400	0.585	0.585	0.706	0.515	0.600	0.577
10	0.450	0.612	0.618	0.736	0.552	0.630	0.607
11	0.500	0.640	0.640	0.755	0.575	0.649	0.631
12	0.550	0.652	0.652	0.756	0.589	0.660	0.642
13	0.600	0.654	0.656	0.743	0.593	0.664	0.645
14	0.650	0.646	0.650	0.706	0.595	0.658	0.643
15	0.700	0.639	0.637	0.667	0.594	0.646	0.625
16	0.750	0.607	0.607	0.618	0.590	0.610	0.597
17	0.801	0.549	0.559	0.535	0.559	0.559	0.548
18	0.825	0.520	0.525	-	-	-	-
19	0.850	0.488	0.488	0.435	0.456	0.488	0.444
20	0.875	0.445	0.445	-	-	-	-
21	0.900	0.399	0.353	0.291	0.318	0.353	0.306
22	0.926	0.273	0.265	-	-	-	-
23	0.951	0.156	0.173	0.145	0.162	0.173	0.154
24	0.975	0.106	0.090	-	-	-	-
25	1.000	0	0	0	0	0	0

shown graphically in Figure 61.

The final values of K_2^1 and K_3^1 were 0.143 and 0.30 respectively. The solid line in Figure 62 was obtained with these values, and it agreed well with the experimental points also shown in the Figure.

The continuous-variations plots obtained when other values of K_2^1 and K_3^1 were used, differed significantly from the experimental plot. Therefore, it may be concluded that $K_2 = 7.0$ and $K_3 = 3.33$. Using the reciprocals of these values and $K_1 = 0.01086$, the equilibrium concentrations of each species present in solution were calculated from equations (c)-10 to (c)-13 and are listed in Appendix XXVIII, Table 5. They will be used later to calculate the continuous-variation plots for 505 and 450 mμ.

With $K_1 = 92.0$, $K_2 = 7.0$ and $K_3 = 3.33$, the continuous-variation plot for SET A was recalculated using equation (c)-20. The roots of the equations were obtained with the use of a conventional computer program for solving fourth-order equations by the modified Downhill-Newton method (120). There was only one positive, real root of equation (c)-20; it was used to calculate the absorbance from equation (c)-9. The calculated absorbances* are compared with the experimental absorbances in Table 73 and in Figure 63.

*The calculated equilibrium concentrations (from equations (c)-10 to (c)-13) of each species present in the solutions are in Appendix XXVIII, Table 6.

FIGURE 61

COMPARISON OF CALCULATED CONTINUOUS-VARIATIONS PLOTS AT 618 mμ USING DIFFERENT COMBINATIONS OF K_2^1 AND K_3^1 FOR THE REACTION OF INDIUM DITHIZONATE WITH OXINE IN BENZENE AT 25°C

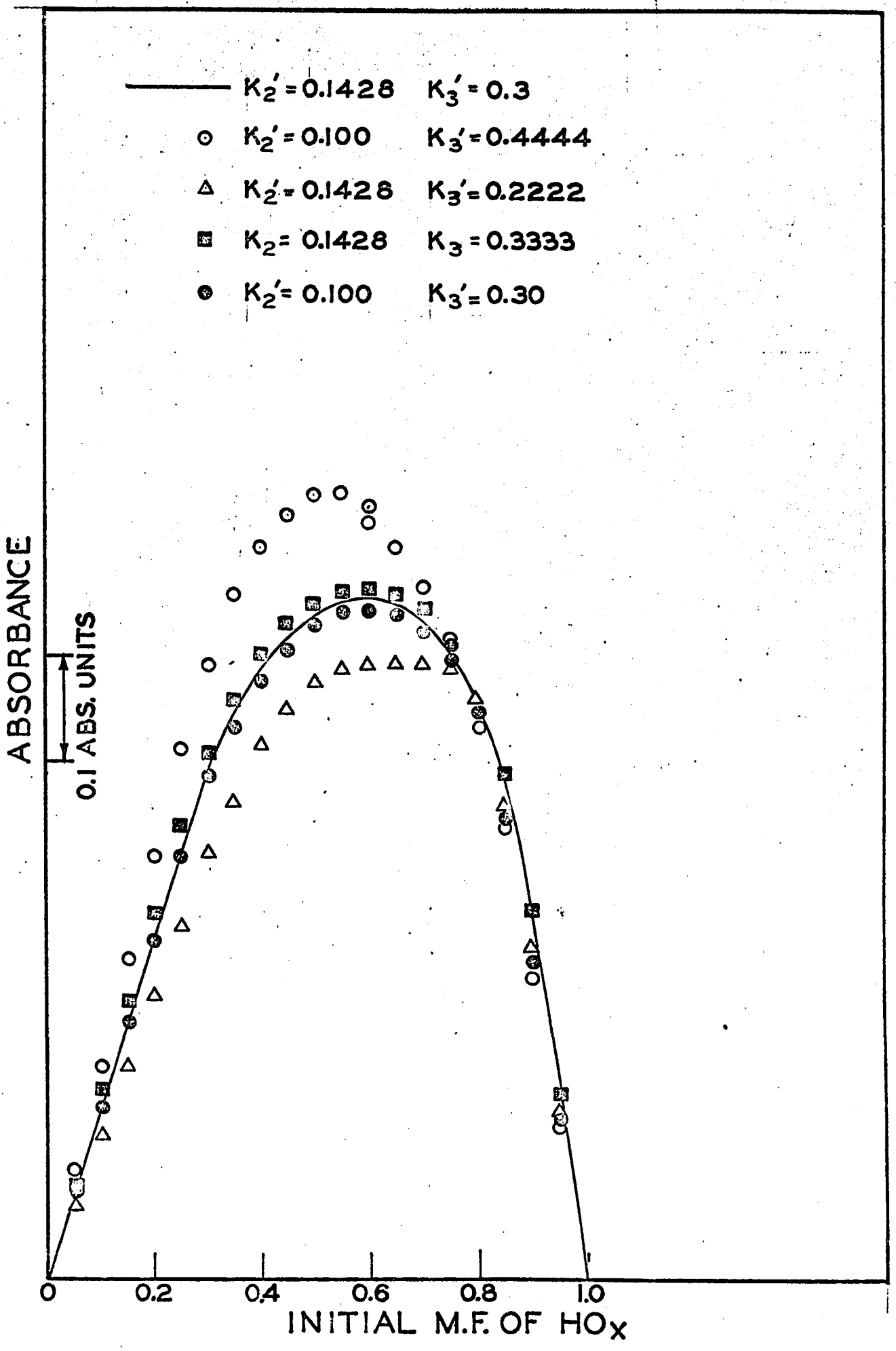

$K_2' = 0.1428$ $K_3' = 0.3$
$K_2' = 0.100$ $K_3' = 0.4444$
$K_2' = 0.1428$ $K_3' = 0.2222$
$K_2 = 0.1428$ $K_3 = 0.3333$
$K_2' = 0.100$ $K_3' = 0.30$
ABSORBANCE
0.1 ABS. UNITS
0
0.2
0.4
0.6
0.8
1.0
INITIAL M.F. OF HO_X

FIGURE 62

COMPARISON OF CALCULATED AND EXPERIMENTAL CONTINUOUS-VARIATIONS PLOTS AT 618 mμ FOR THE REACTION OF INDIUM DITHIZONATE WITH OXINE IN BENZENE AT 25°C

Basic data: SET B, Table 2, Appendix XXVIII

Note: The calculated curve was obtained with the value of $K_2^1 = 0.143$, $K_3^1 = 0.30$ and $K_1^1 = 0.01086$

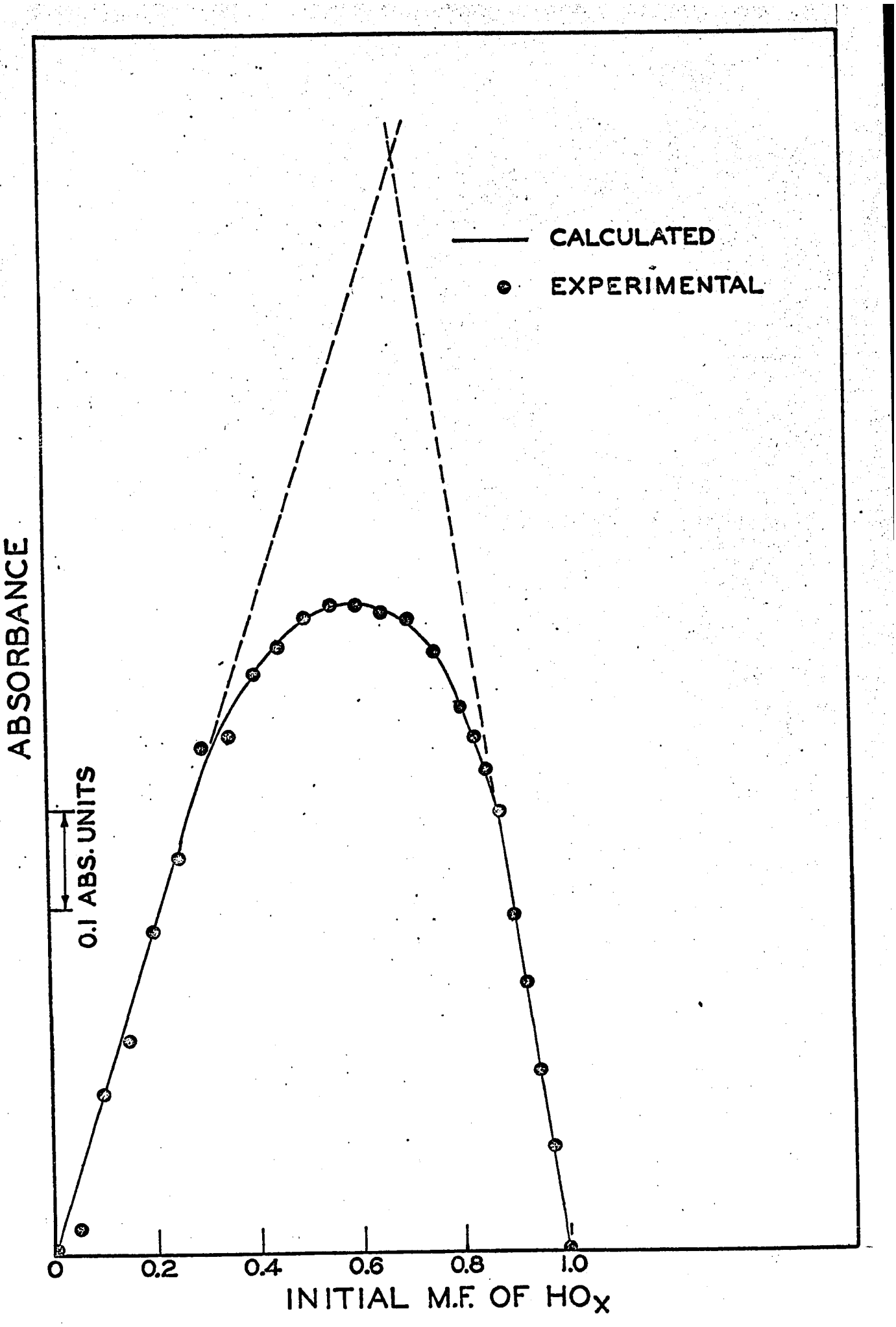

CALCULATED
EXPERIMENTAL
ABSORBANCE
0.1 ABS. UNITS
0
0.2
0.4
0.6
0.8
1.0
INITIAL M.F. OF HOx

TABLE 73

COMPARISON OF EXPERIMENTAL AND CALCULATED ABSORBANCES OF THE CONTINUOUS VARIATION SOLUTIONS FOR THE REACTION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 25°C

Initial Mole Fraction of H_2Dz	Absorbance b = 5 cm											
	SET A				SET C				SET D			
	618 mμ		505 mμ		618 mμ		505 mμ		618 mμ		505 mμ	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0	0	0	0	0	0	0	0	0	0	0	0	0
0.050	0.070	0.033	0.014	0.045	-	0.0012	0.074	0.090	0.008	0.019	0.048	0.065
0.100	0.012	0.070	0.100	0.085	-	0.003	0.172	0.174	0.042	0.038	0.084	0.132
0.150	0.118	0.111	0.136	0.130	-	0.0052	0.252	0.259	0.046	0.057	0.190	0.199
0.200	0.148	0.157	0.152	0.175	-	0.0080	0.345	0.345	0.064	0.075	0.262	0.265
0.249	0.168	0.208	0.215	0.215	0.010	0.012	0.437	0.428	0.98	0.096	0.340	0.333
0.300	0.286	0.264	0.250	0.250	0.012	0.016	0.532	0.514	0.134	0.122	0.398	0.398
0.350	0.340	0.327	0.282	0.285	0.016	0.026	0.614	0.598	0.142	0.154	0.454	0.453
0.399	0.410	0.397	0.322	0.315	0.026	0.032	0.690	0.686	0.206	0.197	0.487	0.501
0.450	0.470	0.473	0.330	0.340	0.048	0.047	0.765	0.760	0.266	0.248	0.546	0.540
0.500	0.566	0.556	0.360	0.360	0.062	0.070	0.822	0.826	0.296	0.311	0.564	0.567
0.549	0.655	0.646	0.370	0.375	0.105	0.102	0.847	0.874	0.398	0.380	0.592	0.587
0.600	0.735	0.744	0.380	0.385	0.155	0.156	0.898	0.898	0.432	0.465	0.586	0.598
0.651	0.832	0.822	0.395	0.390	0.178	0.244	0.885	0.885	0.576	0.576	0.602	0.603
0.699	0.930	0.930	0.394	0.395	0.360	0.365	0.844	0.844	0.690	0.690	0.592	0.594
0.751	1.044	1.043	0.388	0.390	0.524	0.526	0.780	0.780	0.842	0.828	0.560	0.572
0.799	1.148	1.161	0.378	0.380	0.758	0.758	0.706	0.706	0.924	0.975	0.550	0.535
0.850	1.250	1.266	0.364	0.360	0.983	0.988	0.596	0.596	1.132	1.132	0.472	0.478
0.901	1.392	1.392	0.329	0.329	1.150	1.225	0.468	0.482	1.302	1.302	0.402	0.402
0.949	1.520	1.535	0.283	0.292	1.463	1.460	0.367	0.367	1.480	1.490	0.332	0.327
1.000	1.685	1.682	0.246	0.252	1.688	1.682	0.252	0.252	1.672	1.682	0.278	0.252

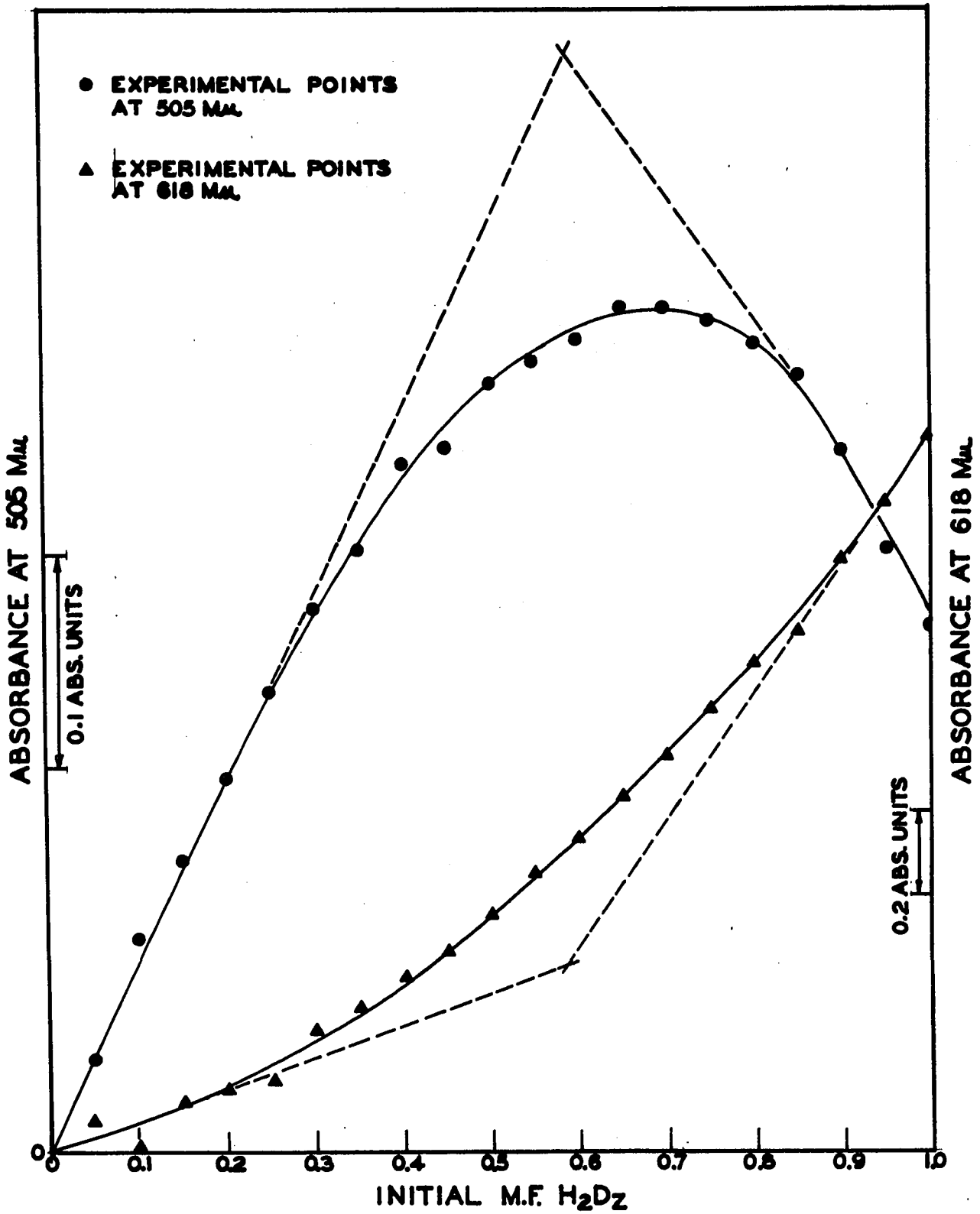
FIGURE 63

COMPARISON OF CALCULATED AND EXPERIMENTAL CONTINUOUS-VARIATIONS PLOTS FOR THE REACTION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 25°C

Basic data: SET A, Table 1, Appendix XXVIII

The solid lines are the calculated curves using

$K_1 = 92.0$, $K_2 = 7.0$ and $K_3 = 3.33$.


EXPERIMENTAL POINTS AT 505 Mμ
EXPERIMENTAL POINTS AT 618 Mμ
ABSORBANCE AT 505 Mμ
0.1 ABS. UNITS
ABSORBANCE AT 618 Mμ
0.2 ABS. UNITS
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
INITIAL M.F. H_2D_2

(iv) Confirmation of K_1, K_2 and K_3 from the data of SETS C and D

The absorbances at 618 mμ were calculated for each solution in SETS C and D, from the positive, real root of equation (c)-20 as was done with SET A. The calculated equilibrium concentrations of the species present in solution are in Tables 7 and 8 of Appendix XXVIII. The experimental and calculated absorbances at 618 mμ are compared in Table 73 and in Figures 64 for SET C, and in Figure 65 for SET D. In both cases the excellent fits with the experimental data confirmed the values of K_1, K_2 and K_3.

To firmly establish the value of K_1, the absorbance curve at 618 mμ of SET D, for mole fractions of H_2Dz from 0.1 to 0.55 (JID-3 to JID-12), was calculated for K_1 = 75, 85, 95, 98 and 108 in turn (7.0 and 3.33 were used for K_2 and K_3 in each case). The resulting curves were compared both with those obtained for K_1 = 92, and with the experimental curve.

The results are given in Table 74 and shown graphically in Figure 66.

A regression analysis was performed on the data in Table 74 to show that the value of K_1 = 92 was the best value as follows:

(1) The equations of each of the curves shown in Figure 66 were obtained by a conventional curve-fitting calculation (121). The best fit was obtained for the general

FIGURE 64

COMPARISON OF CALCULATED AND EXPERIMENTAL CONTINUOUS-VARIATIONS PLOTS FOR THE REACTION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 25°C

Basic data: SET C, Table 3, Appendix XXVIII

Path length = 5 cm

Note: The solid lines are the calculated curves for $K_1 = 92.0$, $K_2 = 7.0$ and $K_3 = 3.33$.

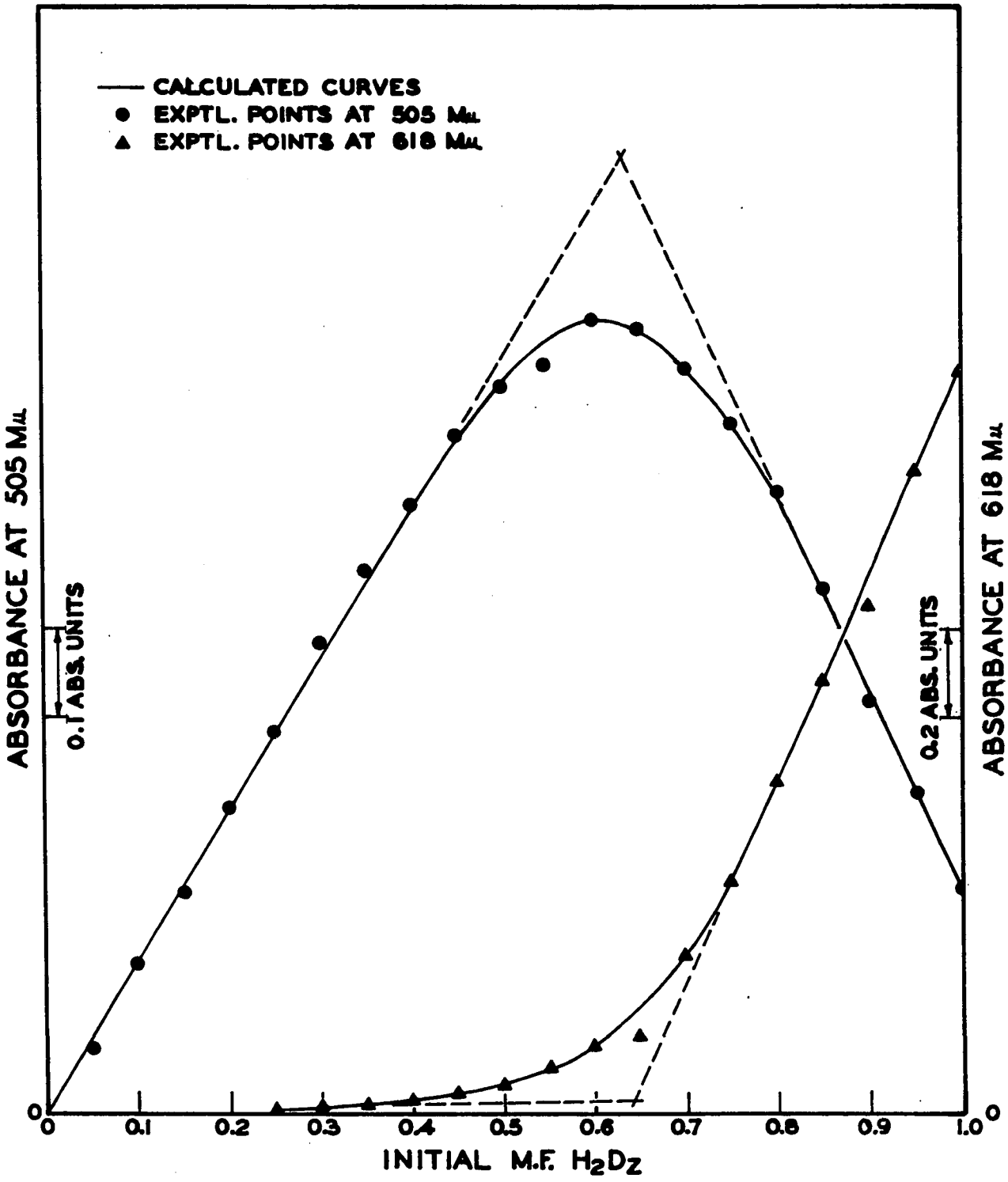

CALCULATED CURVES
EXPTL. POINTS AT 505 Mμ
EXPTL. POINTS AT 618 Mμ
ABSORBANCE AT 505 Mμ
0.1 ABS. UNITS
ABSORBANCE AT 618 Mμ
0.2 ABS. UNITS
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
INITIAL M.F. H_2D_2

FIGURE 65

COMPARISON OF CALCULATED AND EXPERIMENTAL CONTINUOUS-VARIATIONS PLOTS FOR THE REACTION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 25°C

Basic data: SET D, Table 4, Appendix XXVIII

Path length = 5 cm

Note: The solid lines are the calculated curves for $K_1 = 92.0$, $K_2 = 7.0$ and $K_3 = 3.33$.

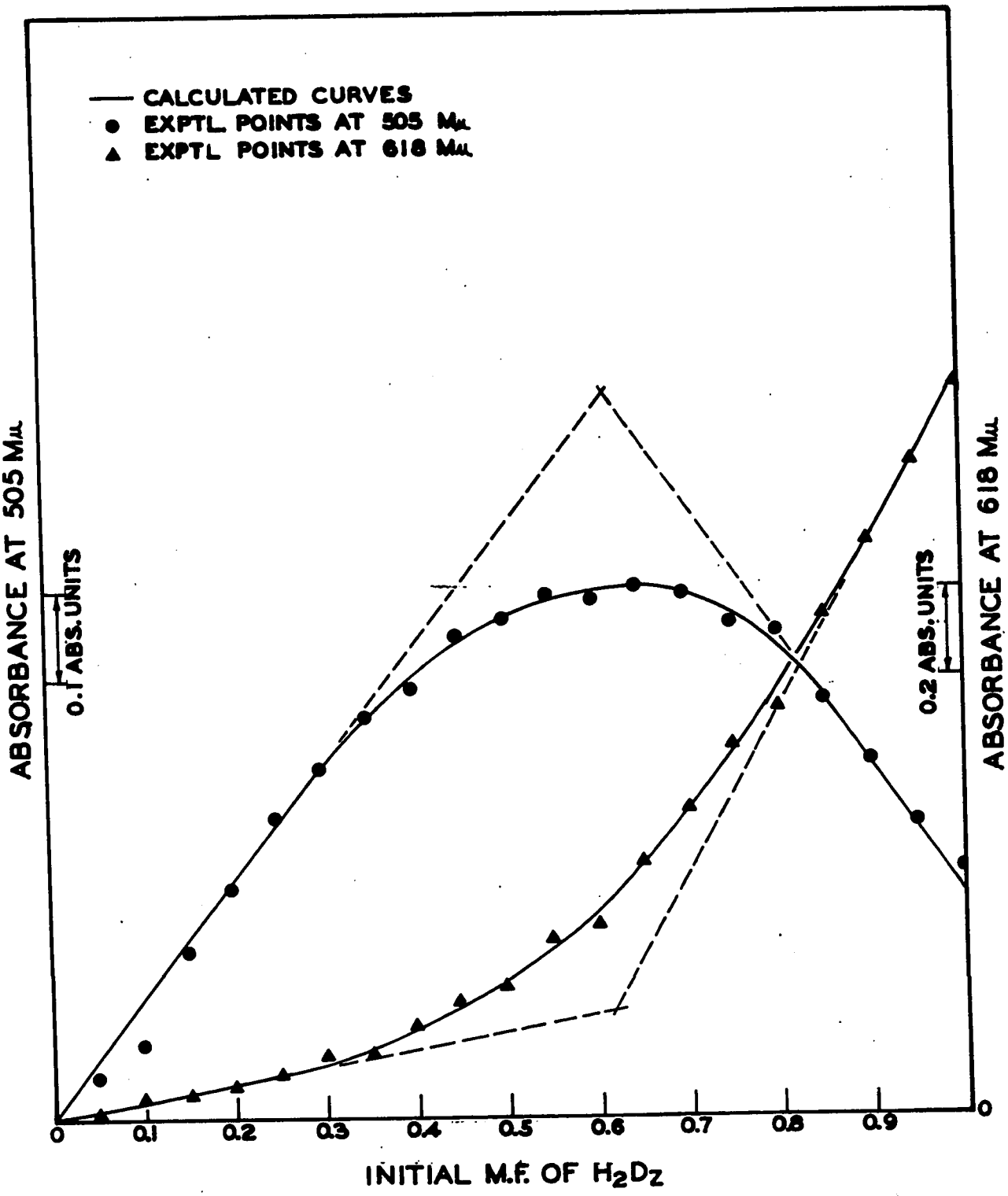

CALCULATED CURVES
EXPTL. POINTS AT 505 Mμ
EXPTL. POINTS AT 618 Mμ
ABSORBANCE AT 505 Mμ
0.1 ABS. UNITS
ABSORBANCE AT 618 Mμ
0.2 ABS. UNITS
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
0
INITIAL M.F. OF H_2D_2

TABLE 74

EXPERIMENTAL ABSORBANCES, AND ABSORBANCES CALCULATED FOR DIFFERENT VALUES OF K_1, AT 618 mμ

Basic Data: SET D, Table 4, Appendix XXVIII

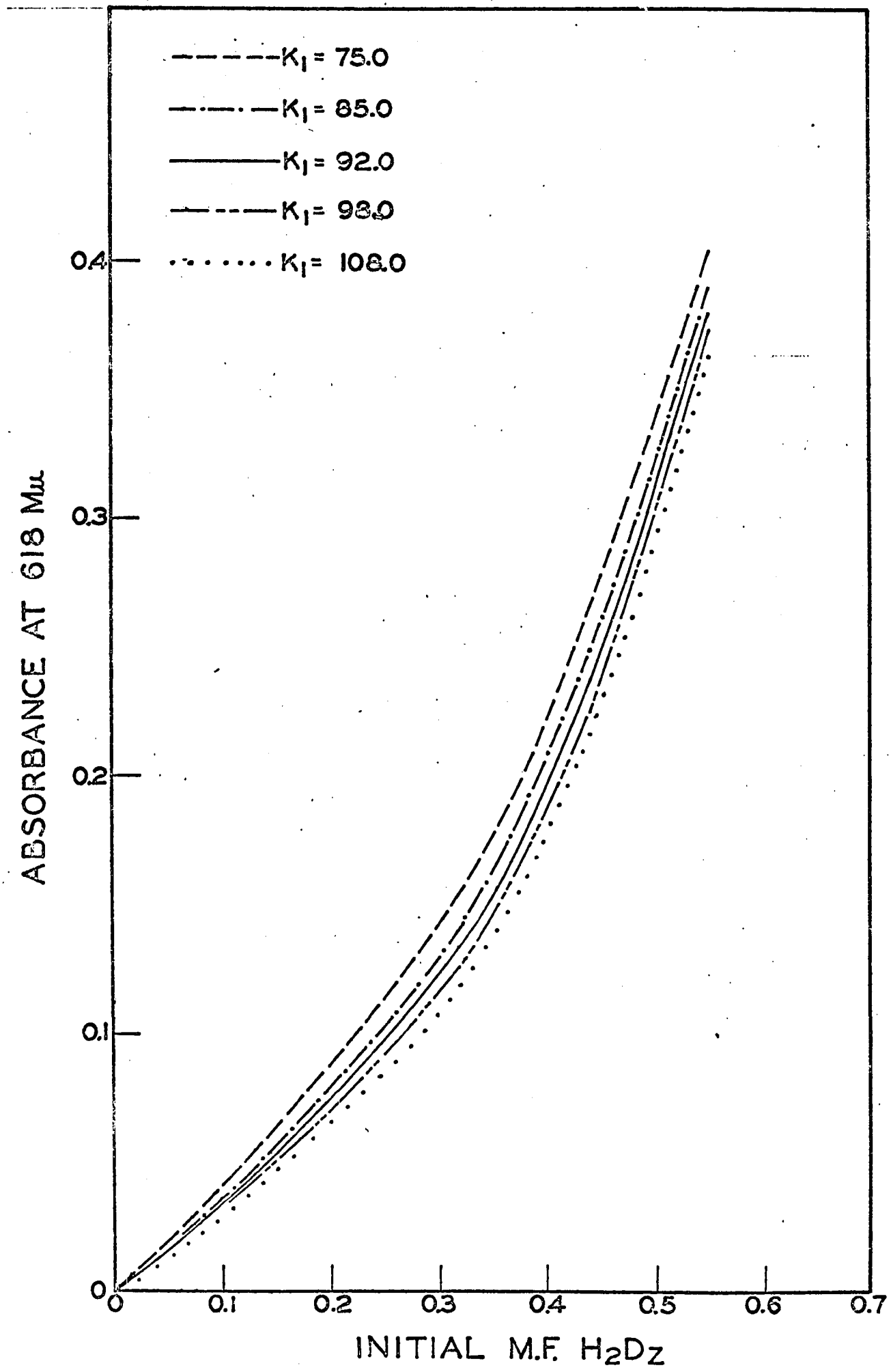
$K_2 = 7.0$; $K_3 = 3.33$

Solution Number	Initial Mole Fraction H_2Dz	Absorbance b = 5 cm							
		K_1							
		75.0	85.0	89.0	92.0	95.0	98.0	108.0	Experimental
JID - 3	0.100	0.042	0.038	0.037	0.038	0.035	0.034	0.031	0.042
4	0.150	0.063	0.057	0.055	0.057	0.052	0.051	0.047	0.046
5	0.200	0.089	0.081	0.078	0.075	0.074	0.072	0.067	0.064
6	0.249	0.112	0.102	0.098	0.096	0.093	0.091	0.084	0.098
7	0.300	0.142	0.130	0.125	0.122	0.119	0.116	0.108	0.134
8	0.350	0.177	0.162	0.157	0.154	0.150	0.147	0.136	0.142
9	0.399	0.222	0.207	0.201	0.197	0.193	0.189	0.178	0.206
10	0.450	0.275	0.259	0.253	0.248	0.244	0.241	0.229	0.266
11	0.500	0.337	0.321	0.315	0.311	0.307	0.304	0.292	0.296
12	0.549	0.404	0.389	0.384	0.380	0.377	0.374	0.363	0.398

FIGURE 66

SECTIONS OF CONTINUOUS-VARIATIONS PLOTS AT 618 mμ, USING DIFFERENT VALUES OF K_1, FOR THE REACTION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 25°C

Data: Table 74


K_1 = 75.0
K_1 = 85.0
K_1 = 92.0
K_1 = 98.0
K_1 = 108.0
ABSORBANCE AT 618 Mμ
0
0.1
0.2
0.3
0.4
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
INITIAL M.F. H_2Dz

equation

$$Y = A_nX + B_nX^2 + C_nX^3 + D_nX^4 + EX^5 \qquad (c)\text{-}27$$

where Y = absorbance at 618 mμ

X = mole fraction of H_2Dz

n refers to the particular equation; let (1) refer to the equation describing the experimental curve, (2) that for $K_1 = 92$, (3) that for $K_1 = 85$ and (4) that for $K_1 = 98$.

The equations for $K_1 = 92, 85, 98$ were of most interest and were further analyzed. The coefficients of these equations are given in Table 75.

(2) The equation of the regression curve for the experimental data was obtained from a conventional, multiple curvilinear regression analysis (121) using equation (c)-27 as the model. The least-square coefficients are listed in Table 75.

(3) The coefficient of each variate (X to X^5) obtained for (1) was compared with the corresponding coefficients of (2), (3) and (4) by a regression analysis (121). The coefficients of X, X^2 and X^3 of (1) were thereby found not to differ significantly from those of (2) at the 95% confidence level; the coefficients were different for X^4 and X^5, indicating that perhaps the model for (1) should have been extended to higher orders of X. However, all the coefficients of (1) were significantly different from those obtained for

TABLE 75

COEFFICIENTS OF THE EQUATIONS OF THE CURVES OBTAINED BY PLOTTING ABSORBANCE AT 618 mμ VERSUS INITIAL MOLE FRACTION

General equation: (c)-27, page
Data: SET D, Table 4, Appendix XXVIII, Table 73, page

Variate (Mole Fraction H_2Dz)	Coefficients			
	Experimental	$K_1 = 92$	$K_1 = 85$	$K_1 = 98$
AX	0.319	0.347	0.273	0.233
BX^2	0.521	0.513	1.819	1.852
CX^3	- 5.334	- 5.241	-10.471	-10.906
DX^4	11.494	13.314	26.492	27.500
EX^5	-10.742	-12.693	-19.740	-20.191

(3) and (4). This fact was sufficient to establish the validity of the value of K_1 being 92. A sample calculation of the comparison of two coefficients is given in Appendix XXVIII, page 144a.

(4) The 95% confidence limits of the regression curve of (1) were calculated. They are plotted as the broken lines in Figure 67, where the solid line is the regression curve itself. The curves obtained for (3) and (4) were found to lie on the positive and negative edges, respectively, of this region.

The above statistical analysis showed that the best fit to the experimental data was obtained with $K_1 = 92.0$, but that K_1 could have a range from 85 to 98 with a 5% risk of it being outside this range.

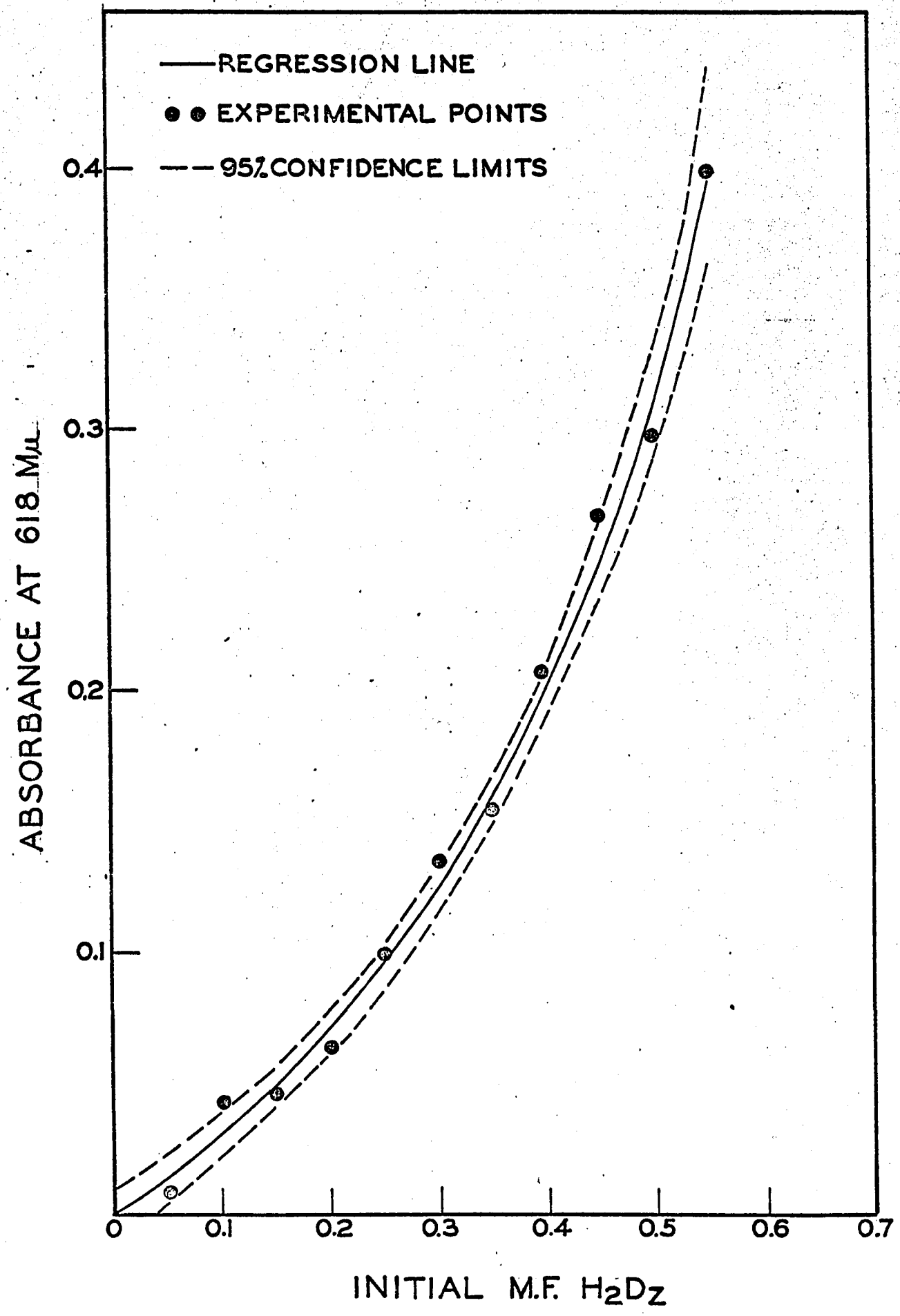
(iv) Calculation of the molar absorptivities of the mixed chelates, $InOx_2(HDz)$ and $InOx(HDz)_2$

Having obtained reliable values for K_1, K_2 and K_3 it was now possible to calculate the absorptivities of the mixed chelates, $InOx_2(HDz)$ and $InOx(HDz)_2$. The data from separate sets of ratio solutions, in which indium oxinate was reacted with dithizone, were used for these calculations. In one set of eleven ratio solutions, hereinafter referred to as SET RI, there was no initial amount of free oxine in the solutions. In the other set of eleven solutions, hereinafter referred to as SET RIH, there was a fiftyfold excess of free oxine with respect to the initial molar concentration

FIGURE 67

EXPERIMENTAL POINTS, REGRESSION LINE AND 95% CONFIDENCE LIMITS FOR PART OF THE CONTINUOUS-VARIATIONS PLOT OF SET D

Basic data: SET D, Table 4, Appendix XXVIII
solutions JID-1 to JID-12 only


REGRESSION LINE
EXPERIMENTAL POINTS
95% CONFIDENCE LIMITS
ABSORBANCE AT 618 Mμ
0.4
0.3
0.2
0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
INITIAL M.F. H2Dz

of indium oxinate present in the solutions. These two sets provided a useful distribution of mixed-chelate concentrations, at equilibrium. Thus, in SET RI, $InOx(HDz)_2$ predominated and in SET RIH, $InOx_2(HDz)$ predominated. The analytical data for these two sets are in Table 9 of Appendix XXVIII.

From the absorbance at 618 mμ the equilibrium concentration of dithizone was calculated for each solution, by using equation (c)-9. Then the equilibrium concentration of oxine was calculated from equation (c)-14. By using equation (c)-10 the equilibrium concentration of indium oxinate was calculated for $K_1 = 92$, $K_2 = 7.0$, $K_3 = 3.33$ in turn. Then from equations (c)-11 to (c)-13 the equilibrium concentrations of all other species were calculated. The resulting data are in Tables 10 and 11 of Appendix XXVIII.

The absorbance of each solution in SETS RI and RIH was measured at 5 mμ intervals, from 600 to 400 mμ. Beer's law equations were set up for each solution. In the general equation

$$A_{p,\lambda_i} = \{a_{\lambda_{i,1}}[In(HDz)_2] + a_{\lambda_{i,2}}[InOx(HDz)_2] + a_{\lambda_{i,3}}[InOx_2(HDz)] + a_{\lambda_{i,4}}[InOx_3] + a_{\lambda_{i,5}}[H_2Dz]\}_p \qquad (c)\text{-}28$$

p is the solution number; the path length is 1 cm; $a_{\lambda_{i,1}}$, $a_{\lambda_{i,4}}$ and $a_{\lambda_{i,5}}$ were known (see Table 4, Appendix XX, Table 3, Appendix XXII and Table 1, Appendix XVIII, respectively) at each wavelength. Since the equilibrium concentrations were

known, the quantities $a_{\lambda_{i,1}}[In(HDz)_2]$, $a_{\lambda_{i,4}}[InOx_3]$ and $a_{\lambda_{i,5}}[H_2Dz]$ were transferred to the left-hand side of the equation and subtracted from $A_{n,\lambda}/b$. There were then 22 equations of the form

$$A^*_{p,\lambda_i} = \{ a_{\lambda_{i,2}}[InOx(HDz)_2] + a_{\lambda_{i,3}}[InOx_2(HDz)] \}_p \qquad (c)\text{-}28$$

where

$$A^*_{p,\lambda_i} = A_{p,\lambda_i} - \{ a_{\lambda_{i,1}}[In(HDz)_3] - a_{\lambda_{i,4}}[InOx_3] - a_{\lambda_{i,5}}[H_2Dz] \}_p$$

This system of equations was then solved* for $a_{\lambda_{i,2}}$ and $a_{\lambda_{i,3}}$ at each wavelength, by a multiple regression (121). An example of one of the system of equations, and a sample calculation is shown in Table 76. Tables of the values thus found for the absorptivities of $InOx(HDz)_2$ and $InOx_2(HDz)$ from 600 to 400 mμ, in 10 mμ intervals, together with the variance and standard deviations are in Tables 13 and 14 of Appendix XXVIII, respectively; and the absorptivity-versus-wavelength curves are shown as solid curves in Figure 68. The dashed curves also included in the Figure represent two-thirds and one-third of the absorptivity of indium dithizonate. A comparison of these various curves shows that absorptivity

*The necessary absorbance data for the above calculation of a_{2_λ} and a_{3_λ} were read from the original spectrometer pen recordings. These bulky charts are not reproduced here. Instead, absorbances at 25-mμ intervals have been read from them, and they are tabulated for illustrative purposes, in Table 12, Appendix XXVIII.

TABLE 76

CALCULATION OF MOLAR ABSORPTIVITIES OF $InOx(HDz)_2$ AND $InOx_2(HDz)$ AT 510 mμ AND 25°C, BY MULTIPLE REGRESSION FROM RATIO-SOLUTION DATA

Basic data: SETS RI and RIH, Tables 9 and 12, Appendix XXVIII

System of Equations for λ = 510 mμ

Solution Number

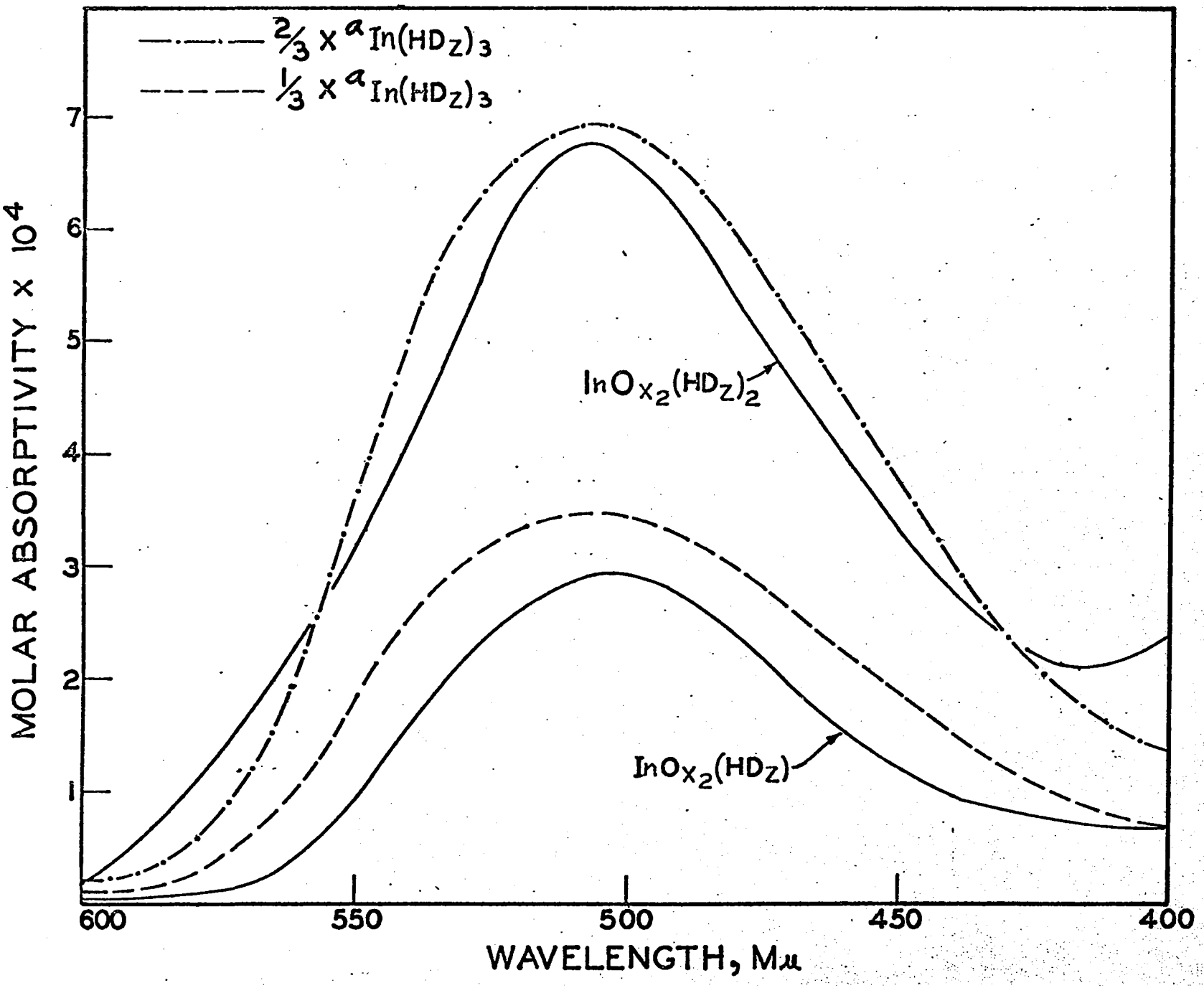
RI - 1	$7.722 \times 10^{-9} a_2^* + 1.023 \times 10^{-6} a_3^* = 2.968 \times 10^{-2}$	
2	$3.297 \times 10^{-8} a_2 + 2.008 \times 10^{-6} a_3 = 5.945 \times 10^{-2}$	
3	$9.939 \times 10^{-8} a_2 + 3.235 \times 10^{-6} a_3 = 9.887 \times 10^{-2}$	
4	$2.532 \times 10^{-7} a_2 + 4.634 \times 10^{-6} a_3 = 0.1490$	
5	$2.680 \times 10^{-6} a_2 + 4.562 \times 10^{-7} a_3 = 0.1928$	
6	$1.173 \times 10^{-6} a_2 + 6.977 \times 10^{-8} a_3 = 8.074 \times 10^{-2}$	
7	$5.363 \times 10^{-7} a_2 + 1.357 \times 10^{-8} a_3 = 3.640 \times 10^{-2}$	
8	$3.469 \times 10^{-7} a_2 + 5.569 \times 10^{-9} a_3 = 0.4095$	
9	$2.562 \times 10^{-7} a_2 + 3.010 \times 10^{-9} a_3 = 1.727 \times 10^{-2}$	
10	$2.030 \times 10^{-7} a_2 + 1.881 \times 10^{-9} a_3 = 1.370 \times 10^{-2}$	
11	$1.682 \times 10^{-7} a_2 + 1.286 \times 10^{-9} a_3 = 1.134 \times 10^{-2}$	
RIH - 1	$3.233 \times 10^{-9} a_2 + 6.734 \times 10^{-7} a_3 = 1.941 \times 10^{-2}$	
2	$1.299 \times 10^{-8} a_2 + 1.308 \times 10^{-6} a_3 = 3.816 \times 10^{-2}$	
3	$3.589 \times 10^{-8} a_2 + 2.086 \times 10^{-6} a_3 = 6.186 \times 10^{-2}$	
4	$8.128 \times 10^{-8} a_2 + 2.976 \times 10^{-6} a_3 = 9.027 \times 10^{-2}$	
5	$2.973 \times 10^{-6} a_2 + 6.030 \times 10^{-6} a_3 = 0.3713$	
6	$4.256 \times 10^{-6} a_2 + 3.889 \times 10^{-6} a_3 = 0.3964$	
7	$4.158 \times 10^{-6} a_2 + 1.770 \times 10^{-6} a_3 = 0.3294$	
8	$3.533 \times 10^{-6} a_2 + 9.732 \times 10^{-7} a_3 = 0.2648$	
9	$2.995 \times 10^{-6} a_2 + 6.083 \times 10^{-7} a_3 = 0.2183$	
10	$2.578 \times 10^{-6} a_2 + 4.142 \times 10^{-7} a_3 = 0.1848$	
11	$2.255 \times 10^{-6} a_2 + 2.996 \times 10^{-7} a_3 = 0.1598$	

Normal Equations		Absorptivity* 510 m	S^2	S	D.F.
$8.660 \times 10^{-11} a_2 + 5.206 \times 10^{-11} a_3 = 7.429 \times 10^{-6}$	a_2	6.72×10^4	1.04×10^7	0.32×10^4	20
$5.206 \times 10^{-11} a_2 + 1.088 \times 10^{-11} a_3 = 6.596 \times 10^{-6}$	a_3	2.85×10^4	8.27×10^6	0.29×10^4	20

*a_2 is the absorptivity of $InOx(HDz)_2$, a_3 is the absorptivity of $InOx_2(HDz)$.

FIGURE 68

MOLAR ABSORPTIVITIES OF $InOx_2(HDz)$ AND $InOx(HDz)_2$
AT 25°C IN BENZENE VERSUS WAVELENGTH


⅔ x a In(HDZ)3
⅓ x a In(HDZ)3
InOX2(HDZ)2
InOX2(HDZ)
MOLAR ABSORPTIVITY x 10⁴
1
2
3
4
5
6
7
600
550
500
450
400
WAVELENGTH, Mμ

per mole of dithizone ligand is not much influenced by the oxinate ligand.

(v) Confirmation of the absorptivities of $InOx(HDz)_2$ and $InOx_2(HDz)$

The correctness of the values calculated for the absorptivities of $InOx(HDz)_2$ and $InOx_2(HDz)$ was confirmed as follows: The continuous-variations plots for 505 mμ SETS A, B, C, and D were calculated by using the equilibrium-concentration data in Tables 6, 5, 7 and 8 of Appendix XXVIII respectively, together with the relevant absorptivities. The continuous-variations plot for 450 mμ of SET B was also calculated. The total absorbance for each point on the curves was obtained from equation (c)-8. These calculated absorbances are compared with the experimental absorbances in Table 73 (page 347) for SETS A, C, and D, and in Table 77 for SET B. The comparisons for SETS A, C, and D are shown graphically in Figure 63-65 respectively, and in Figure 69 for SET B. Agreement between calculated and experimental values was good in all cases, which confirmed the values found for the absorptivities of $InOx(HDz)_2$ and $InOx_2(HDz)$.

(vi) Calculation of the theoretical titration graph for the titration of indium oxinate with dithizone

The analytical data for the titration of indium oxinate with dithizone in benzene at 25°C, (i) when there was no initial free oxine and (ii) when there was a fiftyfold excess with respect to the initial concentration of indium oxinate in the titration solution are in Table 78.

TABLE 77

COMPARISON OF CALCULATED AND EXPERIMENTAL ABSORBANCES FOR SOLUTIONS OF SET B

Solution Number	Initial Mole Fraction Hox	Absorbance b = 1 cm					
		618 mμ		505 mμ		450 mμ	
		Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
JZB - 1	0	0	0	10.34	10.39	5.65	5.61
2	0.050	0.082	0.082	5.46	8.75	3.75	4.68
3	0.101	0.159	0.165	8.25	8.32	4.44	4.49
4	0.149	0.216	0.246	7.65	7.90	4.14	4.30
5	0.200	0.325	0.328	7.42	7.43	4.08	4.09
6	0.250	0.400	0.407	6.93	6.96	3.85	3.87
7	0.300	0.511	0.491	6.58	6.52	3.72	3.68
8	0.350	0.524	0.543	5.95	6.00	3.38	3.42
9	0.400	0.585	0.585	5.48	5.48	3.15	3.15
10	0.450	0.612	0.618	4.94	4.95	2.87	2.88
11	0.500	0.640	0.640	4.44	4.44	2.62	2.62
12	0.550	0.652	0.652	3.91	3.91	2.34	2.34
13	0.600	0.654	0.656	3.40	3.41	2.07	2.07
14	0.650	0.646	0.650	2.91	2.92	1.802	1.808
15	0.700	0.639	0.637	2.43	2.43	1.546	1.543
16	0.750	0.607	0.607	1.96	1.96	1.281	1.281
17	0.801	0.549	0.559	1.488	1.489	0.999	1.011
18	0.825	0.520	0.525	1.259	1.264	0.872	0.877
19	0.850	0.488	0.488	1.048	1.048	0.747	0.747
20	0.875	0.445	0.445	0.839	0.839	0.620	0.620
21	0.900	0.399	0.353	0.642	0.603	0.498	0.456
22	0.926	0.273	0.265	0.395	0.389	0.314	0.307
23	0.951	0.156	0.173	0.202	0.214	0.165	0.179
24	0.975	0.106	0.090	0.089	0.081	0.089	0.078
25	1.000	0	0	0	0	0	0

FIGURE 69

COMPARISON OF EXPERIMENTAL AND CALCULATED CONTINUOUS-VARIATIONS PLOTS FOR THE REACTION OF INDIUM DITHIZONATE WITH OXINE IN BENZENE AT 25°C

(a) At 505 mμ; path length: 0.1 cm.

(b) At 450 mμ; path length: 1.0 cm.

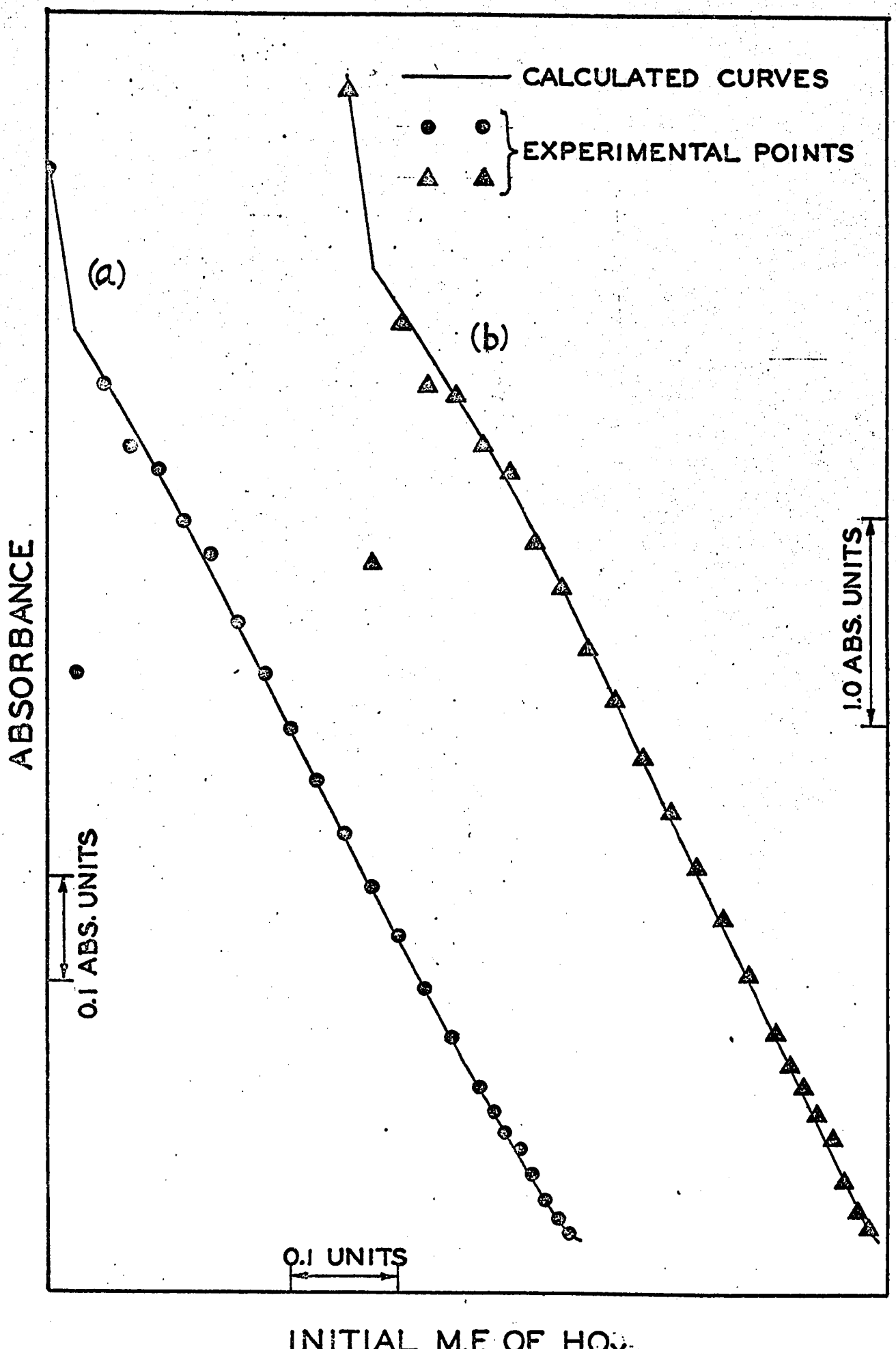

CALCULATED CURVES
EXPERIMENTAL POINTS
(a)
(b)
ABSORBANCE
1.0 ABS. UNITS
0.1 ABS. UNITS
0.1 UNITS
INITIAL M.F. OF HOx

TABLE 78

ANALYTICAL DATA AND COMPARISON OF CALCULATED AND EXPERIMENTAL ABSORBANCES FOR THE TITRATION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 25°C

Molarity of H_2Dz solution in benzene = 1.042×10^{-3} M
Molarity of stock $InOx_3$ solution in benzene = 1.771×10^{-5} M
Initial Molarity of free oxine in titration solution = 8.915×10^{-5} M
Aliquot $InOx_3$ taken = 5 ML
Initial Volume of solution = 50 ± 0.2 ML

	Absorbance b = 5 cm							
	A[1]				B[2]			
ML	618 mμ		505 mμ		618 mμ		505 mμ	
H_2Dz	Exp.[3]	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0	0	0	0	0	0	0	0	0
0.02	0.001	0	0.095	0.091	0.019	0.023	0.039	0.035
0.04	0.003	0.0015	0.186	0.192	0.043	0.051	0.070	0.071
0.06	0.010	0.0061	0.299	0.290	0.083	0.086	0.110	0.107
0.08	0.020	0.020	0.375	0.382	0.127	0.126	0.130	0.142
0.10	0.037	0.039	0.482	0.482	0.181	0.172	0.165	0.175
0.12	0.063	0.063	0.556	0.555	0.215	0.222	0.200	0.207
0.14	0.101	0.092	0.616	0.613	0.274	0.276	0.231	0.236
0.16	0.125	0.126	0.660	0.663	0.332	0.332	0.261	0.264
0.18	0.152	0.164	0.705	0.704	0.393	0.390	0.290	0.291
0.20	0.206	0.207	0.735	0.742	0.452	0.450	0.327	0.317
0.22	0.260	0.254	0.779	0.774	0.516	0.512	0.344	0.342
0.24	0.316	0.305	0.807	0.803	0.576	0.584	0.370	0.370
0.26	0.344	0.359	0.823	0.829	0.639	0.637	0.393	0.389
0.28	0.415	0.416	0.860	0.853	0.705	0.698	0.416	0.410
0.30	0.485	0.476	0.874	0.875	0.766	0.765	0.437	0.434

[1] Titration solution contained no initial free oxine.
[2] Titration solution contained initial free oxine approximately fiftyfold in excess with respect to the initial concentration of $InOx_3$ in the solution for titration.
[3] Experimental absorbances are the average of five replicates.

The equilibrium concentrations of dithizone were calculated for each point on the graphs; equation (c)-20 and a conventional computer program for solving fourth-order polynomials were used. The equilibrium concentrations of all other species were then calculated from equations (c)-10 - (c)-14. These are in Tables 79 and 80. The absorbance at 618 mμ for each point on the graphs was calculated from the known absorptivity and the calculated equilibrium concentrations of dithizone.

The calculated titration graphs for 618 mμ are compared with the experimental ones in Figure 70 and Table 78. The absorbance at 505 mμ for each point on the graphs was calculated from the known absorptivities, and the calculated equilibrium concentrations of all species present in the titration solutions. The calculated titration graph for 505 mμ is compared with the experimental graph in Figure 70 and Table 78.

The calculated and experimental titration graphs at 618 mμ and 505 mμ were almost identical. This agreement confirms the values for K_1, K_2 and K_3 as well as the values of the molar absorptivities of the mixed chelates $InOx(HDz)_2$ and $InOx_2(HDz)$.

(vii) Summary

The values of the equilibrium constants for the reaction of indium oxinate with dithizone were found to be:

$$K_0 = 1144,\ K_1 = 92,\ K_2 = 7.0 \text{ and } K_3 = 3.33$$

TABLE 79

CALCULATED EQUILIBRIUM CONCENTRATIONS OF SPECIES PRESENT IN SOLUTION WHEN INDIUM OXINATE WAS TITRATED WITH DITHIZONE IN BENZENE AT 25°C

$(HDz)_T$ x 10^6	Equilibrium Concentration Moles/litre x 10^6					
	$[InOx_3]$	$[InOx_2(HDz)]$	$[InOx(HDz)_2]$	$[In(HDz)_3]$	[HOx]	$[H_2Dz]$
0	1.771	0	0	0	0	0
0.417	1.354	0.4170	0	0	0.4170	0
0.834	0.8608	0.8449	0.0630	0.0022	0.8248	0.0088
1.250	0.4167	1.108	0.2242	0.0216	1.215	0.0351
1.667	0.1490	0.9950	0.5051	0.1220	1.554	0.1127
2.084	0.0688	0.7734	0.6605	0.2683	1.857	0.2266
2.501	0.0381	0.6010	0.7207	0.4112	2.135	0.3658
2.918	0.0230	0.4708	0.7335	0.5437	2.386	0.5312
3.334	0.0144	0.3697	0.7199	0.6669	2.609	0.7257
3.751	0.0095	0.2939	0.6921	0.7755	2.807	0.9444
4.168	0.0064	0.2342	0.6561	0.8743	2.9767	1.191
4.585	0.0044	0.1880	0.6166	9.9619	3.122	1.462
5.002	0.0031	0.1524	0.5768	1.039	3.246	1.755
5.418	0.0022	0.1245	0.5380	1.106	3.350	2.068
5.835	0.0016	0.1027	0.5016	1.165	3.438	2.398
6.252	0.0012	0.0855	0.4677	1.217	3.510	2.742

TABLE 80

CALCULATED EQUILIBRIUM CONCENTRATIONS OF SPECIES PRESENT IN SOLUTION WHEN INDIUM OXINATE WAS TITRATED WITH DITHIZONE IN BENZENE AT 25°C IN THE PRESENCE OF INITIAL FREE OXINE, APPROXIMATELY FIFTYFOLD WITH RESPECT TO THE INITIAL MOLAR CONCENTRATION OF INDIUM OXINATE

$(HDz)_T$ x 10^6	Equilibrium Concentration. Moles/litre x 10^6					
	$[InOx_3]$	$[InOx_2(HDz)]$	$[InOx(HDz)_2]$	$[In(HDz)_3]$	[HOx]	$[H_2Dz]$
0	1.771	0	0	0	89.15	0
0.417	1.557	0.2120	0.0022	0	89.43	0.1322
0.834	1.350	0.4113	0.0095	0	89.69	0.2967
1.250	1.159	0.5889	0.0227	0	89.90	0.4961
1.667	0.9902	0.7379	0.0418	0.0011	90.09	0.7290
2.084	0.8457	0.8569	0.0660	0.0024	90.24	0.9928
2.501	0.7252	0.9473	0.0940	0.0044	90.37	1.282
2.918	0.6259	1.013	0.1246	0.0073	90.48	1.5900
3.334	0.5440	1.059	0.1567	0.0110	90.57	1.914
3.751	0.4766	1.089	0.1893	0.0156	90.65	2.250
4.168	0.4203	1.108	0.2219	0.0211	90.72	2.596
4.585	0.3732	1.116	0.2538	0.0274	90.78	2.949
5.002	0.3270	1.118	0.2904	0.0359	90.84	3.369
5.418	0.2996	1.114	0.3149	0.0423	90.90	3.670
5.835	0.2716	1.106	0.3425	0.0504	90.96	4.023
6.252	0.2453	1.094	0.3712	0.0599	90.99	4.408

FIGURE 70

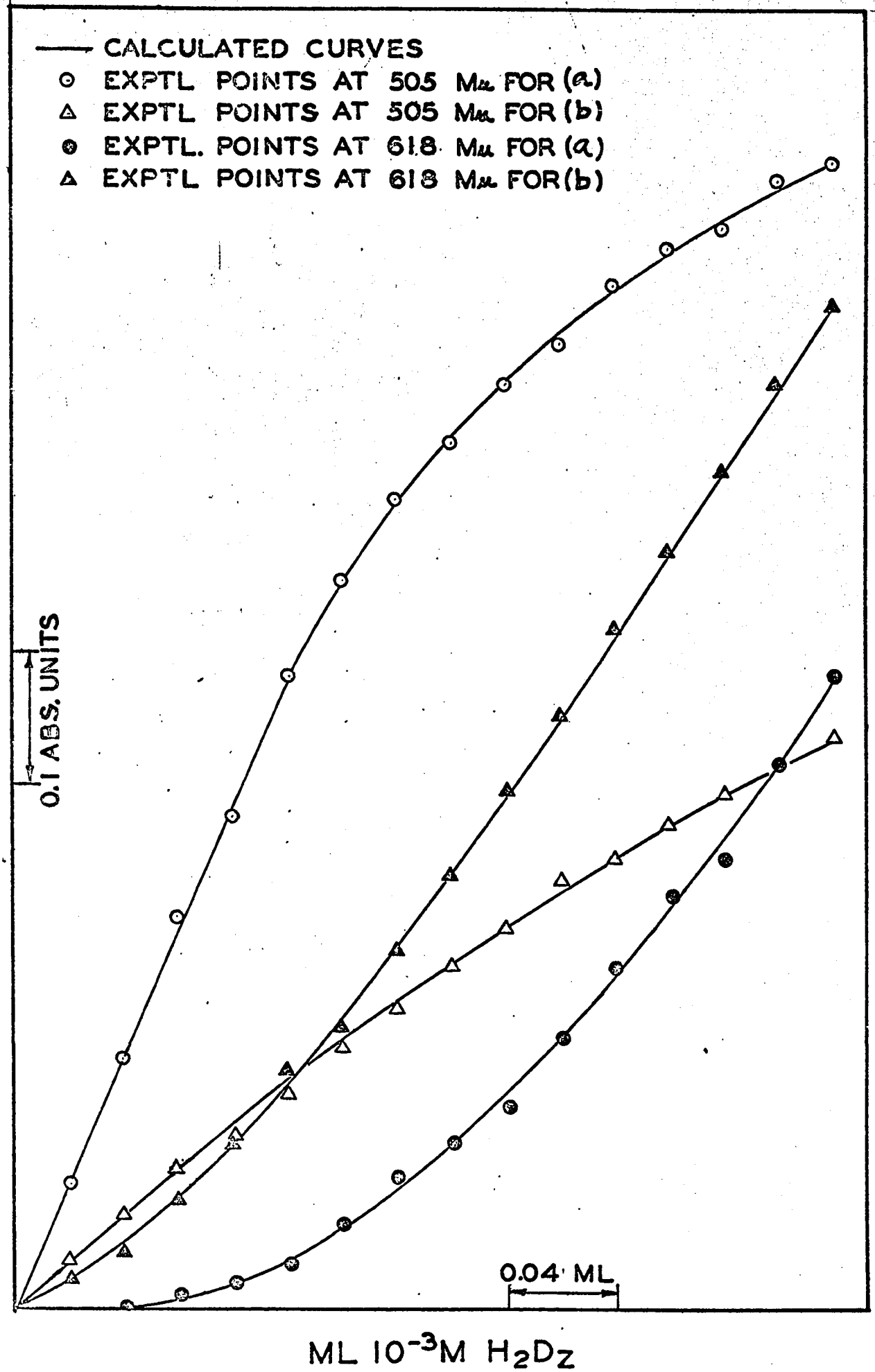
COMPARISON OF CALCULATED AND EXPERIMENTAL TITRATION GRAPHS FOR THE TITRATION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 25°C

Data: Table 78

(a) Curves obtained when initial free oxine was absent from the titration solution.

(b) Curves obtained when there was initial free oxine in the titration solution was approximately fiftyfold with respect to the initial concentration of indium oxinate.

Initial molarity of $InOx_3$ in the titration solution	$= 1.771 \times 10^{-6}$ M
Molarity of H_2Dz solution	$= 1.042 \times 10^{-3}$ M
Initial molarity of free oxine in the titration solution (for (b))	$= 8.915 \times 10^{-5}$ M
Initial volume of solution	= 50 ml
Path length	= 5 cm


CALCULATED CURVES
EXPTL POINTS AT 505 Mμ FOR (a)
EXPTL POINTS AT 505 Mμ FOR (b)
EXPTL. POINTS AT 618 Mμ FOR (a)
EXPTL POINTS AT 618 Mμ FOR (b)
0.1 ABS. UNITS
0.04 ML
ML 10⁻³M H₂Dz

(d) The Lead System

(i) Introduction

1) Experimental Observations

The following facts were observed in the lead chelate reactions:

1. The continuous-variations plot for the reaction of lead oxinate with dithizone (see Figure 71) showed that two moles of dithizone reacted with one mole of lead oxinate. The shape of the graph was only very slightly affected by initial increments of free oxine; but there was increased curvature at the "break" point.
2. In calculations which assumed that $PbOx_2$, $PbDz_2$, HOx and H_2Dz were the only species present at equilibrium, when lead oxinate was reacted with dithizone, the value found for the equilibrium constant varied with the composition of the initial mixture.
3. When the very pale yellow solution of lead oxinate was mixed with the deep red solution of lead dithizonate, the spectra of the resulting solutions was sufficiently different from the sum of the individual spectra of lead oxinate and lead dithizone that a reaction was indicated.
4. Addition of a large excess of oxine to the solutions resulting from (3) above produced further spectral

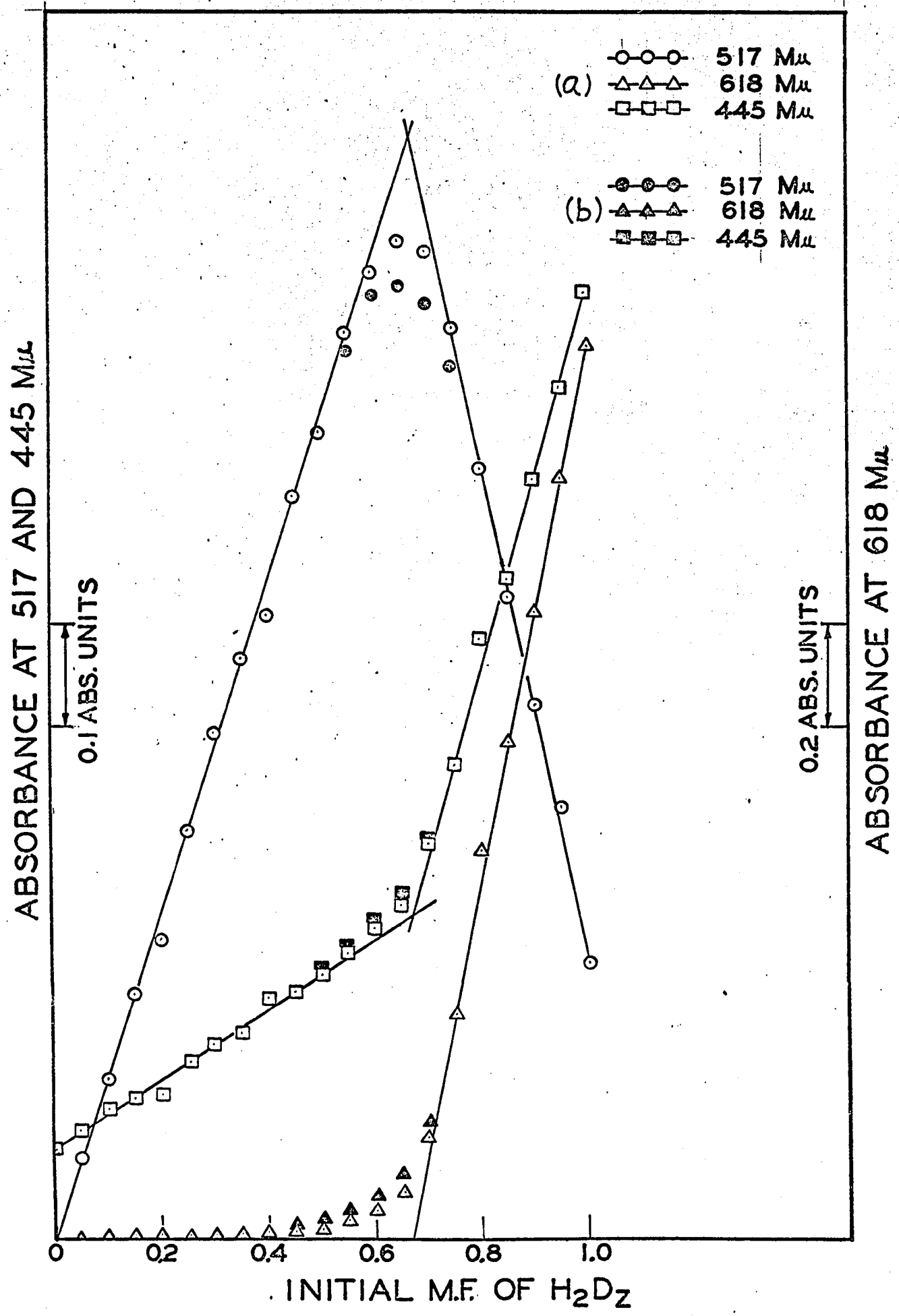
FIGURE 71

CONTINUOUS-VARIATIONS PLOT FOR THE REACTION OF LEAD OXINATE WITH DITHIZONE IN BENZENE AT 25°C

(a) Solutions contained no initial free oxine.

(b) Solutions contained free oxine, onehundredfold in excess with respect to the total concentration of reactants.

Total concentration of reactants: 10^{-5} M
Path length : 5 cm
Basic data: SETS F1 and F2, Tables 11 and 12, Appendix XXIX.


(a) 517 Mμ
618 Mμ
445 Mμ
(b) 517 Mμ
618 Mμ
445 Mμ
ABSORBANCE AT 517 AND 445 Mμ
0.1 ABS. UNITS
ABSORBANCE AT 618 Mμ
0.2 ABS. UNITS
0
0.2
0.4
0.6
0.8
1.0
INITIAL M.F. OF H_2D_Z

changes that indicated further reaction. Free dithizone was not observed.

5. Addition of oxine solutions to lead dithizonate solutions produced spectral changes that indicated a reaction. The spectra of the equilibrium solutions also failed to show the presence of any dithizone.
6. Addition of a large excess of dithizone to solutions of lead oxinate did not produce additional spectral changes which could be interpreted as indicating a reaction. Addition of a large excess of dithizone to lead dithizonate solutions did not produce any spectral change.
7. An adduct of oxine with lead oxinate, $PbOx_2 \cdot nHOx$ was sought for, by spectral studies, but none was found. Thus, benzene solutions of $PbOx_2$ and HOx were prepared in which the ratio $(PbOx_2)_i/(HOx)_i$ was varied from 10:1 to 1:500. The absorptivity versus wavelength curve of $PbOx_2$ was entirely unaffected by the presence of oxine, over the wavelength range 475 to 375; nor did any new peaks or shoulders appear there.

2) Reactions

From observation 1 the overall reaction of lead oxinate with dithizone was postulated to be

$$PbOx_2 + 2H_2Dz \rightleftarrows Pb(HDz)_2 + 2HOx \qquad (d)\text{-I}$$

for which

$$K_0 = \frac{[Pb(HDz)_2][HOx]^2}{[PbOx_2][H_2Dz]^2} \qquad (b)\text{-1}$$

However, Observation 2 indicated that there were additional species present in the solutions at equilibrium; Observations 3, 4, 5 and 6 led to their identification. Thus, as each species in turn was postulated and accounted for in the calculations, so the equilibrium constant, K_0 changed, until it finally became constant within experimental error.

Thus, from Observation 3 it was postulated that a mixed chelate, PbOxHDz, existed:

$$PbOx_2 + Pb(HDz)_2 \rightleftarrows 2PbOxHDz \qquad (d)\text{-II}$$

for which

$$K_3 = \frac{[PbOxHDz]^2}{[PbOx_2][Pb(HDz)_2]} \qquad (d)\text{-2}$$

This postulate permitted reaction (d)-I to be written in steps,

$$PbOx_2 + H_2Dz \rightleftarrows PbOxHDz + HOx \qquad (d)\text{-III}$$

$$PbOxHDz + H_2Dz \rightleftarrows Pb(HDz)_2 + HOx \qquad (d)\text{-IV}$$

for which

$$K_1 = \frac{[PbOxHDz][HOx]}{[PbOx_2][H_2Dz]} \qquad (d)\text{-3}$$

$$K_2 = \frac{[Pb(HDz)_2][HOx]}{[PbOxHDz][H_2Dz]} \qquad (d)\text{-4}$$

The spectral changes noted in Observation 4 required that additional species be postulated:

(1) An adduct of PbOxHDz with oxine, PbOxHDz·HOx. This reaction was postulated to be:

$$PbOxHDz + HOx \rightleftarrows PbOxHDz \cdot HOx \qquad (d)\text{-V}$$

for which

$$K_4 = \frac{[PbOxHDz \cdot HOx]}{[PbOxHDz][HOx]} \qquad (d)\text{-5}$$

(2) An adduct of lead dithioznate with oxine, $Pb(HDz)_2 \cdot HOx$. This reaction was postulated to be:

$$Pb(HDz)_2 + HOx \rightleftarrows Pb(HDz)_2 \cdot HOx \qquad (d)\text{-VI}$$

for which

$$K_5 = \frac{[Pb(HDz)_2 \cdot HOx]}{[Pb(HDz)_2][HOx]} \qquad (d)\text{-6}$$

Observation 5 confirmed the postulate.

Higher oxine adducts i.e. PbOxHDz·nHOx were considered for the two reactions above, but the calculations showed that they did not exist in measurable amounts.

3) Methods for Calculating the Equilibrium Constants

The general method for the calculation of equilibrium constants outlined in subsections (a) (i) and (a) (i)-3) of this Section was used exclusively (with minor variations) except for the calculation of K_2. This equilibrium constant was determined by the Least-squares method outlined in subsection (a) (i)-1) of this Section.

K_1 (reaction (d)-III) could not be evaluated directly because the concentration of free dithizone was always too low to be measured. However, K_1 can be calculated from the relation:

$$K_1 = K_2K_3 \qquad \text{(d)-8}$$

and K_0 can be obtained from:

$$K_0 = K_1K_2, = K_2{}^2K_3 \qquad \text{(d)-9}$$

K_2 could not be calculated until the absorptivities of PbOxHDz, PbOxHDz·HOx, $Pb(HDz)_2$·HOx had been evaluated.

Thus, the sequence of calculations was:

1. Computation of K_3 and the absorptivity of PbOxHDz (reaction (d)-II).
2. Computation of K_5 and the absorptivity of $Pb(HDz)_2$·HOx (reaction (d)-VI).
3. By using the values of K_3 and K_5 and the absorptivities obtained in 1 and 2, K_4 and the absorptivity of PbOxHDz·HOx (reaction (d)-V) were evaluated.
4. Computation of K_2 (reaction (d)-IV) by calculating the equilibrium concentrations of all species present, by using the experimental absorbance data and the relevant absorptivities obtained in 1-3 above.

Finally, by using all the above (equilibrium constants and absorptivities) data a theoretical, calculated titration graph for the titration of lead oxinate with dithizone was calculated.

4) Analytical Data

The equilibrium constants for reactions (d)-I to (d)-VII were calculated from the data of separate experiments. In these experiments the starting concentrations of reactants were chosen to produce the sought-for species. Except for

SET F below, all sets of solutions were ratio solutions; the analytical data are in the specified tables of Appendix XXIX.

The following sets of solutions were prepared:

Set No.	Soln. Nos.	Reaction Studied	Equilib. Const. Calculated	Conc. of Relevant Starting Materials	Table Nos. in Appendix XXIX
A1	PRA1-1 to 9	(d)-II	K_3	$(Pb)_T \sim 10^{-4}$ M	1 and 2
A2	PRA2-1 to 9	(d)-II	K_3	$(Pb)_T \sim 10^{-5}$ M	1 and 2
B1	PRB1-1 to 9	(d)-V	K_4	$(Pb)_T \sim 10^{-4}$ M $(\bar{HOx})$ added $\sim 10^{-2}$ M	3 and 4
B2	PRB2-1 to 5	(d)-V	K_4	$(Pb)_T \sim 10^{-5}$ M $(\bar{HOx})$ added $\sim 10^{-3}$ M	3 and 4
C	PRC-1 to 13	(d)-VI	K_5	$(Pb)_T \sim 4 \times 10^{-5} - 2 \times 10^{-6}$ M $(\bar{HOx})_T \sim 10^{-3} - 10^{-5}$ M	5 and 6
D	PRD-1 to 6	(d)-VII	K_6	$(Pb)_T \sim 2 \times 10^{-5} - 9 \times 10^{-6}$ M $(\bar{HDz})_T \sim 3 \times 10^{-4} - 4 \times 10^{-4}$ M	7 and 8
E1	PRE1-1 to 6	(d)-IV	K_2	$(Pb)_T \sim 8 \times 10^{-5} - 5 \times 10^{-6}$ M $(\bar{HDz})_T \sim 1.6 \times 10^{-4} - 10^{-5}$ M	9 and 10
E2	PRE2-1 to 6	(d)-IV	K_2	As for E2 except (HOx) added $\sim 8 \times 10^{-3} - 5 \times 10^{-4}$ M	9 and 10

The analytical data for the continuous-variations solutions for the reaction of lead oxinate with dithizone (i) when the solutions contained no free oxine and (ii)

when the solutions contained a onehundredfold excess of free oxine with respect to the initial concentration of reactants, are in Tables 11 and 12 of Appendix XXIX. These solutions will be referred to as SETS F1 and F2, respectively.

All of the above solutions were prepared in duplicate, one of which was in regular, spectrophotometric benzene ($[H_2O] \approx 2 \times 10^{-2}$ M) and the other was in benzene dried with silica gel ($[H_2O] \approx 10^{-4}$ M). For all duplicates, the absorbances in the undried and in the dried benzene were identical within experimental error. It was concluded that water did not take part in the reactions.

(ii) Calculation of the Equilibrium Constant for Reaction (d)-II, K_3

The postulated reaction was:

$$PbOx_2 + Pb(HDz)_2 \rightleftarrows 2PbOxHDz \qquad \text{(d)-II}$$

The mass-balance and Beer's law equations were:

$$(Pb)_T = [PbOx_2] + [Pb(HDz)_2] + [PbOxHDz] \qquad \text{(d)-10}$$

$$(HDz)_T = 2[Pb(HDz)_2] + [PbOxHDz] \qquad \text{(d)-11}$$

$$A_{p\lambda_i} = a_{\lambda_i,2}[Pb(HDz)_2] + a_{\lambda_i,3}[PbOxHDz] + a_{\lambda_i,6}[PbOx_2] \qquad \text{(b)-12}$$

where $a_{\lambda_i,2}$ and $a_{\lambda_i,2}$ were the absorptivities at wavelength λ_i for $Pb(HDz)_2$ and PbOxHDz, respectively. The absorptivity for $PbOx_2$ was negligibly small except at wavelengths < 475 mμ; $a_{\lambda_i,2}$ was measured independently for $Pb(HDz)_2$ (see Appendix XX, Table 1); and $a_{\lambda_i,3}$ was unknown for PbOxHDz.

The calculation of K_3 involved two steps:

(1) Step I: From equations (d)-10, (d)-11 and (d)-12 the equilibrium concentrations of the three species in reaction (d)-II were found in terms of the experimental data and $a_{\lambda_i,3}$, for each solution (PRA1-1 to 9, Table 1, Appendix XXIX)

$$D[PbOx_2] = a_{\lambda_i,2}'\{(HDz)_T - (Pb)_T\} - A_{p,\lambda_i} + a_{\lambda_i,3}'\{2(Pb)_T - (HDz)_T\} \quad (d)\text{-}13$$

$$D[Pb(HDz)_2] = a_{\lambda_i,3}(HDz)_T - A_{p,\lambda_i} \quad (d)\text{-}14$$

$$D[PbOxHDz] = 2A_{p,\lambda_i} - a_{\lambda_i,2}(HDz)_T \quad (d)\text{-}15$$

where $D = 2a_{\lambda_i,3} - a_{\lambda_i,2}$, $p = 1$ to 9 and $\lambda_i = 517$ mμ

These expressions for the concentrations were then substituted into equation (d)-2, to give nine equations in K_3 as a function of $a_{\lambda_i,3}$. The resulting equations are shown in Table 81. All different binary combinations of these nine equations were then taken. For each pair K_3 was eliminated, so that 36 quadratic equations in $a_{\lambda_i,3}$ remained. The average value of each of the three coefficients in this quadratic form was calculated, to give an average quadratic equation in $a_{\lambda_i,3}$ (see Table 81) which was then solved for $a_{\lambda_i,3}$. The value thereby found for $a_{\lambda_i,3}$ at 517 mμ was 2.722×10^4.

(2) Step II: The average value of $a_{\lambda_i,3}$ found in Step I was substituted into equations (d)-13 to (d)-15 to give

TABLE 81

EQUATIONS FOR THE EQUILIBRIUM CONSTANT K_3 AS A FUNCTION OF ABSORPTIVITY OF PbOxHDz AT 517 mμ FOR THE REACTION $PbOx_2 + Pb(HDz)_2 = 2PbOxHDz$

Basic data: Set A1, Tables 1 and 2, Appendix XXIX

Solution Number	Equations		
	coeff. of $a^2_{517,3}$	coeff. of $a_{517,3}$	
PRA1- 1	$= 5.390 \times 10^{-8}$	$- 3.221 \times 10^{-3}$	$+ 48.096$
2	$= 1.265 \times 10^{-8}$	$- 7.056 \times 10^{-4}$	$+ 9.480$
3	$= 1.174 \times 10^{-8}$	$- 6.147 \times 10^{-4}$	$+ 8.042$
4	$= 1.350 \times 10^{-8}$	$- 7.027 \times 10^{-4}$	$+ 9.104$
5	$= 8.262 \times 10^{-9}$	$- 4.784 \times 10^{-4}$	$+ 6.894$
6	$= 1.893 \times 10^{-8}$	$- 1.132 \times 10^{-3}$	$+ 16.909$
7	$= 1.496 \times 10^{-8}$	$- 8.395 \times 10^{-4}$	$+ 11.734$
8	$= 2.099 \times 10^{-8}$	$- 1.193 \times 10^{-3}$	$+ 16.913$
9	$= 3.868 \times 10^{-8}$	$- 2.302 \times 10^{-3}$	$+ 34.217$

Average equation of all binary combinations of the above equations is:

$$a^2_{517,3} - 6.4680 \times 10^4 a_{517,3} + 1.0192 \times 10^9 = 0$$

$a_{517,3} = 2.722 \times 10^4$
Variance $= 1.401 \times 10^7$
Std. Dev. $= 0.374 \times 10^4$ (for 8 degrees of freedom)

the equilibrium concentrations of $PbOx_2$, $Pb(HDz)_2$ and PbOxDz. The equilibrium constant K_3 was then calculated from equation (d)-2. The equilibrium concentrations are in Table 82 together with the equilibrium constant, K_3.

A specific example of these calculations is given in Appendix XXIX, page 162a.

The average value of K_3 from all the solutions PRA1-1 to PRA1-9 (excluding PRA1-5)* was found to be 214 ± 41.

Having obtained the equilibrium concentrations of $PbOx_2$, $Pb(HDz)_2$ and PbOxHDz for each of the solutions of SET A1, the absorptivity of PbOxHDz could be calculated from 650 to 400 mμ by resolving the spectral transmission curves by means of the equation

$$\frac{A_{p,\lambda_i} - a_{\lambda_{i,2}}[Pb(HDz)_2] - a_{\lambda_{i,6}}[PbOx_2]}{[PbOxHDz]} = a_{\lambda_{i,3}} \qquad \text{(d)-19}$$

The absorptivities were calculated at 5 mμ intervals. The curve of absorptivity versus wavelength is shown in Figure 72 and a table of values at 10 mμ intervals is given in Table 13 of Appendix XXIX.

The data from SET A2 were used to confirm the value found for K_3. Using the absorptivities calculated above for $a_{\lambda_{i,3}}$ and the known values of $a_{\lambda_{i,3}}$ and $a_{\lambda_{i,6}}$, the equilibrium concentration of each of the species was calculated from the

*It turned out that $[Pb(HDz)_2]$ was essentially zero for this solution.

TABLE 82

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANTS FOR SETS A1 AND A2

Basic Data: See Table 81

Solution Number	Equilibrium Concentration M $[PbOx_2]$ x 10^5	$[Pb(HDz)_2]$ x 10^6	[PbOxDz] x 10^5	K_3
PRA1- 1	0.03014	34.24	5.382	281
2	0.3984	11.68	10.08	218
3	2.162	3.021	12.00	220
4	4.840	1.601	12.07	188
5	3.041	-	2.594	-
6	4.094	0.3570	5.116	179
7	5.027	0.4860	7.785	248
8	6.200	1.103	10.16	151
9	7.211	1.007	12.77	224
PRA2- 1	-	3.450	0.5331	-
2	0.04368	1.207	4.000	190
3	0.2281	0.4209	1.176	144
4	0.4294	0.2438	1.253	150
5	0.3041	-	0.2594	-
6	0.4058	-	0.5188	-
7	0.4978	-	0.7882	-
8	0.6090	-	1.038	-
9	0.7110	-	1.297	-

Average K_3 (PRA1) = 214 Variance = 1675 Std. Dev. = 41 (7 degrees of freedom)

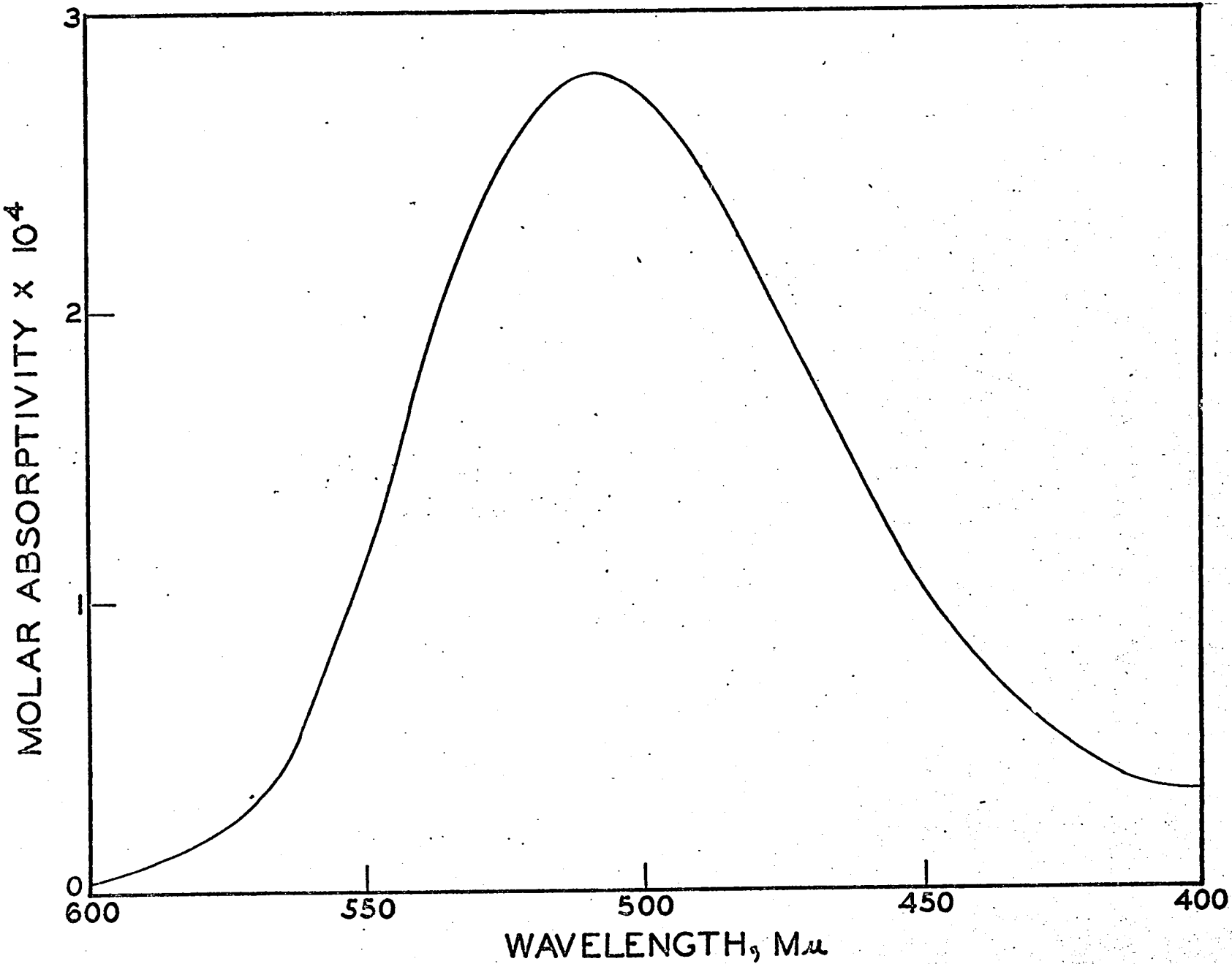
Average K_3 (PRA2) = 161 Variance = 426 Std. Dev. = 21 (2 degrees of freedom)

Grand Average K_3 = 188 Pooled Variance = 1400 Pooled Std.Dev. = 37 (10 degrees of freedom)

FIGURE 72

CURVE OF ABSORPTIVITY VERSUS WAVELENGTH FOR PbOxHDz, IN BENZENE AT 25°C

Basic data: Table 13, Appendix XXIX


MOLAR ABSORPTIVITY x 10^4
3
2
1
0
600
550
500
450
400
WAVELENGTH, Mμ

set of Beer's law equations given in Table 87, pages 401-2 (omitting the terms in species that were known to be absent). In addition to the Beer's law equations, the mass-balance equations (d)-10 and (d)-11 were used. This system of linear equations was solved by the method of least squares outlined in subsection (a)(i)-1), page 279 of this Section. The equilibrium concentrations and the found equilibrium constants are given in Table 82. Unfortunately, the concentration of $Pb(HDz)_2$ in most of the solutions had dropped to a negligible amount, and could not be measured. Thus only three values of K_3 were obtained. The average value was 161 ± 21. This value was not significantly different, at the 95% confidence level, from the value obtained from SET A1, nor were the variances. Thus the grand average was 188, and the pooled standard deviation was 37.

The calculations described on pages 377 - 380 were repeated using the absorbance data for 575, 550, 495, 445, 425 and 400 mμ (Table 2, Appendix XXIX) in order to confirm the absence of species other than $PbOx_2$, $Pb(HDz)_2$ and PbOxHDz. The variability of the data at 575, 550 and 475 mμ did not permit an accurate estimation of the equilibrium constant. The average values of K_3 obtained from the data at 445, 425 and 400 mμ were found to be 257, 196 and 281 respectively. HOwever, the variances were not homogeneous (the inhomogeneity of variance as a function of wavelength was discussed in Section IV C subsection C (ii)page 201), nor were they homogenous

with the variances given in Table 82. Since the above quoted values for K_3 are of the same order of magnitude as those given in Table 82, it was concluded that this was sufficient evidence to exclude the presence of other species. Furthermore the average absorptivites of PbOxHDz at 445, 425 and 400 mμ were not significantly different from those given in Table 13 of Appendix XXIX (calculated by the method given on page 380). It can be argued that species may be present which only absorb above 500 mμ. However, the fact that the average equilibrium constant for SET A2 (see Table 82) was not significantly different from the average value obtained from SET A1 rules out this possibility. Data from 575 to 400 mμ was used in the calculations on SET A2.

Since the variability of the absorbance data was lowest at 517 mμ (the maximum in the spectral absorbance curves), it was concluded that the best estimate of K_3 was obtained at this wavelength. Therefore, the results of the calculations described in the previous paragraph, which were lengthy, are not reported.

(iii) Calculation of the Equilibrium Constant for Reaction (d)-VI, K_5

The postulated reaction was:

$$Pb(HDz)_2 + 2HOx \rightleftarrows Pb(HDz)_2 \cdot HOx \qquad (d)\text{-VI}$$

The species $PbOxHDz \cdot H_2Dz$ was ruled out and the reasons given in Section VC subsection (c), page 461

In the calculations it was assumed that only one oxine adduct was formed. The calculations confirmed this assumption; K_5 was found to be constant over the concentration range studied. It was further assumed that when HOx was not too much in excess (i.e. for $(Pb(HDz)_2)_i:(HOx)_i > 1:50$), species such as PbOxHDz, PbOxHDz·HOx, $PbOx_2$ and H_2Dz were absent in measurable concentrations. Support for this assumption was as follows: Formation of PbOxHDz, PbOxHDz·HOx, or $PbOx_2$ would require the formation also of the dithizone, which absorbs at 618 mμ. The spectra at the low ratio specified did not show any detectable absorbance at 618 mμ.

At ratios of $(Pb(HDz)_2)_i:(HOx)_i < 1:50$ (with $(Pb(HDz)_2)_i = 1.864 \times 10^{-5}$ M), free dithizone was observed. To confirm that a second adduct, $Pb(HDz)_2 \cdot 2HOx$ did not form at these higher ratios, the equilibrium concentrations of PbOxHDz, PbOxHDz·HOx, $Pb(HDz)_2 \cdot HOx$, $Pb(HDz)_2$, $PbOx_2$ and H_2Dz were separately calculated from the absorptivity and equilibrium constant data shown later in subsections (iv) and (v), pages 388 to 406 and using the equations given in subsection (ix), page 409. From these concentrations, and from the known absorptivities of $Pb(HDz)_2$, $PbOx_2$, H_2Dz, PbOxHDz, and PbOxHDz·HOx, spectral transmission curves were calculated from 650 to 400 mμ, and compared with the experimental curves*. They agreed within experimental error even when the ratio of $(Pb(HDz)_2)_i:(HOx)_i$ was 1:500. This evidence proved that the species $Pb(HDz)_2 \cdot 2HOx$

*The data, which is rather lengthy, is not reported.

did not form in measurable amounts.

On using the two assumptions outlined above, the mass-balance and Beer's law equations for reaction (d)-VI became:

$$(Pb)_T = [Pb(HDz)_2] + [Pb(HDz)_2 \cdot HOx] \quad (d)-20$$

$$(Ox)_T = [Pb(HDz)_2 \cdot HOx] + [HOx] \quad (d)-21$$

$$A_{p,\lambda} = a_{\lambda_{i,2}}[Pb(HDz)_2] + a_{\lambda_{i,5}}[Pb(HDz)_2 \cdot HOx] \quad (d)-22$$

The equilibrium concentrations as functions of $a_{\lambda_{i,5}}$ were then

$$D[Pb(HDz)_2] = A_{p,\lambda_i} - a_{\lambda_{i,5}}(Pb)_T \quad (d)-23$$

$$D[Pb(HDz)_2 \cdot HOx] = a_{\lambda_{i,2}}(Pb)_T - A_{p,\lambda_i} \quad (d)-24$$

$$D[HOx] = A_{p,\lambda_i} + a_{\lambda_{i,2}}\{(Ox)_T - (Pb)_T\} - a_{\lambda_{i,5}}(Ox)_T \quad (d)-25$$

where $D = a_{\lambda_{i,2}} - a_{\lambda_{i,5}}$

The experimental data for each of the solutions of SET C (PRC-1 to 13, Tables 5 and 6, Appendix XXIX), were substituted into equations (d)-23 to (d)-25, and the resulting expressions for the equilibrium concentrations substituted into equation (d)-6. The resulting equations of K_5 as a function of $a_{\lambda_{i,5}}$ at 517 mμ are shown in Table 83. All binary combination of these equations were equated to eliminate K_5, as was done in subsection (ii) of this Section, and the average of the 78 equations was then calculated. This average equation is also given in Table 83. This average equation was solved for $a_{\lambda_{i,5}}$, which was found to be 5.872×10^4 at 517 mμ.

TABLE 83

EQUATIONS FOR THE EQUILIBRIUM CONSTANT AS A FUNCTION OF ABSORPTIVITY OF $Pb(HDz)_2 \cdot HOx$ AT 517 mμ FOR THE REACTION $Pb(HDz)_2 + HOx = Pb(HDz)_2 \cdot HOx$ IN BENZENE AT 25°C

Basic data: SET C, Tables 5 and 6, Appendix XXIX

Solution Number	Equations		
		Coeff. of $a^2_{517,5}$	Coeff. of $a_{517,5}$
PRC - 1	$D/K_5 =$	5.990×10^{-8} -	$7.515 \times 10^{-3} + 235.59$
2	$D/K_5 =$	9.053×10^{-8} -	$1.128 \times 10^{-2} + 350.98$
3	$D/K_5 =$	1.765×10^{-7} -	$2.181 \times 10^{-2} + 672.29$
4	$D/K_5 =$	4.645×10^{-8} -	$5.893 \times 10^{-3} + 186.86$
5	$D/K_5 =$	5.996×10^{-8} -	$7.542 \times 10^{-3} + 237.01$
6	$D/K_5 =$	9.023×10^{-8} -	$1.126 \times 10^{-2} + 350.85$
7	$D/K_5 =$	1.794×10^{-7} -	$2.220 \times 10^{-2} + 685.49$
8	$D/K_5 =$	3.053×10^{-8} -	$3.927 \times 10^{-3} + 126.28$
9	$D/K_5 =$	3.116×10^{-8} -	$3.988 \times 10^{-3} + 127.62$
10	$D/K_5 =$	4.504×10^{-8} -	$5.724 \times 10^{-3} + 181.86$
11	$D/K_5 =$	3.108×10^{-8} -	$4.010 \times 10^{-3} + 129.35$
12	$D/K_5 =$	3.357×10^{-8} -	$4.323 \times 10^{-3} + 139.14$
13	$D/K_5 =$	3.207×10^{-8} -	$4.108 \times 10^{-3} + 131.55$

$$D = a_{517,2} - a_{517,5}$$

Average equation of all binary combinations (78) of the above equations was:

$$a^2_{517,5} - 1.562 \times 10^5 a_{517,5} + 2.675 \times 10^9 = 0$$

$$a_{517,5} = 5.872 \times 10^4$$

Variance $= 7.270 \times 10^6$

Std. Dev. $= 0.270 \times 10^4$ (for 12 degrees of freedom)

Substitution of the value of 5.872×10^4 for $a_{\lambda_{i,5}}$ into equations (d)-23 to (d)-25 gave the various equilibrium concentrations, wherefrom the equilibrium constant K_5 was calculated. The equilibrium concentrations and the found equilibrium constants calculated therefrom are given in Table 84. The average value of K_5 was found to be $5.44 \pm 0.37 \times 10^3$ litre $mole^{-1}$.

Having obtained the equilibrium concentrations of $Pb(HDz)_2$ and $Pb(HDz)_2 \cdot HOx$, the absorptivities of $Pb(HDz)_2 \cdot HOx$ from 650 to 400 mμ were calculated by resolving the spectral transmission curves in the same way as outlined in subsection (ii) of this Section. The curve of absorptivity versus wavelength is shown in Figure 73, and the values at 10 mμ intervals are in Table 14 of Appendix XXIX.

(iv) Calculation of the Equilibrium Constant for Reaction (d)-V, K_4

The postulated reaction was

$$PbOxHDz + HOx \rightleftarrows PbOxHDz \cdot HOx \qquad (d)\text{-}V$$

It was assumed that only one adduct was formed. The constancy of the observed equilibrium constant, over a wide concentration range, supported this assumption.

The starting solutions for this study were the equilibrium solutions of SETS A1 and A2, with HOx added to give a concentration of about 10^{-2} M. That is, the equilibrium concentrations of $PbOx_2$, $Pb(HDz)_2$ and PbOxHDz in Solution Nos. PRA1-1 to PRA1-9 and PRA2-5 to PRA2-9 (Table 82) were

TABLE 84

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANTS FOR SET C
Basic data: See Table 83

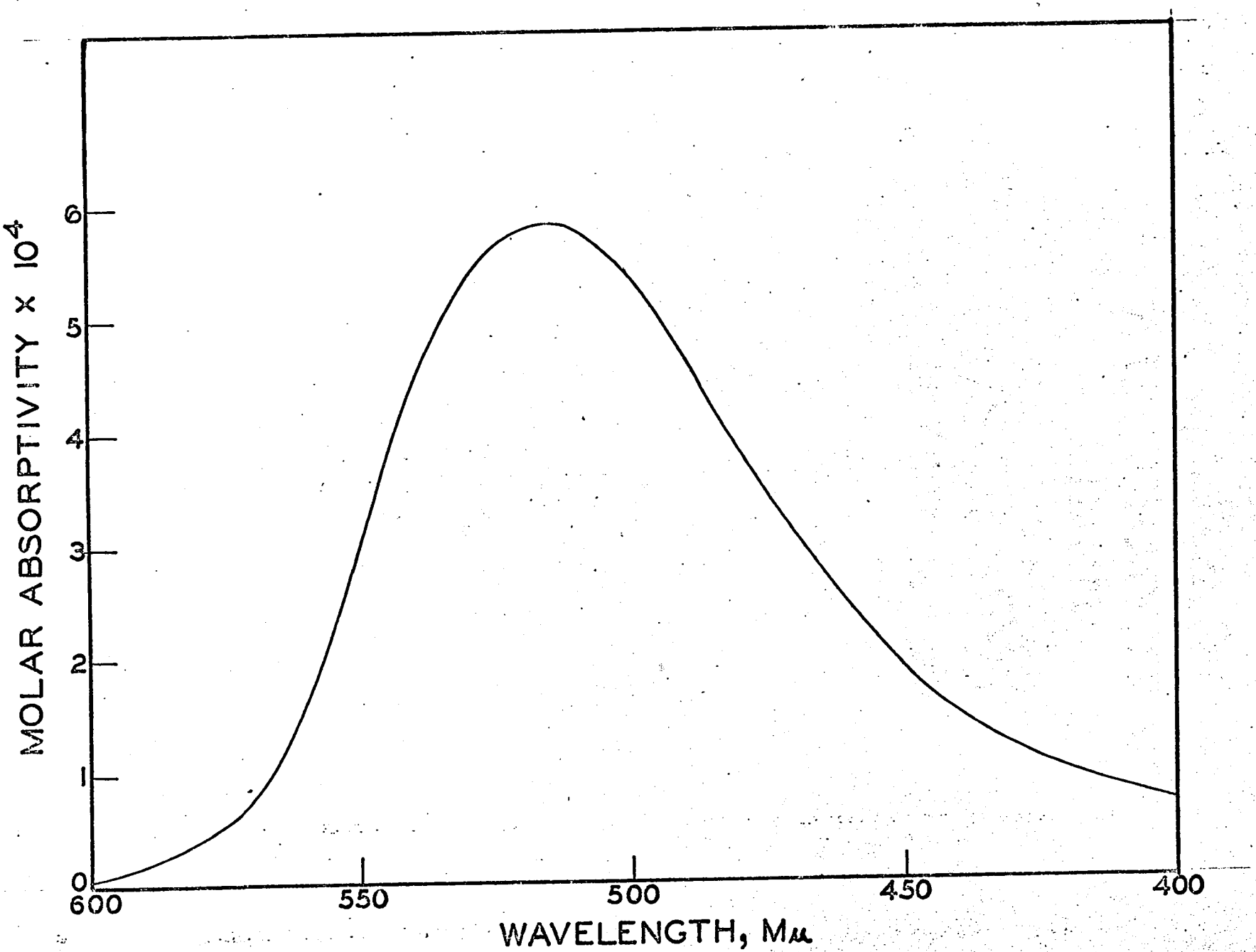
Solution Number	Equilibrium Concentrations M $[Pb(HDz)_2]$ x 10^6	$[Pb(HDz)_2 \cdot HOx]$ x 10^6	[HOx] x 10^5	K_5 litre mole^{-1} x 10^3
PRC- 1	18.53	18.76	18.01	5.5262
2	12.46	24.82	37.29	5.34
3	5.457	31.83	96.26	6.06
4	12.60	6.047	9.339	5.14
5	9.275	9.368	18.95	5.33
6	6.191	12.45	38.53	5.22
7	2.985	15.66	97.87	5.36
8	3.361	0.3680	1.952	5.61
9	3.007	0.7212	3.905	6.14
10	2.481	1.247	9.819	5.12
11	1.774	0.0904	0.9854	5.17
12	1.697	0.1673	1.972	5.00
13	1.514	0.3504	3.942	5.87

Average value of K_5 = 5.44×10^3 litre mole^{-1}
Variance = 13.8×10^4
Std. Dev. = 0.37×10^3 (12 degrees of freedom)

FIGURE 73

CURVE OF ABSORPTIVITY VERSUS WAVELENGTH FOR THE OXINE ADDUCT $Pb(HDz)_2 \cdot HOx$ IN BENZENE AT 25°C

Basic data: Table 14, Appendix XXIX


MOLAR ABSORPTIVITY X 10^4
0
1
2
3
4
5
6
600
550
500
450
400
WAVELENGTH, Mμ

in the present study, the initial concentrations.

These solutions were renumbered to PRB1-1 to PRB1-9 and PRB2-1 to PRB2-5, respectively.

The value of K_4 was calculated in two ways:

(1) In solutions nos. PRA1-5 and PRA2-5 to PRA2-19, the equilibrium concentrations of $Pb(HDz)_2$ were negligibly small (see Table 82, page 381).

Inspection of the spectral transmission curves (not reproduced here) of all solutions of SETS B1 and B2 showed no measurable absorbance at 618 mμ. Therefore, since the lower limit of detection of free dithizone at this, its peak, was 5×10^{-9} M there could have been no significant production of free dithizone by the addition of the oxine. Experiments showed that an adduct of oxine with lead oxinate did not form (observation 7, page 372). Therefore lead oxinate was assumed not to take part in the reaction.

Based on the above assumptions, the mass-balance and Beer's law equations were:

$$(Pb)_T^* = [PbOxHDz] + [PbOxHDz \cdot HOx] \qquad (d)-26$$

$$A_{p,\lambda_i} = a_{\lambda_i,3}[PbOxHDz] + a_{\lambda_i,4}[PbOxHDz \cdot HOx] \qquad (d)-27$$

Since there was such a large excess of HOx compared to $(Pb)_T$, the approximation was used that the equilibrium

---

*$(Pb)_T$ here signifies the $(Pb)_T$ given in Table 1 of Appendix XXIX minus the equilibrium concentration of $PbOx_2$ shown in Table 82. These values are listed in Table 3 of Appendix XXIX.

concentration of HOx was the same as the amount added; represent by $(HOx)_A$.

The expressions for the equilibrium concentrations in terms of $a_{\lambda_{i,4}}$ were:

$$D[PbOxHDz] = a_{\lambda_{i,4}}(Pb)_T - A_{p,\lambda_i} \qquad (d)\text{-}28$$

$$D[PbOxHDz \cdot HOx] = A_{p,\lambda_i} - a_{\lambda_{i,3}}(Pb)_T \qquad (d)\text{-}29$$

where $D = a_{\lambda_{i,4}} - a_{\lambda_{i,3}}$

$$K_4 = \frac{[PbOxHDz \cdot HOx]}{[PbOxHDz][HOx]} \qquad (d)\text{-}5$$

The equilibrium concentrations for solutions PRB1-5 and PRB2-1 to PRB2-5 were obtained by the same method outlined in subsection (ii) of this Section. The equations of K_4 as a function of $a_{\lambda_{i,4}}$ at 517 mμ, and the average equation of all combinations of two of those equations are shown in Table 85. The average value of $a_{\lambda_{i,4}}$ at 517 mμ was found to be $2.008 \pm 0.250 \times 10^4$. The equilibrium concentrations and the equilibrium constants are shown in Table 86.

(2) The data for those solutions which contained appreciable concentrations of $Pb(HDz)_2$ at equilibrium, PRA1-1 to PRA1-4 and PRA1-6 to PRA1-9, had to be treated differently. After the oxine had been added to those solutions, appreciable amounts of $Pb(HDz)_2 \cdot HOx$ would be formed which in turn would alter the equilibrium between $PbOx_2$, $Pb(HDz)_2$ and (PbOxHDz) (Reaction (d)-II, page 373).

TABLE 85

EQUATIONS FOR THE EQUILIBRIUM CONSTANT K_4 AS A FUNCTION OF ABSORPTIVITY OF PbOxHDz·HOx AT 517 mμ (SET B2) AND EQUATIONS IN ABSORPTIVITY ONLY FOR THE REACTION

$$PbOxHDz + HOx \rightleftarrows 2PbOxHDz \cdot HOx$$

IN BENZENE AT 25°C

Basic Data: SETS B1 and B2, Tables 3 and 4, Appendix XXIX

Solution Number	Equations of $a_{517,4}$ As A Function of K_4
PRB1 - 5	$D/K_4 = 6.624 \times 10^{-2} - 2.937 \times 10^{-6}\ a_{517,4}$
PRB2 - 1	$D/K_4 = 3.100 \times 10^{-2} - 1.179 \times 10^{-6}\ a_4$
2	$D/K_4 = 3.838 \times 10^{-2} - 1.450 \times 10^{-6}\ a_4$
3	$D/K_4 = 2.774 \times 10^{-2} - 1.059 \times 10^{-6}\ a_4$
4	$D/K_4 = 2.525 \times 10^{-2} - 9.678 \times 10^{-7}\ a_4$
5	$D/K_4 = 3.155 \times 10^{-2} - 1.199 \times 10^{-6}\ a_4$
	$D = a_{517,4} - a_{517,4}$

Average equation of all binary combinations (15) of the above equations was:

$$1.766 \times 10^{-6} a_{517,4} - 3.545 \times 10^{-2} = 0$$

$$a_{517,4} = 2.008 \times 10^{4}$$

Variance = 6.24×10^{6}

Std. Deviation = 0.250×10^{4} (for 4 degrees of freedom)

(Continued on next page)

TABLE 85 CONTINUED

EQUATIONS FOR THE EQUILIBRIUM CONSTANT K_4 AS A FUNCTION OF ABSORPTIVITY OF PbOxHDz·HOx AT 517 mμ (SET B2) AND EQUATIONS IN ABSORPTIVITY ONLY FOR THE REACTION

PbOxHDz + HOx $\rightleftarrows$ 2PbOxHDz·HOx

IN BENZENE AT 25°C

Basic Data: SETS B1 and B2, Tables 3 and 4, Appendix XXIX

Solution Number	Equations in $a_{517,4}$ Only				Value of $a_{517,4} \times 10^{4}$
	Coeff. of $a^2_{517,4}$		Coeff. of $a_{517,4}$		
PRB - 1	6.078×10^{-4}	-	22.34	$+ 20.14 \times 10^{4} = 0$	1.585
2	5.488×10^{-4}	-	15.12	$+ 8.971 \times 10^{4} = 0$	1.889
3	1.188×10^{-3}	-	21.37	$+ 6.959 \times 10^{4} = 0$	1.372
4	8.478×10^{-4}	-	10.57	$- 9.708 \times 10^{4} = 0$	1.862
6	1.857×10^{-4}	-	2.783	$- 2.206 \times 10^{4} = 0$	2.072
7	2.604×10^{-4}	-	2.468	$- 7.483 \times 10^{4} = 0$	2.234
8	5.813×10^{-4}	-	6.282	$- 16.54 \times 10^{4} = 0$	2.311
9	1.356×10^{-3}	-	10.08	$- 26.11 \times 10^{4} = 0$	1.808

Average value of $a_{517,4} = 1.890 \times 10^{4}$
Variance $= 9.87 \times 10^{6}$
Std. Deviation $= 0.310 \times 10^{4}$ (7 deg. of freedom)

Grand Average value of $a_{517,4} = 1.949 \times 10^{4}$
Variance $= 9.70 \times 10^{6}$
Std. Deviation $= 0.310 \times 10^{4}$ (12 deg. of freedom)

TABLE 86

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANTS FOR SETS B1 AND B2

Basic data: See Table 85

Solution Number	Equilibrium Concentration M $[PbOx_2]$ x 10^5	$[PbOxHDz]$ x 10^5	$[Pb(HDz)_2]$ x 10^7	$[PbOxHDz \cdot HOx]$ x 10^5	$[Pb(HDz)_2 \cdot HOx]$ x 10^5	$[HOx]$ x 10^2	K_4 litre mole^{-1}
PRB1- 1	0.1052	2.470	5.638	2.762	3.443	1.118	100
2	1.124	3.379	3.396	5.253	1.860	1.003	155
3	3.298	3.271	1.754	6.453	1.420	1.483	133
4	6.016	4.703	1.988	5.016	1.336	1.212	88
5	3.041	0.8411	-	1.753	-	1.371	152
6	4.364	1.954	-	2.621	0.3022	1.315	102
7	5.674	3.742	1.263	2.747	0.6838	0.9917	74
8	6.981	4.224	1.382	7.226	0.8775	1.163	89
9	8.099	4.255	1.209	6.738	0.9766	1.480	107
PRB2- 1	0.3041	0.2333	-	0.02606	-	0.1095	102
2	0.4058	0.4699	-	0.04888	-	0.1095	95
3	0.4978	0.6821	-	0.1061	-	0.1095	142
4	0.6090	0.8540	-	0.1840	-	0.1095	111
5	0.7110	1.136	-	0.1606	-	0.1095	121

Average value of K_4 = 113 litre mole^{-1}
Variance = 622
Std. Dev. = 25 (for 13 degrees of freedom).

Therefore, the mass-balance and Beer's law equations for this case were:

$$(Pb)_T = [PbOx_2] + [Pb(HDz)_2] + [PbOxHDz] + [PbOxHDz\cdot HOx] + [Pb(HDz)_2\cdot HOx] \quad (d)\text{-}30$$

$$(HDz)_T^* = 2[Pb(HDz)_2] + [PbOxHDz] + [PbOxHDz\cdot HOx] + 2[Pb(HDz)_2\cdot HOx] \quad (d)\text{-}31$$

$$(Ox)_T = 2[PbOx_2] + [PbOxHDz] + 2[PbOxHDz\cdot HOx] + [Pb(HDz)_2\cdot HOx] + (HOx)_A \quad (d)\text{-}32$$

$$A_{p,\lambda_i} = a_{\lambda_{i,2}}[Pb(HDz)_2] + a_{\lambda_{i,3}}[PbOxHDz] + a_{\lambda_{i,4}}[PbOxHDz\cdot HOx] + a_{\lambda_{i,5}}[Pb(HDz)_2\cdot HOx] \quad (d)\text{-}33$$

$a_{\lambda_{i,4}}$ was unknown, but K_3, K_5, $a_{\lambda_{i,3}}$ and $a_{\lambda_{i,5}}$ were known. Substitution of equation (d)-6 for $[Pb(HDz)_2\cdot HOx]$ into equations (d)-30 to (d)-33 gave:

$$(Pb)_T = [PbOx_2] + [Pb(HDz)_2]\{1 + K_5(HOx)_A\} + [PbOxHDz] + [PbOxHDz\cdot HOx] \quad (d)\text{-}34$$

$$(HDz)_T^* = 2[Pb(HDz)_2]\{1 + K_5(HOx)_A\} + [PbOxHDz] + [PbOxHDz\cdot HOx] \quad (d)\text{-}35$$

$$(Ox)_T - (HOx)_A = 2[PbOx_2] + K_5(HOx)_A[Pb(HDz)_2] + [PbOxHDz] + 2[PbOxHDz\cdot HOx] \quad (d)\text{-}36$$

$$A_{p,\lambda} = \{a_{\lambda_{i,2}} + a_{\lambda_{i,5}}K_5(HOx)_A\}[Pb(HDz)_2] + a_{\lambda_{i,3}}[PbOxHDz] + a_{\lambda_{i,3}}[PbOxHDz\cdot HOx] \quad (d)\text{-}37$$

The above set of equations was solved for the equilibrium concentrations in terms of $a_{\lambda_{i,4}}$:

---

*$(HDz)_T^* = (HDz)_T - [H_2Dz]$. $[H_2Dz]$ was calculated from the absorbance at 618 mμ.

$$D[PbOx_2] = a_{\lambda_i,4}\{K_5^{1}((HDz)_T - (Pb)_T) - K_5^{11}(HDz)_T\}$$

$$- a_{\lambda_i,3}\{((Pb)_T - (HDz)_T)(2K_5^{11}-K_5^{1})\} + a^{1}_{\lambda_i,2}\{(PB)_T - (HDz)_T\}$$

$$+ K_5^{11} A_{p,\lambda_i} \qquad \text{(d)-37}$$

$$D[Pb(HDz)_2] = A_{p,\lambda_i} - a_{\lambda_i,4}(HDz)_T \qquad \text{(d)-38}$$

$$D[PbOxHDz] = a_{\lambda_i,4}\{(HDz)_T(2K_5^{11}-K_5^{1})\} - A_{p,\lambda_i}(2K_5^{11}-K_5^{1}) \qquad \text{(d)-39}$$

$$D[PbOxHDz\cdot HOx] = a^{1}_{\lambda_i,2}(HDz)_T - K_5^{1} A_{p,\lambda_i} - (HDz)_T(2K_5^{11}-K_5^{1}) \qquad \text{(d)-40}$$

$$\text{where } D = a^{1}_{\lambda_i,2} - a_{\lambda_i,4} K_5^{1} - a_{\lambda_i,3}(2K_5^{11}-K_5^{1}) \qquad \text{(d)-41}$$

$$a^{1}_{\lambda_i,2} = a_{\lambda_i,2} + a_{\lambda_i,5} K_5(HOx)_A \qquad \text{(d)-42}$$

$$K_5^{1} = K_5(HOx)_A \qquad \text{(d)-43}$$

$$K_5^{11} = 1-K_5(HOx)_A \qquad \text{(d)-44}$$

The experimental data at 517 mμ of SET B1, excluding #PRB1-5 (Tables 3 and 4, Appendix XXIX), were substituted into equations (d)-37 to (d)-40. The resulting expressions for $[PbOx_2]$, $[Pb(HDz)_2]$ and [PbOxHDz] were then substituted into equation (d)-2 with $K_3 = 188$, to obtain a series of quadratic equations in $a_{\lambda_i,4}$. These equations are shown in Table 85. Each equation was solved for $a_{517,4}$. These individual values for $a_{517,4}$ were then substituted back into equations (d)-37 to (d)-40. From the resulting equations, the equilibrium concentration were evaluated and are given in Table 86, together with the

equilibrium constants evaluated from those concentrations. The average value of $a_{517,4}$ was found to be $1.890 \pm 0.310 \times 10^4$. This was not significantly different from the value found for SET B2 and the variances were not significantly different. Therefore, the grand average of $a_{517,4} = 1.95 \times 10^4$ was calculated, and the standard deviation was 0.310×10^4.

The grand average value of K_4, from SETS B1 and B2 was found to be 113 ± 25 litre mole^{-1}.

The absorptivities of PbOxHDz·HOx from 600 to 400 mμ were calculated from the equilibrium concentrations, by the method outlined in subsection (ii) of this Section. The curve of absorptivity versus wavelength is shown in Figure 74, and a table of values at 10 mμ intervals is given in Table 15 of Appendix XXIX.

(v) Calculation of the Equilibrium Constant for Reaction (d)-IV, K_2

Having calculated all the necessary data, it was now a simple matter to calculate the equilibrium constant, K_2, for reaction (d)-IV which was postulated to be:

$$PbOxHDz + H_2Dz \rightleftarrows Pb(HDz)_2 + HOx \qquad \text{(d)-IV}$$

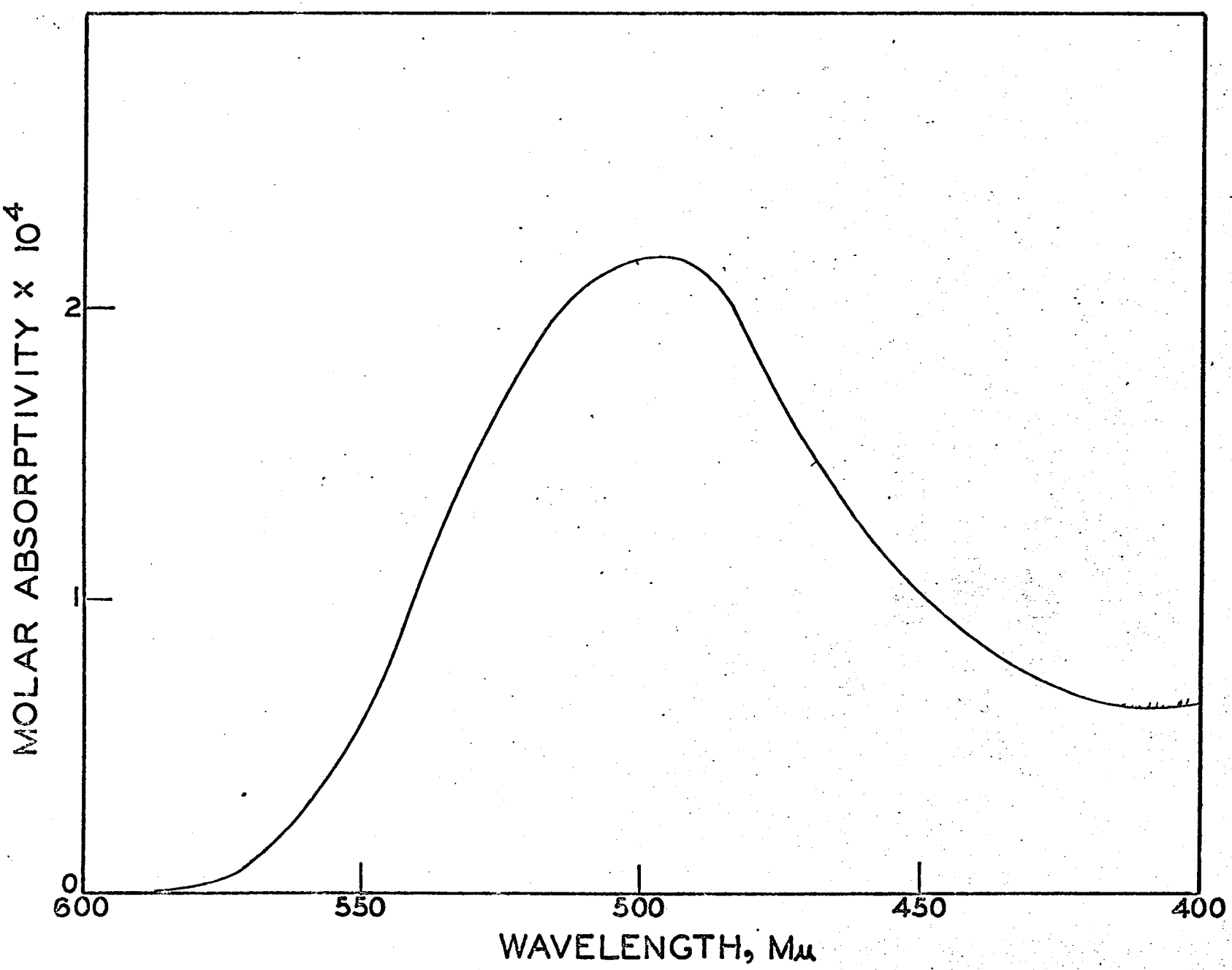
The solutions would also contain PbOxHDz·HOx and $Pb(HDz)_2$·HOx.

The data from SETS E1 and E2 (Tables 9 and 10, Appendix XXIX) were used. In these solutions, the initial concentration of dithizone was twice that of lead oxinate. It was found in the calculations that the concentrations of lead

FIGURE 74

CURVE OF ABSORPTIVITY VERSUS WAVELENGTH FOR PbOxHDz·HOx, IN BENZENE AT 25°C

Basic data: Table 15, Appendix XXIX


MOLAR ABSORPTIVITY X 10^4
2
1
0
600
550
500
450
400
WAVELENGTH, Mμ

oxinate were < 10^{-8} M in all the solutions and are therefore not reported.

The set of Beer's law equations given in Table 87 (excluding the term in $[PbOx_2]$) and the following two mass-balance equations

$$(Pb)_T = [PbOxHDz] + [Pb(HDz)_2] + [PbOxHDz \cdot HOx] + [Pb(HDz)_2 \cdot HOx] \quad (d)-45$$

$$(HDz)_T = [PbOxHDz] + 2[Pb(HDz)_2] + [PbOxHDz \cdot HOx] + 2[Pb(HDz)_2 \cdot HOx] + [H_2Dz] \quad (d)-46$$

were used to calculate the equilibrium concentrations directly, by solving the set of linear equations as outlined in subsection (a)(i)-1) of this Section. The equilibrium concentration of oxine was then calculated from

$$[HOx] = (Ox)_T - [PbOxHDz] - 2[PbOxHDz \cdot HOx] - [Pb(HDz)_2 \cdot HOx] \quad (d)-47$$

In SET E2, the initial concentration of free oxine was large compared to the initial concentrations of $PbOx_2$ and H_2Dz taken, so that this concentration was taken as the equilibrium concentration, $(HOx)_T$.

The equilibrium concentrations, the observed equilibrium constants and the stoichiometry checks are given in Table 88, The value of K_2 from SET E1 was not significantly different at the 95% confidence level, from that found from SET E2, nor were the variances. The grand average value of K_2 was 734 and the pooled standard deviation was 16.

Since the equilibrium concentrations given in Table 88 were calculated directly, they provided a means of confirming other,

TABLE 87

THE SYSTEM OF LINEAR BEER'S LAW EQUATIONS USED FOR THE CALCULATION OF EQUILIBRIUM CONCENTRATIONS IN THE LEAD SYSTEM

Path Length = 1 cm

		$a_{\lambda_{i,6}}[H_2Dz]$	+	$a_{\lambda_{i,2}}[Pb(HDz)_2]$	+	$a_{\lambda_{i,3}}[PbOxHDz]$
A_{618}	=	3.47				
A_{575}	=	2.16	+	0.85	+	0.24
A_{550}	=	1.19	+	3.87	+	1.16
A_{517}	=	0.54	+	6.47	+	2.72
A_{500}	=	0.61	+	5.83	+	2.73
A_{475}	=	1.46	+	3.72	+	1.95
A_{445}	=	1.84	+	1.71	+	0.90
A_{425}	=	1.58	+	1.04	+	0.52
A_{400}	=	0.91	+	0.76	+	0.34

Note: All absorptivities are factored by 10^4.

(Continued on next page)

TABLE 87 CONTINUED

THE SYSTEM OF LINEAR BEER'S LAW EQUATIONS USED FOR THE CALCULATION OF EQUILIBRIUM CONCENTRATIONS IN THE LEAD SYSTEM

Path Length = 1 cm

$a_{\lambda_{i,4}}[PbOxHDz \cdot HOx]$		+ $a_{\lambda_{i,5}}[Pb(HDz)_2 \cdot HOx]$		+ $a_{\lambda_{i,1}}[PbOx_2]$	
		+	0.53		
+	0.59	+	3.00		
+	1.95	+	5.81		
+	2.18	+	5.36		
+	1.67	+	3.45	+	0.036
+	0.94	+	1.66	+	0.214
+	0.71	+	1.09	+	0.377
+	0.65	+	0.68	+	0.453

Note: All absorptivities are factored by 10^4.

TABLE 88

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANTS FOR SETS E1 AND E2

Basic data: Tables 9 and 10, Appendix XXIX

Solution Number	Equilibrium Concentration M [PbOxHDz] x 10^6	[Pb(HDz)$_2$] x 10^6	[PbOxHDz·HOx] x 10^7	[Pb(HDz)$_2$·HOx] x 10^5	[H_2Dz] x 10^6	[HOx] x 10^5
PRE1- 1	2.676	46.56	-	3.088	3.052	12.67
2	2.075	34.12	-	1.385	1.811	8.030
3	1.109	19.44	-	0.4114	0.9995	4.290
4	0.2878	8.442	-	0.0750	0.7276	1.821
5	0.2431	7.330	-	0.0612	0.6084	1.518
6	0.1254	4.336	-	0.0236	0.4271	0.9266
PRE2- 1	3.273	1.758	30.11	7.199	6.024	800.7
2	2.365	1.704	13.01	4.244	5.026	500.0
3	1.806	1.528	4.438	2.055	2.890	250.0
4	0.6360	1.462	0.6067	0.7456	3.107	100.0
5	1.318	1.061	0.1265	0.5763	0.9083	80.00
6	0.9594	1.194	-	0.2812	0.8354	50.00

(Continued on next page)

TABLE 88 CONTINUED

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANTS FOR SETS E1 AND E2

Basic data: Tables 9 and 10, Appendix XXIX

Solution Number	$(Pb)_T$ Found M x 10^5	$(HDz)_T$ Found M x 10^5	Equilibrium Constants K_2	K_4 litre $mole^{-1}$	K_5 litre $mole^{-1}$ x 10^3
PRE1- 1	8.015	16.06	722	-	5.23
2	5.007	9.985	729	-	5.06
3	2.467	4.922	752	-	4.93
4	0.9480	1.940	734	-	4.88
5	0.8186	1.674	752	-	5.50
6	0.4698	0.9698	750	-	5.88
PRE2- 1	8.003	15.98	713	115	5.12
2	4.781	9.698	717	110	4.98
3	2.433	4.930	732	98.3	5.38
4	0.9615	2.164	740	95.4	5.10
5	0.8268	1.600	709	120	6.79
6	0.5009	0.9851	745	-	4.71

(Continued on next page)

TABLE 88 CONTINUED

EQUILIBRIUM CONCENTRATIONS AND EQUILIBRIUM CONSTANTS FOR SETS E1 AND E2

Basic data: Tables 9 and 10, Appendix XXIX

Average value of K_2 from Set E1	= 742
Variance	= 280
Average value of K_2 from Set E2	= 726
Variance	= 226
Grand average value of K_2	= 734
Pooled variance	= 253
Std. Dev.	= 16 (for 11 degrees of freedom)
Average value of K_4 from Set E2	= 108 litre $mole^{-1}$
Variance	= 116
Std. Dev.	= 11 (for 4 degrees of freedom)
Average value of K_5 from Set E1	= 5.25×10^3 litre $mole^{-1}$
Variance	= 14.70×10^4
Average value of K_5 from Set E2	= 5.42 litre $mole^{-1}$
Variance	= 20.60×10^4
Grand average value of K_5	= 5.33×10^3 litre $mole^{-1}$
Pooled variance	= 17.6×10^4
Std. Dev.	= 0.42×10^3 (for 11 degrees of freedom)

previously calculated equilibrium constants, namely:

(1) From the concentrations of PbOxHDz·HOx, PbOxHDz, and HOx in SET E2 of Table 88, K_4 for the reaction

$$PbOxHDz + HOx = PbOx(HDz)HOx$$

was found to be 108 litre moles^{-1}. This value proved not to be significantly different at the 95% level of confidence from the value of 113 already calculated in subsection (iv), page 395.

(2) From the concentrations of $Pb(HDz)_2$, HCx, and $Pb(HDz)_2$·HOx in SETS E1 and E2 in Table 88, K_5 for the reaction

$$Pb(HDz)_2 + HOx \rightleftharpoons Pb(HDz)_2 \cdot HOx$$

was calculated separately for the two sets. However, the value of K_5 from SET E1 was not different from that found from SET E2, so they were combined to give $K_5 = 5.33 \times 10^3$ litre mole^{-1}.

This value proved not to be significantly different from the value 5.44×10^3 already calculated in subsection (iii), page 389.

Since the value of K_3 reported in subsection (ii), page 381 also provided the value of $a_{\lambda_{i,4}}$ used above to evaluate K_4, and since this latter value of K_4 agreed well with that obtained directly in this subsection (Table 88), then this latter agreement indirectly substantiated the value of K_3. If K_3 had been wrong it would have undoubtedly affected the values of K_4 and K_5 in experiments of this subsection.

(vi) Calculation of the Equilibrium Constant for Reaction (d)-III, K_1, and that of the Overall Reaction (d)-I, K_0

Reaction (d)-III was postulated to be

$$PbOx_2 + H_2Dz \rightleftarrows PbOxHDz + HOx \qquad \text{(d)-III}$$

and Reaction (d)-I

$$PbOx_2 + 2H_2Dz \rightleftarrows Pb(HDz)_2 + 2HOx \qquad \text{(d)-I}$$

It was shown in subsection (d)(i)-2) that

$$K_1 = K_2K_3 \qquad \text{(d)-8}$$

and

$$K_0 = K_2^2K_3 \qquad \text{(d)-9}$$

Therefore, on using the values of K_3 and K_2 in Tables 82 and 88 respectively (pages 381 and 403-5),

$$K_1 = 1.380 \pm 0.105 \times 10^5$$

$$K_0 = 1.013 \pm 0.086 \times 10^8$$

(vii) Summary of the Reactions of the Lead Chelates and their Equilibrium Constants

The prescribed reactions were:

$$PbOx_2 + H_2Dz \overset{K_1}{\rightleftarrows} PbOxHDz + HOx \qquad \text{(d)-III}$$

$$PbOxHDz + H_2Dz \overset{K_2}{\rightleftarrows} Pb(HDz)_2 + HOx \qquad \text{(d)-IV}$$

$$PbOx_2 + Pb(HDz)_2 \overset{K_3}{\rightleftarrows} 2PbOxHDz \qquad \text{(d)-II}$$

$$PbOxHDz + HOx \overset{K_4}{\rightleftarrows} PbOxHDz \cdot HOx \qquad \text{(d)-V}$$

$$Pb(HDz)_2 + HOx \overset{K_5}{\rightleftarrows} Pb(HDz)_2 \cdot HOx \qquad \text{(d)-VI}$$

$K_1 = 1.380 \pm 0.105 \times 10^5$ (d)-48

$K_2 = 734 \pm 16$ (11 deg. of freedom) (d)-49

$K_3 = 188 \pm 37$ (10 deg. of freedom) (d)-50

$K_4 = 110 \pm 19$ litre mole^{-1} (18 deg. of freedom) (d)-51

$K_5 = 5.38 \pm 0.40 \times 10^3$ litre mole^{-1} (24 deg. of freedom) (d)-52

(viii) Note of the Formation of an Adduct of Dithizone with Lead Dithizonate

The data of SET D were used to investigate the formation of the adducts, $Pb(HDz)_2 \cdot nH_2Dz$. Experiments had shown that when $Pb(HDz)_2$ was mixed with dithizone in benzene, there was no reaction; and in benzene dried with silica gel and with calcium hydride there was again no evidence of reaction. However, when lead oxinate was mixed with a large excess of dithizone (SET D), the absorbance data indicated a reaction hitherto unspecified in the present work. However, the calculations proved to be inconclusive. Thus, the concentration of the suggested adduct, $Pb(HDz)_2 \cdot H_2Dz$ was never higher than the value expected merely from statistical fluctuations. The difference between the experimental absorbances in the region 600 to 400 mμ and those calculated assuming that only $Pb(HDz)_2$, $Pb(HDz)_2 \cdot HOx$ and H_2Dz were present in the solution was found to be on the edge of the 95% confidence limits of the standard error of the mean of the calculated absorbances, The experimental absorbances, however, were all consistently greater than the calculated absorbances. Unfortunately higher concentrations of dithizone could not be used because then the absorbance of the benzene solutions would have been higher than the upper limit that the instrument could measure, i.e. 2.00 with a 0.1 cm cell.

(ix) Calculation of the Titration Graph for the Titration of Lead Oxinate with Dithizone in Benzene at 25°C

The theoretical titration graph for the titration of lead oxinate with dithizone in benzene was calculated only for the case when the titration solution contained a one-hundredfold excess of free oxine with respect to the initial concentration of lead oxinate. In this case, the approximation could be made that the equilibrium concentration of oxine was the same as the concentration added to the solution. Without this approximation, such as would be the case when no initial free oxine was present, it was impossible to derive a solvable equation in one unknown variable. Other approximations such as examining portions of the titration graph, and making assumptions that certain species were not present, were attempted without success.

However, the calculations of this subsection used all the equilibrium constants evaluated in the previous subsections. Thus, the results of the calculations may be considered to verify the accuracy of the equilibrium constants for all titrations.

The analytical data for the titration of lead oxinate with dithizone in the presence of initial free oxine is given in Table 89. The mass-balance equations were:

$$(Pb)_T = [PbOx_2] + [Pb(HDz)_2] + [PbOxHDz] + [PbOxHDz \cdot HOx] + [Pb(HDz)_2 \cdot HOx] \qquad (d)-53$$

TABLE 89

CALCULATED EQUILIBRIUM CONCENTRATIONS OF SPECIES PRESENT IN SOLUTION WHEN $PbOx_2$ WAS TITRATED WITH DITHIZONE IN BENZENE AT 25°C, FOR THE CASE WHERE THE SOLUTION CONTAINED FREE OXINE, ONEHUNDREDFOLD IN EXCESS WITH RESPECT TO THE INITIAL $PbOx_2$ CONCENTRATION

Molarity of stock H_2Dz solution in benzene = 2.5×10^{-3} M
Initial Molarity of $PbOx_2$ in titration solution = 3.02×10^{-6} M
Molarity of HOx in titration solution = 3.012×10^{-4} M
Volume of solution = 50 ML

ML H_2Dz Added	$(HDz)_T$ M $\times 10^6$	Equilibrium Concentration M $[PbOx_2] \times 10^7$	$[PbOxHDz] \times 10^7$	$Pb(HDz)_2 \times 10^6$	$[PbOxHDz \cdot HOx] \times 10^8$	$[Pb(HDz)_2 \cdot HOx] \times 10^6$	$[H_2Dz] \times 10^6$
0	0	30.20	0	0	0	0	0
0.02	1.0	20.26	9.546	0.0021	3.335	0.0034	-
0.04	2.0	10.63	18.52	0.0151	6.472	0.0248	0.0033
0.06	3.0	2.856	24.01	0.943	8.389	0.1551	0.0161
0.08	4.0	0.4925	19.49	0.3604	6.811	0.5928	0.0760
0.10	5.0	0.1018	12.05	0.6666	4.210	1.096	0.2273
0.12	6.0	0.0197	6.156	0.9003	2.151	1.480	0.6009
0.14	7.0	0.0048	3.224	1.016	1.126	1.670	1.294
0.16	8.0	0.0018	2.014	1.063	0.7038	1.748	2.168
0.18	9.0	-	1.435	1.086	0.5014	1.785	3.108
0.20	10.0	-	1.108	1.098	0.3870	1.806	4.074
0.22	11.0	-	0.8998	1.106	0.3144	1.819	5.052
0.24	12.0	-	0.7568	1.112	0.2644	1.828	6.037

$$(HDz)_T = 2[Pb(HDz)_2] + [PbOxHDz] + [PbOxHDz \cdot HOx] + 2[Pb(HDz)_2 \cdot HOx] + [H_2Dz] \qquad (d)-54$$

$$(Ox)_T = 2[PbOx_2] + [PbOxHDz] + 2[PbOxHDz \cdot HOx] + [Pb(HDz)_2 \cdot HOx] + (HOx) \qquad (d)-55$$

$$(HOx)_A = [HOx]$$

The mass-law equations were

$$K_1 = \frac{[PbOxHDz][HOx]}{[PbOx_2][H_2Dz]} \qquad (d)-3$$

$$K_2 = \frac{[Pb(HDz)_2][HOx]}{[PbOxHDz][H_2Dz]} \qquad (d)-4$$

$$K_4 = \frac{[PbOxHDz \cdot HOx]}{[PbOxHDz][HOx]} \qquad (d)-5$$

$$K_5 = \frac{[Pb(HDz)_2 \cdot HOx]}{[Pb(HDz)_2][HOx]} \qquad (d)-6$$

(see subsection (vii), page 407, of this section for the numerical values of the equilibrium constants). Substitution of equations (d)-3 to (d)-6 into equations (d)-53 and (d)-54 gave:

$$(Pb)_T = [PbOx_2]\{1 + K_1K_2\frac{[H_2Dz]^2}{(HOx)_A^2} + K_1\frac{[H_2Dz]}{(HOx)_A} + K_1K_4[H_2Dz] + K_1K_2K_5\frac{[H_2Dz]^2}{(HOx)_A}\}$$

$$(HDz)_T = [PbOx_2]\{2K_1K_2\frac{[H_2Dz]^2}{(HOx)_A^2} + K_1\frac{[H_2Dz]}{(HOx)_A} + K_1K_4[H_2Dz] + 2K_1K_2K_5\frac{[H_2Dz]^2}{(HOx)_A}\} + [H_2Dz]$$

Let

$$K_0 = K_1K_2$$

$$K_A = K_1(HOx)_A$$

$$K_B = K_1K_4(HOx)_A^2$$

$$K_C = K_1K_2K_5(HOx)_A^2$$

$$K_A + K_B = K_A^1$$

$$K_0 + K_C = K_0^1$$

Then

$$[PbOx_2] = \frac{(Pb)\ (HOx)_A^2}{\{(HOx)_A^2 + K_A^1[H_2Dz] + K_0^1[H_2Dz]^2\}} \qquad (d)\text{-}56$$

$$[PbOx_2] = \frac{\{(HDz)_T - [H_2Dz]\}(HOx)_A^2}{\{K_A^1[H_2Dz] + 2K_0^1[H_2Dz]^1\}} \qquad (d)\text{-}57$$

On equating these two equations, an expression in $[H_2Dz]$ alone was obtained:

$$[H_2Dz]^3 + [H_2Dz]^2\{\frac{K_A^1}{K_0^1} + 2(Pb)_T - (HDz)_T\} + [H_2Dz]$$

$$\{\frac{(HOx)_A^2}{K_0^1} + \frac{K_A^1}{K_0^1}((Pb)_T - (HDz)_T)\} - \frac{(HOx)_A^2(HDz)_T}{K_0^1} = 0 \quad (d)\text{-}58$$

By using the analytical data given in Table 89 and the numerical values of the relevant equilibrium constants, the coefficients of equation (d)-58 were calculated for each increment of dithizone added. The resulting cubic equations were then solved by a computer program for solving polynomials. There was only one real positive root of each equation, and it was substituted into equation (d)-56 to obtain $[PbOx_2]$. The values of $[PbOx_2]$ and $[H_2Dz]$ were then substituted where necessary into equations (d)-3 to (d)-6, to obtain the equilibrium concentrations of each of the species. These results are given in Table 89.

From the equilibrium concentrations and the relevant absorptivities (given in Table 87, pages 401-2) the absorbances

at 618 mμ and 517 mμ were calculated. The calculated absorbances are compared with the experimental absorbances in Table 90 and graphically in Figure 75.

The agreement is very good. The very good agreement between calculated and experimental absorbances serves to confirm the values of K_1, K_2, K_4, K_5, $a_{517,3}$, $a_{517,4}$ and $a_{517,5}$ obtained in the previous subsections.

As further proof that a mixed chelate and adducts must be postulated in order to explain the experimental titration graph, a titration graph was calculated by assuming the existence of only $PbOx_2$, $Pb(HDz)_2$, HOx and H_2Dz. This graph required the use only of the value of K_0 (subsection (vi) page 407). The required equation in $[H_2Dz]$ was

$$[H_2Dz]^3 + [H_2Dz]^2\{2(Pb)_T - (HDz)_T\} + [H_2Dz]\frac{(HOx)_A^2}{K_0} - (HDz)_T\frac{(HOx)_A^2}{K_0} = 0$$

The equilibrium concentrations of $PbOx_2$ and $Pb(HDz)_2$ were calculated in the same way as given above, wherefrom the absorbances at 618 and 517 mμ were calculated. In Table 90 and Figure 75 these absorbances are compared with the experimental ones. The degree of disagreement demonstrates that the species PbOxHDz, PbOxHDz·HOx and $Pb(HDz)_2$·HOx must be postulated. Furthermore, only by including these latter species in the calculations can the curvature in the experimental graph be accounted for; curvature would be negligibly

TABLE 90

COMPARISON OF EXPERIMENTAL AND CALCULATED ABSORBANCES FOR THE TITRATION OF $PbOx_2$ WITH DITHIZONE IN BENZENE FOR THE CASE WHERE THE SOLUTION CONTAINED FREE OXINE, ONE-HUNDREDFOLD IN EXCESS WITH RESPECT TO THE INITIAL $PbOx_2$ CONCENTRATION

Initial Molarity of stock H_2Dz solution in benzene = 2.500×10^{-3} M
Molarity of $PbOx_2$ in titration solution = 3.020×10^{-6} M
Molarity of HOx in titration solution = 3.012×10^{-4} M
Volume of solution = 50 ML
Pathlength = 5 cm

ML H_2Dz Added	Absorbance					
	618 mμ		517 mμ		*	
	Calc.	Exp.	Calc.	Exp.	618 mμ	517 mμ
0	0	0	0	0	0	0
0.02	0	0.001	0.135	0.144	0.002	0.160
0.04	0.001	0.001	0.270	0.289	0.003	0.321
0.06	0.003	0.004	0.411	0.423	0.005	0.482
0.08	0.013	0.013	0.563	0.583	0.007	0.642
0.10	0.039	0.040	0.708	0.721	0.010	0.801
0.12	0.104	0.083	0.823	0.834	0.027	0.950
0.14	0.224	0.210	0.893	0.892	0.167	1.002
0.16	0.376	0.384	0.937	0.931	0.340	1.030
0.18	0.539	0.541	0.972	0.975	0.514	1.057
0.20	0.707	0.717	1.004	1.002	0.687	1.084
0.22	0.877	0.905	1.033	1.022	0.861	1.111
0.24	1.047	1.032	1.062	1 040	1.034	1.138

* Calculated on the assumption that only $PbOx_2$, $PbDz_2$; HOx and H_2Dz were present in the titration solution.

FIGURE 75

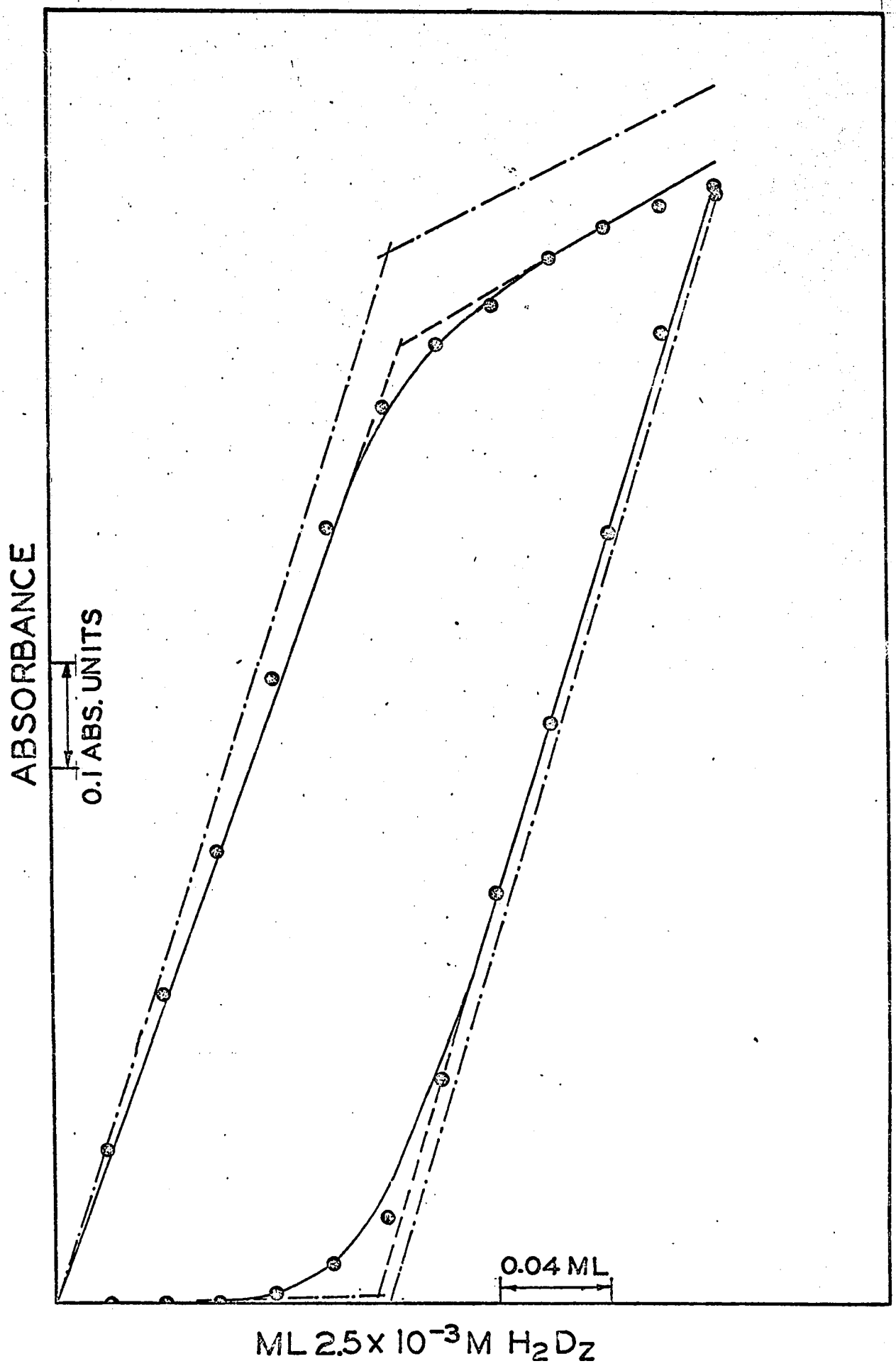
CALCULATED AND EXPERIMENTAL TITRATION GRAPHS FOR THE TITRATION OF LEAD OXINATE WITH DITHIZONE IN BENZENE AT 25°C FOR THE CASE WHERE THE SOLUTION CONTAINED INITIAL FREE OXINE, ONEHUNDREDFOLD IN EXCESS WITH RESPECT TO THE INITIAL CONCENTRATION OF LEAD OXINATE

Basic data: See Tables 89 and 90
Path length = 5 cm

● Experimental points

---- Calculated graph assuming the species given in Table 89 were present

-·-·- Calculated graph assuming only $PbOx_2$, $Pb(HDz)_2$, HOx and H_2Dz were present


ABSORBANCE
0.1 ABS. UNITS
0.04 ML
ML 2.5 x 10⁻³ M H₂Dz

small if they were assumed absent, because the value of K_0 is so large.

The species also account for the slight negative (at 618 mμ) and positive (at 517 mμ) errors in the end points (see Table 40, subsection 1(c), Section (IV-D, page 246). The reason for these errors is that the species have changed the slope of the second branch of the curve at 618 mμ, and the first branch of the curve at 517 mμ.

V DISCUSSION

A. TITRATIONS

1. Sources of Error

(a) Titration of Metal Dithizonates in Chloroform with Sodium Diethyldithiocarbamate in Ethanol

(i) Effect of free dithizone

The effect of free dithizone on the error of a titration was found to be negligible except in the case of silver dithizonate (pages 224 to 229) up to a free dithizone concentration of 10^{-4} molar. The effect of higher concentrations could not be explored because then the initial absorbance of the titration solution was beyond the range of the instrument. This negligible effect of free dithizone indicated a high equilibrium constant for the relevant reaction.

$$M(HDz)_n + nNaD = MD_n + nNa^+ + nHDz^-$$

The curvature observed in the titration graphs (see Figure 45, page 231) was attributed to intermediate species such as mixed chelates and adducts in the solutions.

The presence of initial free dithizone in the silver dithizonate titrations increased the percentage error as the initial concentration of dithizone was increased (Table 32, page 224). Therefore the equilibrium constant of the reaction between silver dithizonate and sodium diethyldithiocarbamate probably is lower than the others. The curvature at the end-point also increased as the initial

free dithizone concentration was increased (see Figure 45(d) and (e)) which further indicates a lower equilibrium constant and, in addition, the presence of adducts*.

(ii) Effect of wavelength

In general, equally accurate and precise results were obtained both at 615 mμ and at the absorption peak of the metal dithizonate. The means and variances were not significantly different (see Table 56 page 276).

(iii) Effect of concentration on the accuracy and precision of titrations

The accuracy and precision of the chelate-exchange titrations was unaffected by a ten-fold change in the concentration of the metal dithizonate (see Tables 32-34 pages 224-226).

(b) Titrations of Mixtures of Metal Dithizonates with Sodium Diethyldithiocarbamate

Not all mixtures were successfully titrated (see page 230). In the successful cases, the end-points for the various components titrated were generally accurate and precise (Tables 38 and 39 pages 233 and 234). It was found that the optimum wavelength was at the

---

* It is assumed that since the formulae of silver dithizonate and diethyldithiocarbamate are AgHDz and AgD respectively mixed chelates did not form.

absorption peak of the second component titrated in a binary mixture, and at the peak of the middle component titrated in the case of a ternary mixture. Only equimolar mixtures were studied in the present work; changing the ratio of one component to another could affect the accuracy.

The component that was titrated first, second and, in the case of ternary mixtures, third was correctly predicted by calculating a titration graph from absorptivity data and the expected concentrations of the participating species and then comparing the shape with the experimental graph. For example, in the titration of copper and zinc dithizonates at 530 mμ, if zinc dithizonate were to be titrated first, the titration graph would have a steep negative slope, followed by a much less negative slope representing the titration of copper dithizonate. If copper dithizonate were to be titrated first, the graph should have a slightly negative slope, followed by a steep negative slope representing the titration of zinc dithizonate. The latter was the shape of the experimental graph (see Figure 46(a), page 235).

(c) Titration of Metal Oxinates with Dithizone in Benzene

(i) Effect of free oxine

The accuracy of the titration of zinc, cadmium and lead oxinates with dithizone was unaffected by the initial presence of free oxine.

Consequently the equilibrium constant for the overall reaction

$$MOx_2 + 2H_2Dz = M(HDz)_2 + 2HOx$$

must have been high for all three metals and in the case of lead was in fact measured and found to be 1.013×10^8. However, initial free oxine did affect the accuracy of the titration of copper and indium oxinates. In the case of indium oxinate the measured value of the equilibrium constant was 1.144×10^3. With this relatively low value, initial free oxine would be expected to affect the accuracy of the titration. Unlike the titration of zinc, cadmium and lead oxinates, the accurate titration of indium oxinate required that a correction be applied for the presence of free oxine, and this correction has been described in section IV D subsection 2(d).

In the case of copper the overall equilibrium constant was 2.64×10^7. Therefore the observed effect of free oxine on the accuracy of the titration did not seem to be attributable to an incomplete reaction. The complete study undertaken for this reaction, however, provided a satisfactory explanation.

The reactions found to take place up to the end-point for this particular titration were:

$$CuOx_2 + Cu(HDz)_2 = 2CuDz + 2HOx \qquad (V)\text{-I}$$

$$CuOx_2 + 2H_2Dz = Cu(HDz)_2 + 2HOx \qquad (V)\text{-II}$$

$$CuDz + H_2Dz = Cu(HDz)_2 \qquad (V)\text{-III}$$

The production of the secondary copper dithizonate, CuDz, caused initial free oxine to affect the position of the end-point. The effect was produced in the following way: it was shown in section IV D subsection 3(b) page 322 that during the early part of a titration, when the initial concentration of copper oxinate greatly exceeded the amount of added dithizone, that CuDz was primarily produced. Thus during the early stages of the titration the predominant reaction can be formulated from reactions (V)-I, (V)-II to be:

$$CuOx_2 + H_2Dz = CuDz + 2HOx \qquad (V)\text{-IV}$$

The value of K for this reaction is the product of K_1 and K_2 (pages 331 and 332); $K_1K_2 = 0.0384$. With such a low equilibrium constant it is clear that initial oxine will greatly affect the extent of reaction (V)-IV at any point during the early part of the titration (see Figure 60, page 332). That is to say this reaction will determine the slopes of the first branch of the titration graphs at 618 mμ and 545 mμ. The latter part of the graph before the end-point would represent predominantly the conversion of the secondary to the primary copper dithizonate. Since these two dithizonates have different absorptivities, the first branch of the titration graph would be expected to be curved (see Figure 59, page 329). In fact it was found to be essentially a straight line. The reason for this discrepancy is that the titration was carried out under reproducible, but non-equilibrium conditions. This non-equilibrium fortuitously

lead to a straight line. Nevertheless, increasing amounts of free oxine initially present affected the extent of reaction (V)-IV so that the slope of the first branch of the titration graph was reduced. This in turn placed the intersection point, that is, the end-point, further to the right which thereby introduced the positive error into the titration.

It was found that the slope of the correction curve for titrations performed at 618 mμ was lower and significantly different from that at 545 mμ (section IV D subsection (c)-(iii) and Figure 53, page 265). The explanation proposed is as follows: at 618 mμ the absorptivities of CuDz and $Cu(HDz)_2$ are low and not very different from each other (0.68×10^4 for CuDz versus 1.24×10^4 for $Cu(HDz)_2$). At 545 mμ the absorptivities are higher and their difference is more pronounced (0.79×10^4 for CuDz versus 4.11×10^4 for $Cu(HDz)_2$). Thus, the change of slope in the first branch of the titration graph at 618 mμ due to increasing initial concentrations of free oxine is less pronounced than at 545 mμ and this results in a less positive error.

The difference in precision at the two wavelengths (as shown by the 95% confidence-limit curves in Figure 53) must also be attributed to the non-equilibrium conditions of the titration and the curvature in the graphs as noted above.

The variance of the slope of the first branch of the titration curve at 618 mμ would be greater than it was at 545 mμ due to the different effects of curvature. This in fact was the effect observed. It must be noted that the curvature that is being discussed was slight, and in fact was not visible to the eye in the plotted titration graphs.

Table 40 page 246 shows that the results for the titration of lead oxinate with dithizone were negative at 618 mμ and positive at 517 mμ. Furthermore, the grand means at 618 and 517 mμ were significantly different (Table 55 page 273). The results of Section IV D subsection 3(d), page 409 showed that this was to be expected. Figure 75 showed that at 618 mμ, intersection of the linear portions of the graph came before the stoichiometric end-point and that at 517 mμ after it. Thus, the presence of the species PbOxHDz, PbOxHDz.HOx and $Pb(HDz)_2$.HOx caused a less positive slope in the first branch of the titration graph at 517 mμ. The concentration of $Pb(HDz)_2$ from the overall reaction:

$$PbOx_2 + 2H_2Dz = Pb(HDz)_2 + 2HOx \qquad (V)\text{-}VI$$

was less than expected because the species listed above were present. After the end-point the slope was not greatly affected by the changing proportions of the various species, because of the relatively low absorptivity of dithizone (0.54×10^4) at 517 mμ. At 618 mμ the slope of the first branch of the titration graph was almost zero because it was

dependent solely on the concentration of free dithizone which itself was very small. In this case the changing proportions of PbOxHDz, PbOxHDz.HOx; $Pb(HDz)_2$.HOx and $Pb(HDz)_2$ had little noticeable effect on the slope because they did not absorb at 618 mμ. However, just preceding, and also after the end-point the concentration of free dithizone became relatively large in the titrations. In the absence of intermediates and adducts the slope of the second branch of the titration graph would be dependent solely on Reaction (V)-VI. In fact the experimental slope was less than that calculated by the use of equation (V)-VI. This decrease in slope is satisfactorily explained by the presence of the adducts and the mixed chelates. The effect is clearly evident in Figure 75.

Approximately the same effect was observed for the titration of zinc oxinate at 42.4°C (Table 47 page 253) but the reverse effect was observed for the titration of cadmium oxinate (Table 42 page 248). However, Table 55 page 273 showed that unlike the behaviour of copper and lead, there was no significant difference between the titration results obtained at 618 mμ and those obtained at the absorption peaks of cadmium and zinc dithizonates.

(ii) Note on the theoretical and experimental titration graphs for the titration of copper oxinate with dithizone

The disagreement between the theoretical and experimental titration graphs (Figures 59 and 60, pages 329

and 332) is due to the non-equilibrium conditions of the experimental titration graph, as noted above. This explanation is as follows: Figure 48, page 238 demonstrated that when a solution of dithizone was added to a solution copper oxinate, $Cu(HDz)_2$ was produced first (shown by the rate curve at 545 mμ). This species then reacts slowly with the excess copper oxinate to form CuDz, by reaction (V)-I (the absorbance at 442 mμ increases sharply after about 3 hours). The final absorbance corresponds to that obtained for a comparable point on the theoretical titration graph.

(iii) Effect of concentration on accuracy and precision of the titrations

The accuracy and the precision of titrations of the metal oxinates was found not to vary when the initial concentration of metal oxinate was varied over a ten fold concentration range (see Figures 53 page 265 and Figure 54 page 271).

2. Kinetics

Figures 48-50 pages 239-240 show the rate curves when dithizone was added to $CuOx_2$, $ZnOx_2$ and $CdOx_2$ respectively.

The titrations of copper oxinate were carried out under non-equilibrium conditions, but the rate curve showed that the absorbance was constant for a much longer period of time than it took to perform a titration. In fact,

the results of the titrations were not affected.

The rate curves of zinc and cadmium oxinates were unusual and require interpretation. Since quantitative measurements to determine rate constants were not made, this interpretation is qualitative.

The shapes of the rate curves indicated that two reactions were simultaneously taking place. For example in Figure 49 the absorbance at 618 mμ for the reaction of zinc oxinate with dithizone at 25°C decreased slowly for a period and then rapidly dropped to a more or less constant level. If it is assumed that zinc oxinate formed a mixed-chelate then the reaction mechanism would be written as:

$$ZnOx_2 + H_2Dz = ZnOxHDz + HOx \qquad (V)\text{-VII}$$

$$ZnOxHDz + H_2Dz = Zn(HDz)_2 + HOx \qquad (V)\text{-VIII}$$

wherein reaction (V)-VII is postulated to be the rate-determining step. The presence of initial free oxine decreased the rate. This is to be expected from the above reaction mechanism since the rate would depend on the concentration of ZnOxHDz. With a large excess of free oxine, less ZnOxHDz would be present for a given concentration of added dithizone. The effect of temperature on the rate of reaction of $ZnOx_2$ with dithizone is also illustrated in Figure 49. The rate increased with increasing temperature.

The rate of reaction of cadmium oxinate with dithizone (Figure 50) was higher than that of zinc oxinate. Totally unexpected was the fact that increasing temperature

decreased the rate of reaction. Increasing the concentration of free oxine also decreased the rate. Thus a reaction mechanism similar to reactions (V)-VII and (V)-VIII may not apply to the reaction of cadmium oxinate with dithizone.

3. Application to Solvent Extraction

A major purpose of the present work was to develop a simple, yet accurate analytical method to determine the concentration of the extracted metal for liquid-liquid extraction methods. The method has been successfully demonstrated for the determination of a metal dithizonate and a metal oxinate in benzene which was nearly saturated with water.

In most solvent extraction methods, it is necessary to add a large excess of extractant to obtain complete extraction, and in general it is both inconvenient and less accurate to remove the excess reagent.

When a metal is extracted by dithizone from basic solution, any excess dithizone remains in the aqueous phase and presents no problem. In extraction from acid solutions, excess free dithizone remains in the nonaqueous phase. Most methods require that either (i) the concentration of added dithizone be exactly equivalent to the metal, or (ii) the free dithizone be removed by shaking with basic solution or (iii) allowing the dithizone to remain, measuring

the absorbance at 618 mμ and subtracting the concentration of free dithizone calculated from this absorbance and its known absorptivity. In the titrimetric method recommended in the present work, none of the above conditions need be met. The only requirement is that the concentration of free dithizone in the nonaqueous phase not be so high as to increase the absorbance at the peak of the metal dithizonate, beyond the range of the spectrophotometer.

The presence of free oxine was found to affect the accuracy of the titration of $CuOx_2$ and of $InOx_3$ and therefore correction curves were devised. The use of these correction curves depends on knowing the concentration of free oxine in the organic extract. Two methods for determining this concentration are suggested. Method one applies only when the concentration of free oxine is much greater than that of the metal oxinates. Method two is a general method and applies for any concentration of oxine.

1. Measurement of the absorbance of free oxine at 313 mμ, and computation of its concentration from its absorptivity at this wavelength (2.50×10^3). The absorptivities of the metal oxinates at 313 mμ are similar to that of oxine (see Figure 42, page 210) so that there will be some error. However in most metal oxinate extraction methods the concentration of free oxine must be much greater than that of the metal oxinate (122). Consider the extraction of copper oxinate with a onehundredfold

excess of free oxine and let the concentration $CuOx_2$ be 3.463×10^{-6}M and that of oxine, 3.67×10^{-4}M. The absorptivity of $CuOx_2$ at 313 mμ is 2.37×10^3 and that of oxine 2.5×10^3. In a 5-cm cell the absorbance due to $CuOx_2$ would be 0.008, while that due to oxine would be 0.920. If the total absorbance of 0.928 were taken to be due only to free oxine, the calculated concentration of HOx would be 3.71×10^{-4}M; the difference is <1% with respect to the actual concentration of 3.67×10^{-4}M. It was shown in Section IV D subsection 2(c) that an error of 5% in the oxine concentration could be tolerated without causing a significant error in the copper oxinate concentration obtained for the correction curve.

2. Determination of the oxine concentration in a separate aliquot using the procedure outlined in Section IV C subsection 3(b). This method will give the most accurate result for the oxine concentration.

B. RANGE OF TITRATABLE CONCENTRATIONS

1. Range of Concentration

The upper and lower limits for the titration of single metal dithizonates and oxinates were calculated by using the absorptivities given in Appendix XX. These calculated limits are given in Table 91. They are based on the following conditions:

1. For the titration of metal dithizonates in which the absorption peak used was that of the metal dithizonate, the initial absorbance was 1.95 and decreased towards 0 during the titration.
2. For the titration of metal oxinates using the absorption peak of metal dithizonate, the initial absorbance was 0 and increased to 1.95 at the end-point.
3. For the titration of metal dithizonates at 618 mμ the initial absorbance was 0 and rose to a value 1.95 at the end-point.
4. For the titration of metal oxinates at 618 mμ, the initial absorbance was 0 and remained there up to the end-point.

The lower limits in Table 91 could be improved by two evident techniques:

1. Evaporation of the sample solutions to 25 ml* and thereby

---

* 25 ml is about the smallest volume that could be used with the 60-ml titration cell, and still keep the solution fully in the light path.

TABLE 91

RANGE OF TITRATABLE CONCENTRATIONS FOR THE TITRATION OF METAL DITHIZONATES IN CHLOROFORM WITH SODIUM DIETHYLDITHIOCARBAMATE IN ETHANOL, AND OF METAL OXINATES WITH DITHIZONE IN BENZENE, AT 25°C

	Titration of $M(HDz)_2$ in Chloroform				Titration of MOx_n in Benzene			
	Upper Limit*		Lower Limit**		Upper Limit*		Lower Limit**	
METAL	$M \times 10^5$	ug	$M \times 10^7$	ug	$M \times 10^5$	ug	$M \times 10^7$	ug
Wavelength setting: Peak of Metal Dithizonate[1]								
Ag	14	76	7.2	3.9	-	-	-	-
Cu	9.5	30	5.0	1.6	7.3	23	5.0	1.6
Pb	6.0	62	3.0	3.1	4.6	48	3.0	3.1
Zn	4.1	13	2.1	0.7	3.1	10	2.1	0.7
Cd	4.9	27	2.5	1.4	3.8	21	2.5	1.4
In	3.8	22	1.9	1.1	2.9	17	1.9	1.1
Wave length setting: Peak of Dithizone[1]								
ALL METALS STUDIED	5.5×10^{-6}	-	3.0×10^{-7}	-	(2)	-	2.0×10^{-8}	-

TABLE 91 CONT.

(1) See Tables 32-37 and 40-50 pages 224-229 and 246-256 for the wavelengths.
(2) Determined by the solubility of the metal oxinate in benzene (see Appendix XII)
* Based on a 5-ml sample solution, diluted to 50ml before titration
** Based on a 50-ml sample solution, titrated without dilution

concentrating the metal chelate by factor of two.

2. Evaporation of the sample solutions to 2.5 ml and using the micro-titration cell described in Section IV A subsection (1) page 115. The lower limits could thereby be reduced by a factor of approximately 10.

2. Comparison with Other Techniques

The spectrophotometric titration method developed for the metals studied in the present work has lower limits of determinable concentrations than have conventional polarography and emission spectroscopy, and slightly higher limits than have colorimetric methods (mostly with dithizone). This titration method fills a need for a rapid and inexpensive method of determining trace metals. The concentration range lies approximately between that attainable with conventional polarography and that attainable with the more expensive instrumentation of atomic absorption spectroscopy or neutron activation analysis. Moreover in the determination of trace metals the chelate-exchange titration method is more advantageous and than colorimetric methods in that it is more rapid, and more convenient to use.

A comparison of typical lower limits obtainable with various instrumental methods is given in Table 92.

TABLE 92

TYPICAL LOWER LIMITS OF DETERMINABLE CONCENTRATIONS FOR VARIOUS INSTRUMENTAL METHODS

Metal	Colorimetry	Conventional Polarography	Atomic-Absorption Spectroscopy*	Emission Spectroscopy*	Spectrophotometric Titration **
	M x 10^7	M x 10^6	M x 10^8	M x 10^6	M x 10^7
Ag	6 (2)	5 (3)	9	0.1	7
Cu	5 (4)	50 (5)	8	0.8	5
Pb	2 (6)	1 (5)	5	20	3
Zn	0.8(4)	1 (5)	3	60	2
Cd	0.9(4)	1 (5)	9	2	2.5
In	0.6(7)	10 (5)	40	90	2

*(1) V. A. Fassel and D. W. Golightly, Anal. Chem.,39,466(1967)
(2) G. C. B. Cave and D. N. Hume, Anal. Chem., 24,1503 (1952) ("Rhodanine" Method)
(3) G. C. B. Cave and D. N. Hume, Anal. Chem., 24,588 (1952)
(4) F.D. Snell and C. T. Snell, "Colorimetric Methods of Anaysis", Vol.II, 3rd Ed., D. Van Nostrand Co. Ltd., New York (1959). (Dithizone methods)
(5) G. W. C. Milner, "The Principles and Applications of Polarography", Longmans, Green and Co., London (1957).
(6) O. B. Mathre and E. B. Sandell, Talanta, 11, 295 (1964). (Dithizone method)
(7) I. May and J. I. Hoffman, J. Washigton Acad. Sci., 38, 329 (1948). (Dithizone method)

**This work

C. REACTIONS OF THE METAL CHELATES

1. Introduction

Before discussing the chemistry of the chelate-exchange reactions studied in the present work, it is necessary briefly to review the pertinent chemistry of dithizone and the metal dithizonates, and of oxine and the metal oxinates. The reactions studied in the present work are then discussed.

2. Dithizone and the Metal Dithizonates

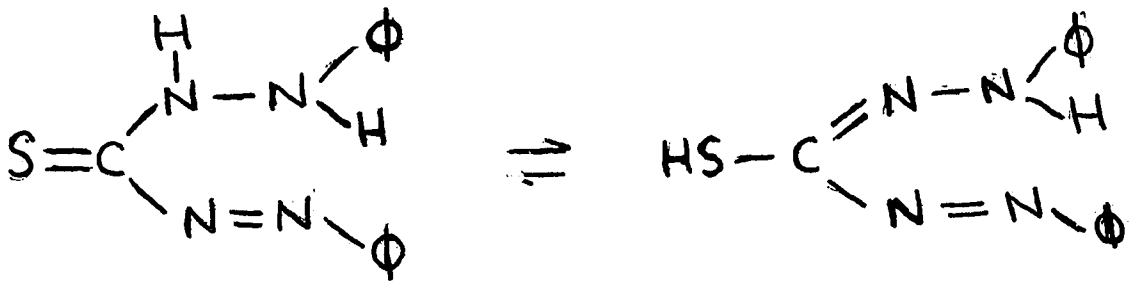
Dithizone is a dibasic acid:

$$H_2Dz = H^+ + HDz^- \qquad K_1 = 2 \times 10^{-5} \text{ at } 25°C \qquad (V)\text{-IX}$$

$$HDz^- = H^+ + Dz^= \qquad K_2 \sim 10^{-15} \text{ at } 25°C \qquad (V)\text{-X}$$

but it behaves primarily as a monobasic acid in its reactions with metals. It dissolves in basic solutions to produce a brown solution characteristic of the primary dithizonate anion (HDz^-). It is insoluble in acid solutions. It forms primary and secondary dithizonates (see Section IV B subsection 9(b) page 145).

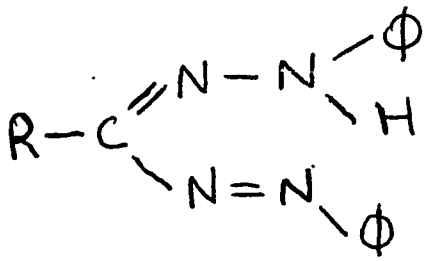
Dithizone is readily soluble in benzene, chloroform and carbon tetrachloride to form green solutions. The absorption spectra of these solutions have two maxima, one at ~620 mμ and the other at ~450 mμ. These may be identified with the absorption of the so-called enol- and keto- forms of dithizone, respectively, which are in mobile equilibrium (123, 124):



ϕ = phenyl group

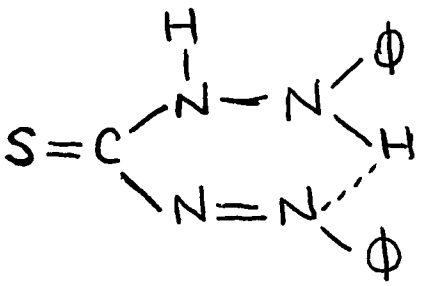
It is well known from studies of thiols and thiones that in such a tautomeric equilibrium the thione form almost always predominates (125-128).

Infrared studies of shifts at the N-H stretching frequency in compounds which have structures similar to that of dithizone i.e. C-alkyl formazans (136)



(R= H, Cl, I, CH_3, C_2H_5)

showed that the hydrogen was intramolecularly hydrogen-bonded to nitrogen; even in 0.1M chloroform solution. It may be postulated that dithizone behaves similarly, and that its structure is:



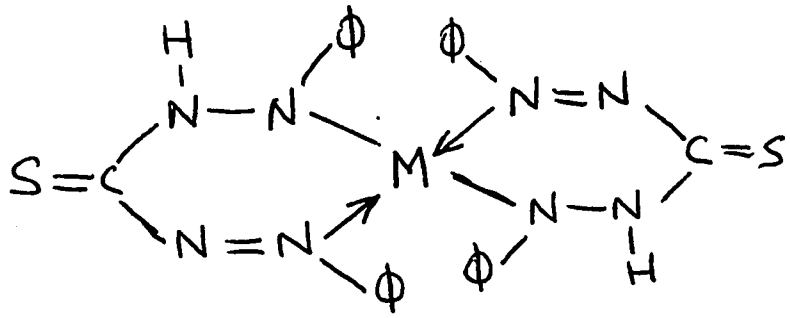
Irving et al. (137) determined the molecular weight of dithizone by ebullioscopic and isopiestic methods. These methods confirmed the absence of association in chloroform, chlorobenzene and carbon tetrachloride when the concentration of dithizone was 0.018M. They too suggested that dithizone may be stabilized by intramolecular hydrogen bonding.

It was, therefore, concluded that dimers of dithizone were absent from solutions used in the present work, because the concentrations of dithizone were never greater than 10^{-2}M.

Dithizone forms highly coloured complexes with metals. H. Fischer (74) observed that the "dithizone elements" either were transition metals, or else belonged to the B sub-groups of the periodic table with closed shells of 18 or 18 + 2 electrons (138). Irving and Cox (123) noted that "the small number of elements which form such complexes (dithizonates) are also those for which the stability of their halide complexes increases in the order $F^- \ll Cl^- < Br^- < I^-$, and which show a greater tendency to combine with sulphur-donors than with oxygen-donors; these have been referred to as Class (b) metals (139). The more numerous Class (a) cations, whose halides decrease in

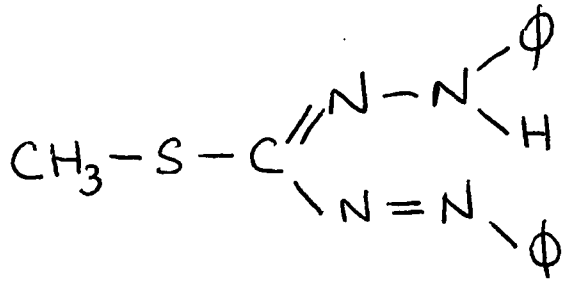
stability in the order $F^- \gg Cl^- > Br^- > I^-$ do not appear to form stable dithizone complexes." All the metals studied in the present work were class (b) metals.

There has been considerable discussion in the literature (72, 74, 129-133) on which part of the dithizone molecule bonds to the metal atom. Early papers (72, 74, 132) assumed that the metal atom was bonded to dithizone through the nitrogens:

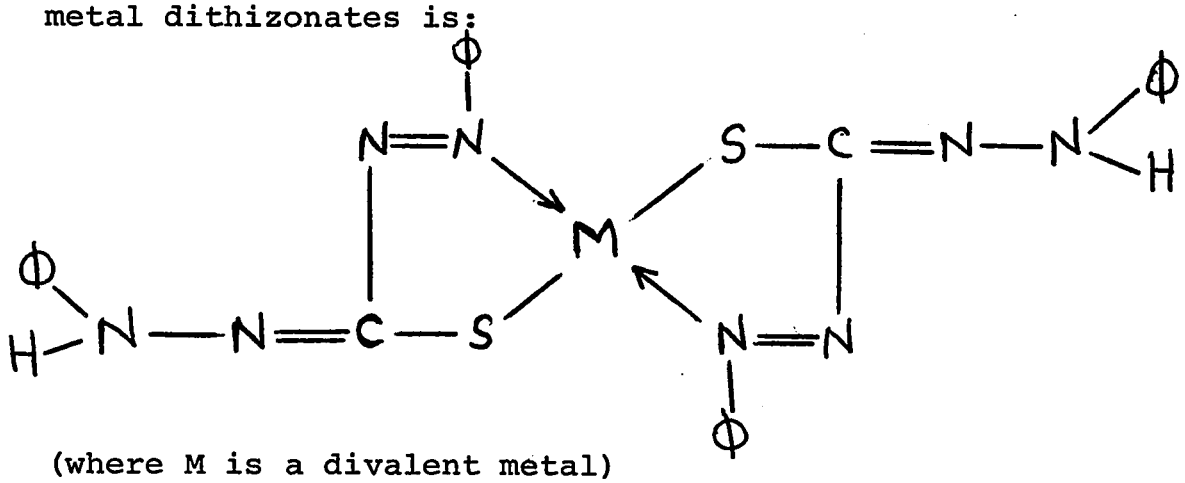


(where M is a divalent metal)

and indeed there is evidence that this is the structure of nickel dithizonate (131). However, Irving and Bell prepared S-methyldithizone (129, 130);



and then attempted to react it with metals under the same conditions as those known to be favourable for the formation of dithizonates. They did not obtain any reaction with Cu(II), Ag, Hg, Zn or Cd. In another paper (133) Irving et al. concluded that the general structure of metal dithizonates is:



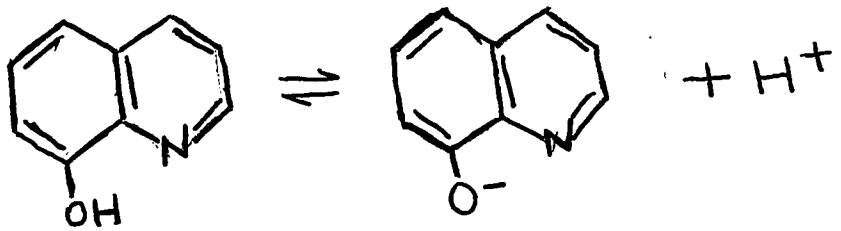
(where M is a divalent metal)

This type of bonding was confirmed in two X-ray crystallographic studies. In one study, Harding (134) found that in mercury dithizonate, the mercury atom was bonded to sulphur. In the other study, Bryan and Knopf (135) found the same bonding in the primary cupric dithizonate.

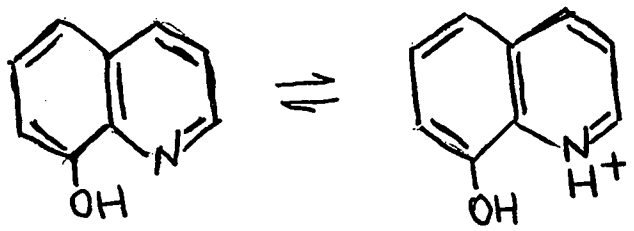
At the present time, no data exist on the structures of the secondary metal dithizonates e.g. CuDz.

3. Oxine and the Metal Oxinates

Oxine is sparingly soluble in water but is soluble both in acid and in basic solutions. The reactions are (88):

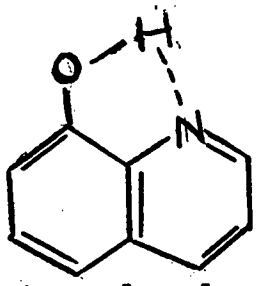


$K_a = 2 \times 10^{-10}$



$K_b = 2.3 \times 10^{-10}$

It dissolves readily in most organic solvents, including benzene, chloroform and carbon tetrachloride. There is strong evidence for intramolecular hydrogen-bonding (141-143) of the type:



but no evidence for intermolecular hydrogen bonding until the concentration exceeds 1M (141). This concentration was never reached in the present work, so the concentration of dimers was taken as being negligibly small.

Oxine forms metal chelates with many metals (88); the metal is reported to be covalently bonded to oxygen and a nitrogen coordinatively bonded with the vacant s or d orbitals of the metal (88). The anhydrous metal oxinates are soluble in low dielectric constant solvents.

Anhydrous zinc oxinate has been found by X-ray crystallography (144-146) to be tetrahedral; the dihydrate,

$ZnOx_2.2H_2O$, was found to be a distorted octahedron. In reference 144 it was postulated that cadmium and lead oxinates have the same structure as zinc oxinate. Two forms of copper oxinate may be prepared by adjusting the reaction conditions (147), namely the so-called α and β forms. The beta form was found by X-ray crystallographic studies (148) to be square planar, while its dihydrate was octahedral (149). It has been postulated that the α form is tetrahedral (141). In the present work only the β form was used.

4. Interpretation of Absorption Spectra

The visible and ultraviolet absorption spectrum of dithizone in benzene has peaks at 618, 445, 326 and 296 mμ (see Figure 37 page 191). The peaks at 618 and 445 mμ, which have high absorptivities, have been assigned (123, 124) to the thiol and thione forms respectively.

The band at 445 mμ probably originates from $n \rightarrow \pi^*$ transitions of the thione group (150) (the visible absorption spectrum of thioketones, for example, is due to the transition of a sulphur lone-pair electron to the thiocarbonyl π^*-orbital (151)), coupled with $\pi \rightarrow \pi^*$ transitions of the azo (N=N) group. The second visible band at 618 mμ could arise from an $n \rightarrow \pi^*$ transition of the thiol group together with $\pi \rightarrow \pi^*$ transitions of the conjugated azo group (n=N-$\overset{\overset{SH}{|}}{C}$=N-).

The ultraviolet band at 296 mμ may possibly be

due to $n \rightarrow \pi^*$ transitions of the C=N bond (152). The band at 326 mμ may be due to $n \rightarrow \pi$ transitions of the C=S bond (153).

In the metal dithizonates, the two bands of dithizone at 618 mμ and 445 mμ converge to a single band at about 500 mμ. This band may be due either to $n \rightarrow \pi^*$ or more likely to $\pi \rightarrow \pi^*$ transitions. However, in the metal dithizonates there is strong covalent-bond formation with the metal, including back-double-bonding by the metal's π electrons with the sulphur p orbitals (134). In these compounds, the nature of the molecular orbitals or the ligand may be significantly changed, including both the energy levels and the probability of transition of electrons to or from other orbitals. Therefore, it is not possible to distinguish transitions within the ligand itself from those involving electron shifts to or from the metal ion.

The ultraviolet spectrum of oxine in benzene consisted of one band at 313 mμ which was found to be a composite of two $\pi \rightarrow \pi^*$ bands and an $n \rightarrow \pi^*$ band (154). Ohnesonge and Rogers (155) suggested that in the metal oxinates the long-wavelength absorptions (those in the visible or near ultraviolet) are also due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The bands at the shorter wavelengths (see Figure 42, page 210) have lower absorptivities. A $\pi \rightarrow \pi^*$ band has been suggested, with the low intensities probably indicating that the transitions are forbidden ones

(155).

5. Mixed Chelates

(a) Introduction

Mixed chelates have been reported (156-163)* in solvent extraction studies with chloroform, carbon tetrachloride and benzene as the organic phases. In those studies, extraction constants for the mixed chelates were reported but not formation constants. Sekine and Dyrssen (158) noted that the mixed chelates of zinc, and of copper with 2-thenoyltrifluoroacetone (TTA) and isopropyltropolone (IPT) had higher distribution ratios than those of $M(TTA)_2$ or $M(IPT)_2$ alone and they concluded that the mixed chelates were more stable.

(b) Mixed Chelates Discovered in the Present Work

(i) Evidence for the mixed chelate, PbOxHDz

1. The equilibrium constant for the overall reaction of

$$PbOx_2 + 2H_2Dz = Pb(HDz)_2 + 2HOx$$

was found from the spectrophotometric data to be a function of the initial concentration of lead oxinate. This fact clearly indicated that additional species were present during the titration. It was in fact necessary

---

* In reference 156 a mixed chelate of indium with oxine and 5-methyloxine was reported. In references 157-163 mixed chelates of copper, zinc, europium, thorium, indium, calcium and strontium with such chelating agents as dimethylglyoxime, acetylacetone, 2-thenoyltrifluoroacetone and β-isopropyltropolone have been reported.

to postulate three such species. One was an adduct of lead dithizonate, namely $Pb(HDz)_2HOx$; it is discussed in a later section. The second was a mixed chelate, PbOxHDz; the third was an adduct of the mixed chelate, PbOxHDz.HOx which also is discussed in a later section.

When these two and the mixed chelate were taken into account then it was found that the equilibrium constant of the overall reaction was independent of the initial concentration of lead oxinate. This fact is considered to represent strong evidence for the existence of the three new species.

Additional evidence for the existence of the mixed chelate PbOxHDz was the fact that the equilibrium constant of the postulated reaction

$$PbOx_2 + Pb(HDz)_2 = 2PbOxHDz \qquad (V)\text{-}XI$$

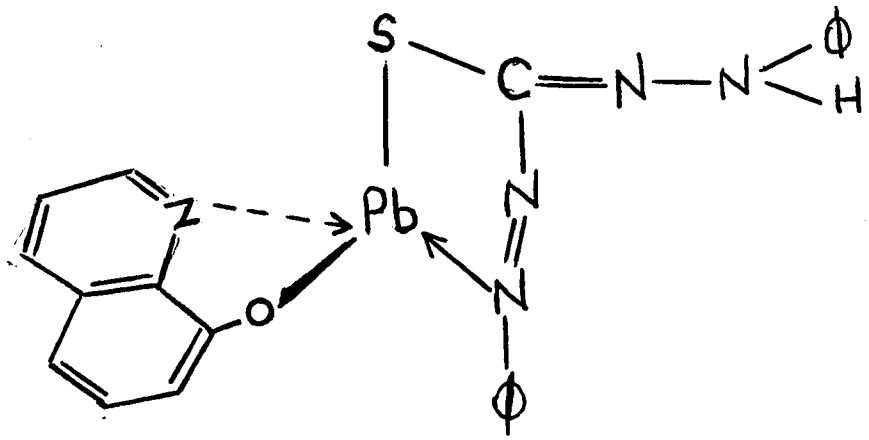
was constant over a wide range of concentrations of the reactants.

2. The infrared spectrum of the solid, prepared by means of reaction (V)-XI, provided evidence that it was PbOxHDz (see Figure 43 page 219). The intensities of the bands of the mixed chelate were much less than those of the parent compounds $PbOx_2$ and $Pb(HDz)_2$. This reduction could be attributed in part to differences in particle size in the Nujol mull. However, $PbOx_2$ showed an intense doublet at 354 and 343 cm^{-1}, which have been attributed to Pb-O

stretching. The band appeared in the prepared mixed chelate but (i) it shifted to a shorter wavelength (356 cm^{-1}); (ii) the doublet disappeared; (iii) the relative intensity was much less than that for $PbOx_2$; and (iv) the band was much broader. This infrared evidence indicates that the prepared compound was not in fact a mixture of $PbOx_2$ and $PbHDz_2$ but was indeed a mixed chelate.

3. In a microscopic examination of the crystals of PbOxHDz, $PbOx_2$ and $Pb(HDz)_2$ it was found that PbOxHDz was anisotropic, while $PbOx_2$ and $Pb(HDz)_2$ were isotropic.
4. The X-ray powder patterns were inconclusive since some difficulty was encountered in obtaining clear patterns in a reasonable length of irradiation time.

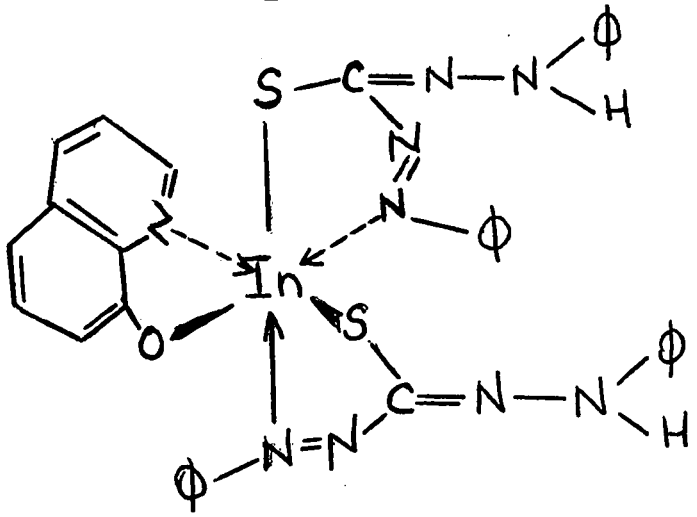
It was concluded that the mixed chelate PbOxHDz existed. It is postulated to have a tetrahedral structure similar to the structures of $PbOx_2$ and $Pb(HDz)_2$ which are believed to be tetrahedral (144):



(ii) Evidence for the mixed chelates, $InOx_2(HDz)$ and $InOx(HDz)_2$

It was not possible to prepare the individual solids since they were always present together in equilibrium. The only evidence available, therefore, was that the titration graph for the titration of indium dithizonate in benzene could be interpreted only by postulating the mixed chelates.

Sekine and Dyrssen (161) identified, by solvent extraction studies, two mixed chelates of indium in chloroform extracts. The formulae were InA_2B and $InAB_2$, where A was 2-thenoyltrifluoroacetone and B was isopropyltropolone. Irving (156) also reported that indium formed mixed chelates with oxine and 5-methyloxine in benzene. He postulated (156) the structure of these mixed chelates to be octahedral, which was the structure also of the parent compounds. In the present work, the structure of $InOx(HDz)_2$ is postulated to be



with a similar structure for $InOx_2(HDz)$.

(iii) The mixed chelate, CuOxHDz

All attempts in the present work to prepare a mixed chelate of the type CuOxHDz by mixing copper oxinate and primary copper dithizonate in solution failed. Secondary copper dithizonate (CuDz) and oxine were shown spectrophotometrically to be the only products. The fact that the equilibrium constant for the reaction:

$$CuOx_2 + Cu(HDz)_2 = 2CuDz + 2HOx$$

was constant over a wide range of concentrations (Tables 59 and 60, pages 297 and 298), confirmed the absence of a mixed chelate.

Sekine and Dyrssen (158) stated that mixed chelates of copper(II) with TTA and IPT were more stable than the parent chelates. Donor π-bonding of the p orbitals of the sulphur atom of the dithizonate ligand with the vacant d orbitals of copper (165) is possible in the case of CuDz. In Sekine and Dyrssen's mixed chelates the extent of back π-bonding in the Cu-O bonds is small (139). The existence of CuDz, and not of CuOxHDz in the solutions of the present work appears to be due to the difference in the strength of the π-bonding in the Cu-S bonds.

6. Adduct Formation

Enhancement of the distribution ratio of a metal chelate in solvent extraction by the formation of an adduct

with the chelating agent or with some other reagent in the organic phase (synergistic effect) has been extensively studied (166-174).

In general, the formation constants of adducts of metal-TTA chelates with reagents such as tributylphosphate (TBP) or tri n-butylphosphine oxide (TBPO) in low-dielectric constant solvents are of the order of 10^{0} to 10^{4}, depending on the solvent and the metal (166). The formation constants of adducts of bis copper dimethylglyoximate with amines are of comparable magnitude (171). Examples of the formation constants of some adducts of copper(II) chelates are in Table 93.

(b) The Copper System

(i) Formation of the adducts $Cu(HDz)_2.H_2Dz$ and $Cu(HDz)_2.2H_2Dz$

The only adducts found in the present work were those of primary copper dithizonate with dithizone, $Cu(HDz)_2.H_2Dz$ and $Cu(HDz)_2.2H_2Dz$. The stepwise formation constants were $K_{31} = 6.32 \times 10^{5}$ and $K_{32} = 1.08 \times 10^{4}$, respectively, in dry benzene. The values are higher than those obtained on other systems, by the other workers (see Table 93). This difference is to be expected; all adducts studied by other workers have involved donation of electrons by nitrogen and/or oxygen into the vacant orbitals of the metal. It is known that sulphur possesses greater donor properties than do nitrogen and oxygen (139). According to Dyrssen and Petkovic (171) "the adduct formation constant reflects the

TABLE 93

ADDUCT-FORMATION WITH COPPER CHELATES

Acceptor	Donor	Solvent**	log K	Reference
$Cu(AcAc)_2$	pyridine	C_6H_6 (dry)	0.94	4
"	4-picoline	"	1.04	4
$Cu(TTA)_2$	hexone*	$CHCl_3$ (wet)	<0	3
"	"	CCl_4 (wet)	0.47	3
"	TBP	$CHCl_3$ (wet)	0.65	3
"	"	CCl_4 (wet)	2.27	3
$Cu(IPT)_2$	hexone*	"	<0	3
"	TBP*	"	<0	3
$Cu(HD)_2$	triethylamine*	C_6H_6 (dry)	<0	2
"	dodecylamine	"	3.62	2
"	pyridine	"	3.50	2
"	quinoline	$CHCl_3$ (wet)	2.04	5
"	aniline	"	1.92	2
"	TBP*	"	<0	2
"	hexone	"	<0	2
$Cu(HDz)_2$	dithizone	C_6H_6 (dry)		1
$Cu(HDz)_2.H_2Dz$	"	"		1

TABLE 93 CONT.

TABLE 93 CONT.

(1) This work
(2) D. Dyrssen and D. Petkovic, Acta.,Chem..Scand. 19,653 (1965)
(3) T. Sekine and D. Dyrssen, J.Inorg, Nucl.,Chem,, 26,1727 (1964)
(4) W. R. May and M. M. Jones, J. Inorg, Nucl., Chem., 25,507 (1963)
(5) D. Dyrssen and M.Hennichs, Acta.,Chem.,Scand., 15,47 (1961)

AcAc = Acetylacetonate
TTA = 2 - Thenoyltrifluoroacetonate
IPT = β - Isopropyltropolonate
HD = Dimethylglyoximate

---

* No adduct formation was detected for this system

** Wet solvent indicates that the solvent extraction method was used for determination of log K.

residual coordination power of the copper chelates for a certain type of donor electrons .....". Now the Cu-S bond is stronger than either the Cu-O or the Cu-N bond. Therefore the higher formation constants of $Cu(HDz)_2.H_2D_z$ and $Cu(HDz)_2.2H_2Dz$ are not unexpected.

(ii) Structure of the adducts

Primary copper dithizonate was found to have a square-planar structure (135). Now, Irving and Edgington (166) have postulated that when adducts form that involve square-planar complexes "another ligand is introduced into a bis square-planar complex along the z-axis (axial) and a square pyramidal, five-coordinate molecule ($4s4p^34d$) results. On the addition of a further molecule a tetragonal field leading to a six-coordinate complex ($4s4p^34d^2$) would result".

In the present work, it was found from models* that in the case of the two dithizone adducts of $Cu(HDz)_2$ the phenyl groups were not sterically hindered. In the solution the thione form of dithizone predominates (121), and one of the hydrogens is intramolecularly hydrogen bonded to the azo nitrogen (see page 436). Therefore it is postulated that the dithizone donor molecule bonds through its sulphur

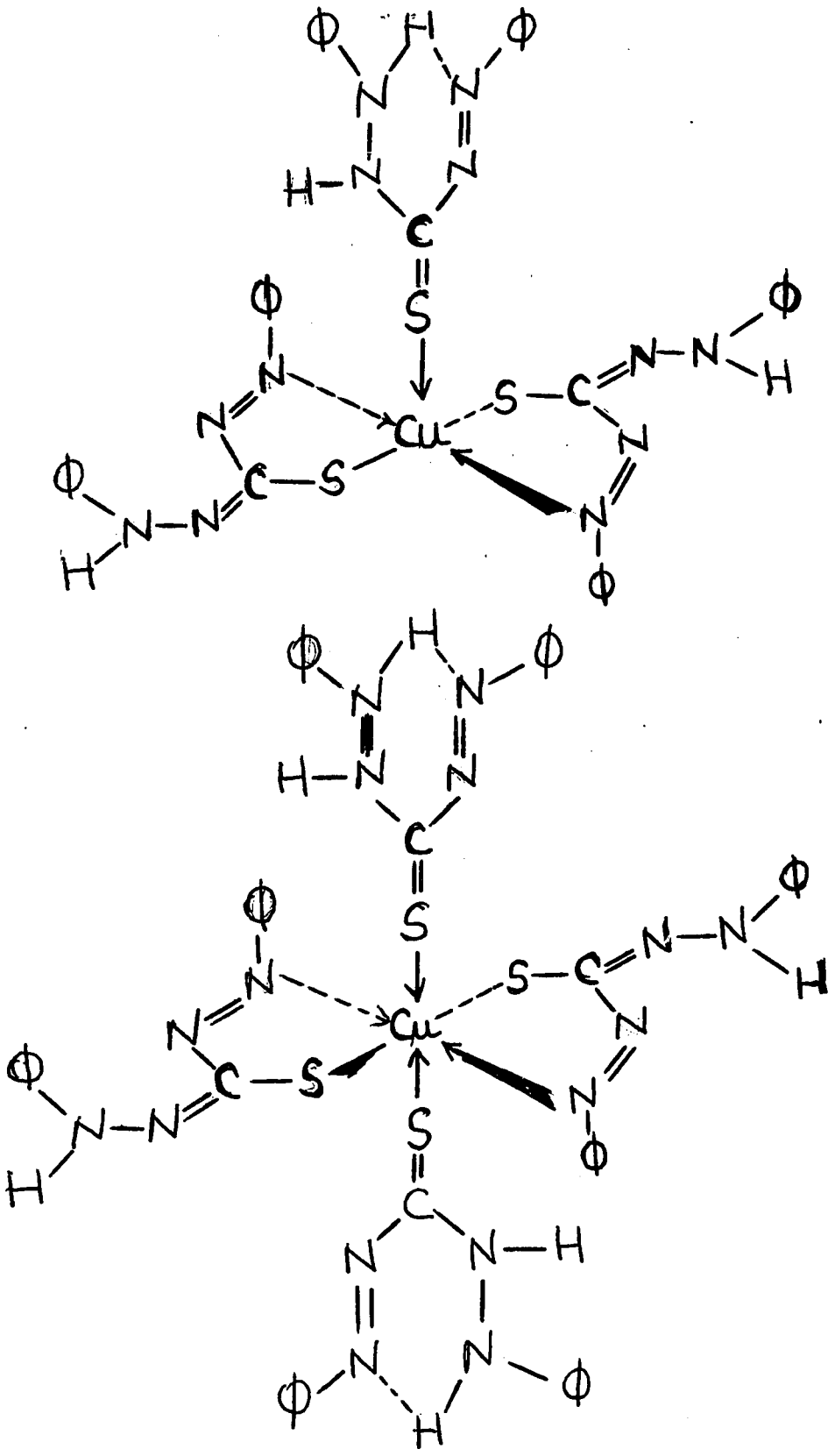
---

*Fisher-Taylor-Hirschfelder Models

atom. This postulate is supported by the fact that the formation constants of $Cu(HDz)_2.H_2Dz$ and $Cu(HDz)_2.2H_2Dz$ are higher than the constants reported for those adducts which bond to copper via nitrogen atoms (Table 93). Thus the structures of the adducts of primary copper(II) dithizonate with dithizone are postulated in the present work to be those given on the next page.

It is well established that square-planar complexes of copper tend to take up only one further unidentate ligand (166). For example, bis copper dimethylglyoximate takes up only one molecule of quinoline or laurylamine (174); and a variety of bis-chelates with diketones and keto-esters take up only one molecule of a heterocyclic base such as pyridine on its homologues (175-177). The fact that primary copper(II) dithizonate form two adducts is also interpreted in terms of the greater stability of the Cu-S bond in the adduct, over that of Cu-O or Cu-N bonds for other ligands.

The second stepwise formation constant, for attaching a dithizone molecule to $Cu(HDz)_2.H_2Dz$ was found to be about 60 times smaller than the first one, for attaching a dithizone molecule to $Cu(HDz)_2$. This fact is consistent with the tendency of square-planar complexes of copper to prefer a five-coordinate structure. In the "di-adduct", the structure is six-coordinate.



(iii) Effect of water

The effect of water on the adduct formation of $Cu(HDz)_2$ with dithizone was shown in Section IVD subsection 3(b), page 316. As reported there, the concentrations of the adducts in benzene were found to be reduced by the introduction of water into the benzene. The causes are not apparent. Irving and Al-Niaimi (170) studied the adduct formation of copper(II) acetylacetonate with quinoline. They evaluated the formation constant of the quinoline adduct in dry benzene (dried by calcium hydride) by a spectrophotometric method, and in water-saturated benzene by a solvent-extraction method. The values of the constant found by the two methods were not significantly different. However, the values found for the adduct with isoquinoline, in the dry and "wet" benzene respectively, did not agree; the formation constant of the isoquinoline adduct was lower in the "wet" benzene. They suggested that the difference may have been due to the presence of water, although they conceded that the explanation was inconclusive. Yet Dyrssen and Petkovic (171) argued that donor molecules must compete with water molecules when adducts form with copper dimethylglyoximate*

In the present work, if copper prefers the five-coordinate structure, one hydrate would be expected; and this agrees with the opinion of Irving and Al-Niaimi (170) and of Dyrssen and Petkovic (171). In that case, reactions

---

*Donor molecules: dibutylamine, pyridine, ammonia, dodecylamine.

(b)-VIII and (b)-IX on page 320 should be written:

$$Cu(HDz)_2.H_2O + H_2Dz = Cu(HDz)_2.H_2Dz + H_2O \qquad (V)\text{-XII}$$

$$Cu(HDz)_2.H_2Dz + H_2Dz = Cu(HDz)_2.2H_2Dz \qquad (v)\text{-XIII}$$

Thus, only the first reaction should be affected by water. The data used in Section IVD subsection 3(b), page 316 (see also Tables 13 and 14 of Appendix XXVIII) were therefore now recalculated* for equation (V)-XII instead of the equation:

$$Cu(HDz)_2 + H_2Dz = Cu(HDz)_2.H_2Dz;$$

the value of K_{32} (for equation (V)-XIII) was assumed to be unaffected by the presence of water. The results of these calculations caused the calculated continuous-variations curve to resemble in shape the curve for dry benzene (see Figure 57, page 287) and to resemble even less the experimental curve for wet benzene. Therefore it is necessary to postulate a dihydrate of primary copper(II) dithizonate in order to account for the experimental data. Further work is needed to confirm this postulate.

(iv) Absorption curves of the adducts

The curves of absorptivity versus wavelength (Figure 58, page 308) for the adducts $Cu(HDz)_2.H_2Dz$ and $Cu(HDz)_2.2H_2Dz$ in benzene dried with calcium hydride are consistent with the addition of molecules of dithizone to $Cu(HDz)_2$. The absorptivity of the mono-adduct was greater than that of primary copper(II) dithizonate, but less than

---

*Calculations not shown

that of the di-adduct. Further, the spectrum of the di-adduct is not very different from the composite curve of free dithizone and primary copper(II) dithizonate*, although the absorptivities of the dithizone peaks were enhanced in the adduct. The fact that the spectral component due to $Cu(HDz)_2$ is not altered by adduct formation indicates that the chelate rings remain intact.

(c) The Lead System

The following adducts were found in the lead chelate reactions:

$PbOxHDz.HOx$ and $Pb(HDz)_2.HOx$.

Adducts of mixed chelates are known (157). Until the present investigation, no work had been done on lead chelate-adduct formation; but some work has been reported on zinc chelate-adduct formation (166). It is generally thought that reactions of lead chelates resemble those of zinc chelates. It seem reasonable to suppose that this resemblance extends to adducts.

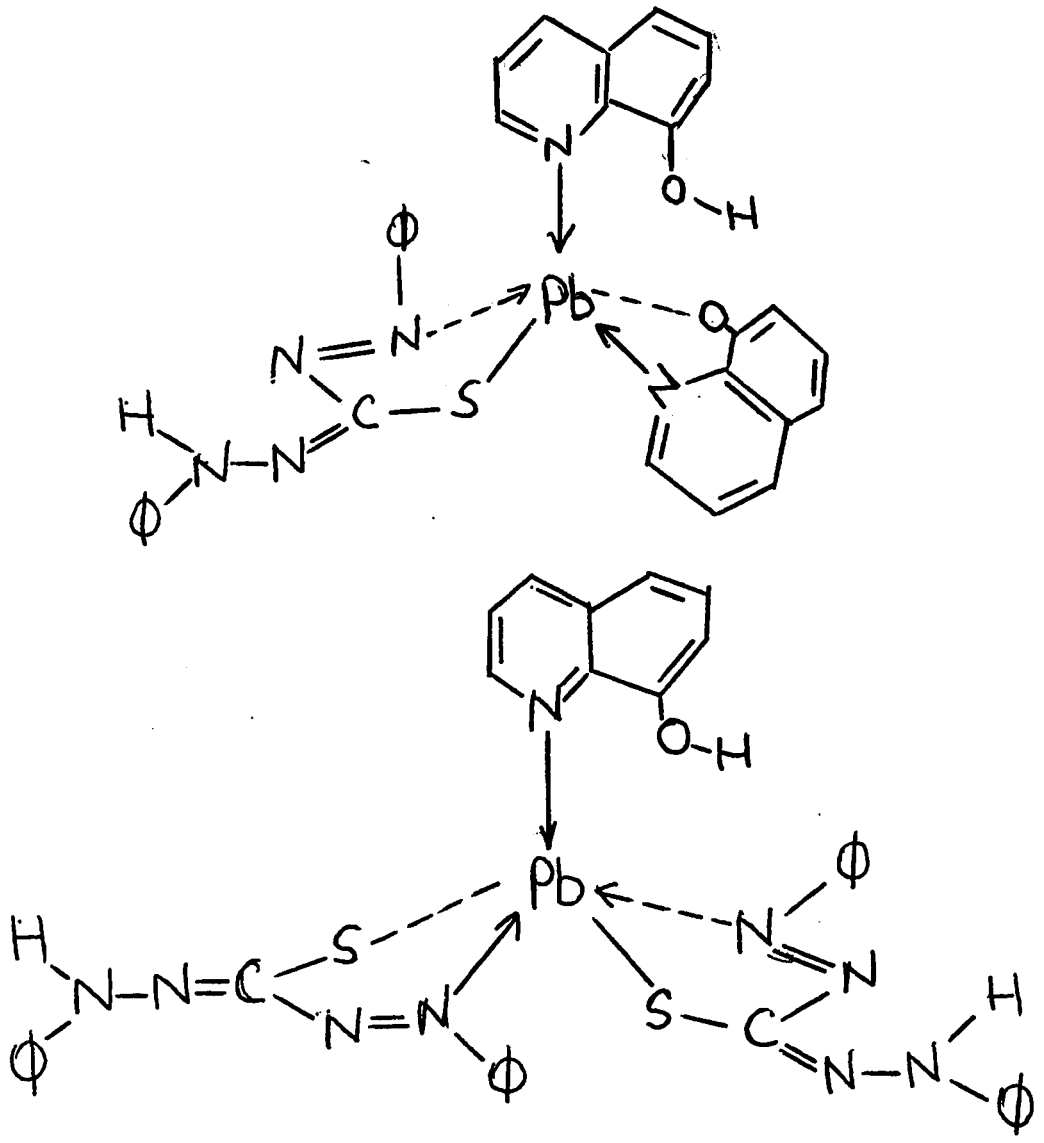
Zinc does not readily expand its coordination from four to five or six (178) although (i) a five-coordinate complex, zinc bis-N,N'-disalicylidineethylenediamine hydrate has been reported (179) and (ii) the crystal structure of solid, dihydrate of zinc oxinate was shown to be a distorted octahedron (146,180).

The results obtained with lead were consistent with the above experimental results for zinc.

---

*See Figures 37 and 39 on pages 191 and 202, respectively.

If PbOxHDz and $Pb(HDz)_2$ have tetrahedral structures, then the adducts with oxine should be five-coordinate and pyrimidal, as shown:



Moreover these adducts should not be easily formed. In

fact the formation constants for the adducts (113 for PbOxHDz.HOx and 5.34×10^3 for $Pb(HDz)_2$.HOx) were low compared to those for the formation of the mono-adduct of copper dithizonate with dithizone. The fact that the adducts are five-coordinate is consistent with di-adducts not having been found.

It is postulated in the present work that the oxine molecule bonds to the central lead atom through its nitrogen rather than through its oxygen. It has been found that in general, the formation constants of adducts of metal chelates with amines have been higher ($K \sim 10^3$) than those with oxygenated compounds ($K \sim 0$ to 10) (166, 167, 170, 171). The formation constants for PbOxHDz.HOx and $Pb(HDz)_2$.HOx evaluated in this work (noted above) are of the same order of magnitude as the formation constants of the amine adducts of several metal chelates reported in the literature (see Table 93 for examples with some copper chelates). Therefore in PbOxHDz.HOx and $Pb(HDz)_2$, bonding of the oxine through its nitrogen to the central lead atom seems more reasonable than through its oxygen.

The fact that the formation constant of $Pb(HDz)_2$.HOx was found to be approximately 50 times larger than the formation constant of PbOxHDz,HOx requires comment. This difference may be interpreted in terms of structure. From molecular models, it was seen that in the tetra-

hedral $Pb(HDz)_2$ molecule there would be some mutual repulsion between the phenyl groups on the opposite dithizonate ligands. This particular source of repulsion would be absent in the PbOxHDz molecule. When the adducts of both molecules are formed the models indicate that the dithizonate ligands are pushed further apart and so are the ligands of the mixed chelate. In the formation of these two adducts only the repulsion of the phenyl groups on the opposite dithizonate ligands in $Pb(HDz)_2$ would be expected to contribute to the energy change at absolute zero. This statement is based on the assumption that the partition function quotients at 25°C for the two reactions are the same. Then, and only then, can the differences in $\Delta F°$ (i.e. equilibrium constants) be interpreted in terms of energy (195).

It would be interesting to determine whether or not a substituted 8-quinolinate ligand attached to lead in the mixed chelate increased the formation constant of the adduct.

It was surprising that an adduct of lead oxinate with oxine was not found. Freiser (181) found from solvent-extraction studies that zinc oxinate formed an adduct, $ZnOx_2.HOx$. It is also known that divalent metal oxinates such as $MgOx_2$, $CaOx_2$, $SrOx_2$ and AgOx form adducts with oxine in nonaqueous solutions (88).

In the present work it was found that the visible

spectrum of lead oxinate in benzene was unchanged by the addition of oxine. However, this fact is not sufficient for rejecting the formation of an adduct. Dyrssen and Petkovic (171) found that adduct formation had little effect on the spectrum of bis copper dimethylglyoximate; but they were able to show from solvent-extraction data that adducts were in fact formed.

Strong evidence for rejecting the formation of an adduct of lead oxinate with oxine resulted from the calculations to evaluate the equilibrium constants of the lead chelate (Section IVD subsection 3(d)). The value of K_2 (see Table 88, page 404) for the reaction:

$$PbOxHDz + H_2Dz = Pb(HDz)_2 + HOx$$

was evaluated directly from spectrophotometric measurements, both in solutions which contained no free oxine, and also in solutions that contained a large excess of free oxine. The values of K_2 for both sets of solutions were calculated on the basis of an adduct such as $PbOx_2.HOx$ being absent. The values of K_2 were not significantly different. An adduct would certainly have led to a discrepancy in the values of K_2.

Lead dithizonate did not form an adduct with dithizone, yet it formed one with oxine. The reason is not clear. With lead sulphur forms stronger bonds than does nitrogen (139), so an adduct of lead dithizonate with dithizone would be expected. The visible spectrum of lead dithizonate was unchanged by the presence of free dithizone,

but this is not sufficient justification for rejecting the formation of an adduct. Therefore further work is recommended.

It is possible to postulate a further adduct, $PbOxHDz.H_2Dz$, which has the same empirical formula as $Pb(HDz)_2.HOx$. No evidence was found for its existence. The value of the equilibrium constant K_2 (Table 88, page 404) for the reaction:

$$PbOxHDz + H_2Dz = Pb(HDz)_2 + HOx$$

was constant over a wide rangeof concentrations of reactants on the basis of there being no $PbOxHDz.H_2Dz$ present.

(d) The Indium System

Adducts were not found for the indium chelates. The chelates of indium(III) are known to be octahedral.(182). Therefore, if adducts were to be formed the coordination number of indium would have to expand to seven or eight. Such a coordination number is unlikely for indium. Dyrssen and Sekine (162) found that tris 2-thenoyltrifluoroacetylacetonates of indium did not form adducts with tributylphosphate, dibutylsulphoxide or methyl isobutyl ketone.

7. The Reaction of Cobalt Oxinate with Dithizone

In the present work cobalt(II) oxinate did not react with dithizone in benzene. This finding required an explanation, because the dithizonate of cobalt is well known (190). However, the valence of the cobalt in the dithizonate was not established by these workers. Subsequently, Duncan and Thomas (191) found from solvent-extraction

studies that cobalt formed a tris dithizonate, $Co(HDz)_3$ rather than $Co(HDz)_2$. If the earlier preparations were cobalt(III) dithizonate, it would mean that Co(II) dithizonate has never been prepared, even though Co(II) was the starting material. Therefore it was not surprising that Cobalt(II) oxinate did not react with dithizone, because there was no way for the cobalt to be oxidized.

D. EQUILIBRIUM CONSTANTS

1. Activity Coefficients

The activity coefficient of every participating species was assumed to be unity. The concentrations of the participating species were of the order of 10^{-4} to 10^{-7}M. At these low concentration levels the activity coefficients of the monomers would be expected to be very close to unity. Dimerization is treated as a separate effect below, and is not considered to be represented by a contribution to the activity coefficient of the monomer.

Even if activity coefficients were not unity, it is to be noted that except for the mass-law expression for adduct formation, the activity coefficients would almost cancel out. For example, in the expression:

$$K = \frac{[Pb(HDz)_2][HOx]^2}{[PbOx_2][H_2Dz]^2} \cdot \frac{\gamma_{Pb(HDz)_2} \cdot \gamma^2_{HOx}}{\gamma_{PbOx_2} \cdot \gamma^2_{H_2Dz}}$$

the activity coefficients of $Pb(HDz)_2$ and $PbOx_2$ would probably be similar and so would those of HOx and H_2Dz.

2. Formation of the Compound, $H_2Dz.HOx$

The existence of $H_2Dz.HOx$ was sought. However at the concentration levels studied (mixture of $\sim 10^{-4}$M H_2Dz and $\sim 10^{-2}$M HOx) there was no spectrophotometric evidence for this compound. Furthermore, the calculations performed on the metal-chelate-reaction data assumed the absence of $H_2Dz.HOx$. The equilibrium constants obtained were constant over a wide range of concentrations of reactants, which ruled out the presence of $H_2Dz.HOx$.

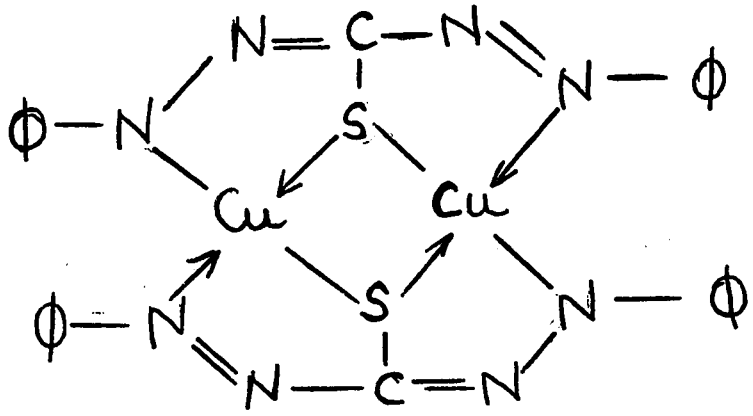
3. Dimers

Parallel with all the calculations of Section IVD subsection 3, complementary calculations were carried out in which the existence of dimers was assumed. However, in every case the inclusion of dimers caused the otherwise constant value of the equilibrium constant to become a function of the initial concentration of reactants.

There is strong evidence in the literature (183-186) for dimer formation by metal complexes; but in all cases but one the concentrations of the metal complexes were much higher ($\sim 10^{-3}$M) than they were in the present work. The exception was the copper chelate of salicyl-aldehyde (187), which was found to dimerize in cholorform in the range 10^{-5} to 10^{-4}M and to tetramize above 10^{-4}M.

From the above-described evidence of the present work, and from the evidence in the literature on metal-chelate dimerization, it was concluded that in the metal chelate reactions studied in the present work dimers were not present in significant concentrations.

In the present work all evidence indicated that the secondary copper dithizonate, CuDz, existed solely as a monomer in solution. However, from molecular models, with copper assumed to be square-planar it proved impossible to arrange the bidentate dithizonate ligand around the copper atom without imposing severe strain on the chelate ring. By postulating a dimer instead, a structure can be formulated which is sterically stable, as shown below:



Sulphur bridge bonds have been found by X-ray crystallographic studies (188,189) on the polymeric thiocyanate cobalt(II) complex of thiourea.However, the formation constant (see Table 60, page 298) of CuDz was not a function of the concentration of the reactants, on the basis of the product being a monomer. There is a possibility that the molecule is stabilized with water because the reactions were carried out in "wet" benzene. Further work clearly is needed in order to remove the discrepancy between the solution evidence which indicates a monomer and the molecular-model evidence which indicates a dimer.

4. Effect of Water

It does not seem possible from the literature (167,171 and references therein) to prescribe the exact environment in which hydrates of metal chelates will form and the environment in which they will not form. In the present work equilibrium constants were measured in benzene for which the water content varied onehundredfold without any change in the values of the equilibrium constants. Therefore, it seems unlikely that water plays a significant role in the chelate-exchange titrations. However, unequivical proof would have to await their study in very intensively dried benzene. In this connection it is relevant to point out that it would be impractical to require that the chelate-exchange titrations be carried out with intensively dried solvents. It is for this reason that the equilibrium constants were evaluated in solvents that were not completely anhydrous.

The oxinates of Ni(II),Cu(II),Pb,Zn and Cd all form dihydrates (88) which are octahedral, some with distortion. The dihydrates of nickel,zinc and cadmium oxinates were found to be almost insoluble in benzene dried with silica gel. The anhydrous oxinates of the same metals, on the other hand, were found to be relatively soluble in benzenendried with silica gel. This suggests that a general relationship may exist; dihydrates of the metal oxinates are almost insoluble, and the anhydrous

oxinates are soluble in dried benzene. Anhydrous copper oxinate and its dihydrate were found to be soluble in wet or dried benzene. Either this represents an exception to the rule or else $CuOx_2.2H_2O$ is unstable in benzene and dissociates into the anhydrous copper oxinate which is then stable. This latter explanation seems to be the reasonable one. In this connection X-ray crystallographic measurements have shown that the bond distance between Cu-OH_2 in $CuOx_2.2H_2O$ is 2.53A°(149) compared to a bond distance of 2.07A° for the Cu-O bond to the oxinate ligand. In the case of $ZnOx_2.2H_2O$, X-ray crystallographic measurements have shown that the bond distance of the Zn-OH_2 bond is 2.27A° and the Zn-O bond to the oxinate ligand to be 2.05A° (144). Thus, one might infer that water molecules are bonded tightly to $ZnOx_2$ and less tightly to $CuOx_2$. This inference is consistent with the $CuOx_2.2H_2O$ dissociating into $CuOx_2$ when it dissolves in benzene and with the insolubility of $ZnOx_2.2H_2O$, that is, its inability to dissociate in benzene into anhydrous zinc oxinate.

Now the ready solubility of $PbOx_2.2H_2O$ in benzene suggests that the dihydrate dissociates into $PbOx_2$. This further suggests that the Pb-OH_2 bond is relatively large. Unfortunately, this distance has not been measured. In fact, little is known about the structure of lead oxinate. The only relevant information appears to be that zinc oxinate is isomorphous with lead oxinate (144). Finally, the dissociation temperature of $ZnOx_2.2H_2O$ is

140°C whereas those of $PbOx_2.2H_2O$ and $CuOx_2.2H_2O$ are 105°C, which again supports the contention that the water molecules are more tightly bonded in zinc oxinate than they are in lead and copper oxinates.

It may be concluded from the above discussion, that water probably plays an insignificant role in the metal chelate reactions studied in the present work. The one exception is the formation of adducts of primary copper dithizonate with dithizone which has been discussed elsewhere.

5. Effect of Temperature

The effect of changing the temperature from 25°C to 40°C in the metal chelate systems studied, was to change most of the overall absorbances by not more than 5%. This change would correspond to a value of $\Delta H°$ of the order of 5-8 Kcal/mole. From the point of view of practical titrations the temperature dependence of the absorbance measurements indicated that close control of temperature was unecessary for the titrations. From the point of view of evaluation of the thermodynamic property $\Delta H°$ for the various reactions, it was considered that the change in absorbance with temperature was too small to have provided an accurate value of $\Delta H°$ because the statistical error in the absorbance readings was itself about 2% of the absorbance measurement.

By not measuring $\Delta H°$ the interpretation of the

thermodynamic data was necessarily restricted. However, even if ΔH° had been evaluated, its interpretation in terms of bond energies would still have been questionable because it would have been impossible in the present state of our knowledge to evaluate the partition functions of the species participating in the various reactions.

VI SUMMARY AND CONCLUSIONS*

1. Chelate-exchange titrimetry was conceived in the present work, and was successfully applied to the determination of the dithizonates of Cu(II),Pb,Zn,Cd,Ag, and In in chloroform with sodium diethyldithiocarbamate, and to the oxinates of Cu(II), Pb, Zn, Cd and In with dithizone in benzene.

   This titration procedure was also successfully applied to the determination of 1:1 mixtures of the dithizonates of Cu+Zn, Cu+Cd, Cu+Pb, Pb+Ag, In+Pb, Cu+Ag, Cu+Pb+Ag, Cu+Zn+Cd and Cu+Pb+Zn.

2. The molar absorptivities of dithizone and the metal dithizonates listed in (1) were determined in benzene at 25°C, in the region from 750 to 350 mu. The molar absorptivities of oxine and the metal oxinates listed in (1) were determined in benzene at 25°C, in the region from 500 to 250 mu.

3. Estimates of the components of the population variances due to: (i) the presence of free chelating agent in the titration solution; (ii) titrations at different wavelengths and (iii) reproducibility, were obtained from a rigorous treatment of the titration data of the chelate-exchange titrations in (1).

4. A rapid and accurate spectrophotometric titration procedure was developed for the determination of oxine

*For Part I, see page 95

dithizone and sodium diethyldithiocarbamate in non-aqueous solvents.

5. The following new species were discovered in benzene:

   Mixed chelates: PbOxHDz, $InOx_2(HDz)$ and $InOx(HDz)_2$

   Adducts : $Cu(HDz)_2.H_2Dz$, $Cu(HDz)_2.2H_2Dz$, PbOxHDz.HOx, $Pb(HDz)_2.HOx$

6. The equilibrium constants for the following reactions in benzene at 25°C were evaluated:

$CuOx_2 + Cu(HDz)_2 = 2CuDz + 2HOx$	5.61×10^9 mole^{2}litre^{-2}
$CuDz + H_2Dz = Cu(HDz)_2$	6.85×10^{-7} litre mole^{-1}
$CuOx_2 + 2H_2Dz = Cu(HDz)_2 + 2HOx$	2.64×10^7
$Cu(HDz)_2 + H_2Dz = Cu(HDz)2.H_2Dz$	6.32×10^5 litre mole^{-1}
$Cu(HDz)_2.H_2Dz + H_2Dz = Cu(HDz)_2.2H_2Dz$	1.08×10^4 litre mole^{-1}
$PbOx_2 + Pb(HDz)_2 = 2PbOxHDz$	188
PbOxHDz + HOx = PbOxHDz,HOx	113 litre mole^{-1}
$Pb(HDz)_2 + HOx = Pb(HDz)_2.HOx$	5.34×10^3 litre mole^{-1}
$PbOxHDz + H_2Dz = Pb(HDz)_2 + HOx$	734
$PbOx_2 + 2H_2Dz = Pb(HDz)_2 + 2HOx$	1.072×10^8
$InOx_3 + H_2Dz = InOx_2HDz + HOx$	92
$InOx_2HDz + H_2DZ = InOx(HDz)_2 + HOx$	7.0
$InOx(HDz)_2 + H_2Dz = In(HDz)_3 + HOx$	3.33

7. With the use of the equilibrium constants listed in (6), theoretical titrations graphs were calculated for the chelate-exchange titrations of lead, copper and indium oxinates with dithizone in benzene at 25°C. The theoretical graphs and the experimental graphs of lead and indium agreed well. Those of copper did not agree.

The discrepancy was satisfactorily explained by the non-equilibrium yet reproducible conditions of the experimental graphs.

8. The effects of the variables listed in (3) on the variances of the chelate-exchange titrations of metal oxinates with dithizone were interpreted in terms of the reactions listed in (6).

VII SUGGESTIONS FOR FURTHER WORK*

1. An investigation into the use of zinc dibenzyldithiocarbamate as a titrant in the chelate-exchange titrations of metal dithizonates. This titrant is readily soluble in low-dielectric constant solvents such as carbon tetrachloride. Evaluation of the equilibrium constants for the reactions should be practicable, and this could lead to the discovery of new mixed chelates and adducts.
2. Investigation into the use of derivatives of dithizone such as di-β-naphthylthiocarbazone as titrants for metal oxinates. Comparison of the results with the data of the present work might lead to new information on the structure of mixed chelates and adducts.
3. The chelate-exchange titration of amino-, thio- and seleno-oxinates of metals with dithizone as the titrant, and evaluation of the equilibrium constants of the reactions. The values of these equilibrium constants might be found to correlate with certain fundamental properties of the metal chelates.
4. The extension of chelate-exchange titrations to other systems of metal chelates and chelating agents, and also to the use of the ultraviolet region of the spectrum for following the course of the titration.

* For Part I, page 97

5. A complete X-ray crystallographic investigation of the structure of secondary cupric dithizonate.
6. A detailed kinetic study of the reaction of dithizone with the oxinates of copper, zinc and cadmium, as a means of adding to present knowledge of chelate-exchange reactions.
7. The development of analytical procedures based on the kinetics of chelate-exchange reactions.
8. A detailed study of the effect of water on chelate-exchange reactions.

VIII CLAIMS TO ORIGINAL WORK*

1. A spectrophotometric titration procedure (named chelate-exchange titrimetry) was conceived and developed, which was based on chelate-exchange reactions in low-dielectric constant solvents such as benzene, carbon tetrachloride and chloroform. The method proved to be rapid, accurate and precise.
2. Chelate-exchange titrimetry was successfully applied to the determination of microgram amounts of the dithizonates of silver, copper(II), lead, zinc, cadmium and indium singly and in certain binary and ternary mixtures in chloroform; sodium diethyldithiocarbamate in ethanol was the titrant.
3. Chelate-exchange titrimetry was also successfully applied to the determination of microgram amounts of the oxinates of lead, copper(II), zinc, cadmium and indium in benzene; dithizone in benzene was the titrant.
4. Rapid, convenient and accurate spectrophotometric titration methods were developed for the determination of dithizone, oxine and sodium diethyldithiocarbamate in nonaqueous solvents.
5. The molar absorptivities of dithizone and oxine in benzene at 25°C in the region 750 to 250 mμ, were evaluated.

* For Part I, see page 98

6. The molar absorptivities of lead, zinc, cadmium, copper(II) and indium oxinates in benzene at 25°C in the region 500 to 250 mu were evaluated.
7. The molar absorptivities of lead, indium, zinc, cadmium, silver and primary and secondary copper(II) dithizonates in benzene at 25°C in the region 750 to 400 mu were evaluated.
8. The mixed chelates PbOxHDz, $InOx_2HDz$, and $InOx(HDz)_2$ were discovered in solution, and their molar absorptivities in benzene at 25°C in the region 750 to 400 mu were evaluated.
9. The adducts $Cu(HDz)_2.H_2Dz$, $Cu(HDz)_2.2H_2Dz$, PbOxHDz.HOx and $Pb(HDz)_2$.HOx were discovered in solution and their molar absorptivities in benzene at 25°C in the region 750 to 400 mu were evaluated.
10. The equilibrium constants for the following reactions in benzene at 25°C were evaluated:

$$PbOx_2 + H_2Dz = PbOxHDz + HOx$$

$$PbOxHDz + H_2Dz = Pb(HDz)_2 + HOx$$

$$PbOx_2 + Pb(HDz)_2 = 2PbOxHDz$$

$$PbOxHDz + HOx = PbOxHDz.HOx$$

$$Pb(HDz)_2 + HOx = Pb(HDz)_2.HOx$$

$$CuOx_2 + Cu(HDz)_2 = 2CuDz + 2HOx$$

$$CuDz + H_2Dz = Cu(HDz)_2$$

$$Cu(HDz)_2 + H_2Dz = Cu(HDz)_2.H_2Dz$$

$$Cu(HDz)_2.H_2Dz + H_2Dz = Cu(HDz)_2.2H_2Dz$$

$$InOx_3 + H_2Dz = InOx_2HDz + HOx$$

$$InOx_2HDz + H_2Dz = InOx(HDz)_2 + HOx$$

$$InOx(HDz)_2 + H_2Dz = In(HDz)_3 + HOx$$

11. It was demonstrated that the presence of even very low concentration of water must be taken into account in a rigorous study of nonaqueous systems containing metal chelates.

12. Structures for the newly discovered mixed chelates and adducts (Claims 8 and 9) have been suggested.

13. The differences in the magnitudes of the equilibrium constants referred to in Claim 10 have been tentatively explained in terms of structure.

14. Theoretical titration graphs were constructed for the chelate-exchange titrations reported in Claims 2 and 3, by using the equilibrium constants referred to in Claim 10.

15. Evaluation of chelate-exchange titrimetry as an analytical method was carried out, by a rigorous statistical treatment of the titration data.

APPENDICES

APPENDIX I

CALCULATION OF THE FIRST BRANCH OF THE TITRATION GRAPH FOR THE ARGENTIMETRIC TITRATION OF AN EQUIMOLAR MIXTURE OF CHLORIDE AND BROMIDE

In the argentimetric titration of an equimolar mixture of chloride and bromide there was an experimental error of 8% in the bromide end point. In the following calculation it is assumed that solid-solution formation has taken place to the extent of 8 per cent. Therefore 8% of the chloride has been precipitated (prematurely) and 8% of the bromide remains in solution. Consider the following example: 10-ml aliquots of 5×10^{-3} M sodium chloride and sodium bromide are mixed in the titration cell and diluted to 120 ml with methanol. The solution is then titrated with 0.01-N silver nitrate in methanol. Therefore, theoretically, 5 ml of silver nitrate is required for the bromide end point and 10 ml for the total halide end point. Thus:

Initial concentration of sodium chloride $= 4.17 \times 10^{-4}$ M

Initial concentration of sodium bromide $= 4.17 \times 10^{-4}$ M

In the absence of solid-solution formation:

Concentration of NaCl at the bromide end point

$$= 4.17 \times 10^{-4} \times \frac{120}{125}$$
$$= 4.00 \times 10^{-4}$$

Concentration of $NaNO_3$ resulting from the precipitation of bromide, at the bromide end point

$$= 4.17 \times 10^{-4} \times \frac{120}{125}$$
$$= 4.00 \times 10^{-4}$$

With 8% solid-solution formation the concentrations at the bromide end point will be:

Concentration of NaCl = $\frac{92}{100}$ x 4.0×10^{-4} M = 3.68×10^{-4} M

Concentration of NaBr = $\frac{8}{100}$ x 4.0×10^{-4} M = 3.20×10^{-5} M

Concentration of $NaNO_3$ = 4.00×10^{-4} M

Ionic strength at the bromide end point = 8.00×10^{-4} M

The individual response of the electrolytes at 8.00×10^{-4} M ionic strength taken from their respective response curves are (see Figures 14, 15 of Section III D subsection 3):

NaCl = 15880 instrument divisions
NaBr = 16060 instrument divisions
$NaNO_3$ = 16200 instrument divisions

The composition of the solution at the bromide end point is:

NaCl = 46.0%
NaBr = 4.0%
$NaNO_3$ = 50.0%

Contribution to the apparent capacitance due to NaCl = $\frac{46.0}{100}$ x 15880
= 7304 instrument divisions

Contribution to the apparent capacitance due to NaBr = $\frac{4}{100}$ x 16060
= 642 instrument divisions

Contribution to the apparent capacitance due to $NaNO_3$ = $\frac{50}{100}$ x 16200
= 8100

Net apparent capacitance due to the solution is the sum of the above individual responses = 16046

It was found, from a similar calculation for the titration of a single halide that the precipitate contributed to the apparent capacitance in an amount of 33 instrument divisions.

If this is added onto the above reading to account for the presence of precipitate the net apparent capacitance will be 16079.

In summary the calculated apparent capacitances at the bromide end point are:

Without solid-solution formation or precipitate	:	16040
With 8% solid-solution formation but without precipitate	:	16046
With 8% solid-solution formation and in the presence of precipitate	:	16079
Experimental apparent capacitance	:	16082

The calculated titration graph with the corrections corresponds closely with the experimental titration graph, for the portion which represents the precipitation of bromide. Similar calculations can be made for any amount of solid-solution formation.

APPENDIX II

THE SOLUBILITY PRODUCTS OF SILVER HALIDES IN SOME SOLVENTS

	Solubility Product at 25°C			
	Water	Absolute Methanol	Absolute Ethanol	Acetone
AgCl	1.56×10^{-10}(1) 1.77×10^{-10}(2) 1.95×10^{-10}(3)	8.9×10^{-14}(6)	9.22×10^{-15}(7) 1.16×10^{-14}(8)	-
AgBr	7.7×10^{-13}(1) 6.3×10^{-13}(3)	5.8×10^{-16}(6)	1.37×10^{-17}(7) 1.04×10^{-16}(8)	-
AgI	1.5×10^{-16}(1) 0.97×10^{-16}(3)	6.0×10^{-19}(6)	4.41×10^{-20}(7) 1.41×10^{-19}(8)	1.10×10^{-22}(9)
AgSCN	1.16×10^{-12}(1) 1.40×10^{-12}(4) 1.08×10^{-12}(5)	1.8×10^{-14}(6)	4.73×10^{-15}(8)	-

(1) "Handbook of Chemistry and Physics", 48th Ed., (1968).

(2) J. A. Gledhill and G. McP. Malan, Trans. Far. Soc. 48, 258 (1951).

(3) K. Hess and K. Jellinek, Z. physik. Chem., A162, 153 (1932).

(4) S. Aditya and B. Prasod, J. Indian Chem. Soc. 29, 293 (1952).

(5) I. Leden and R. Milsson, Svensk Kem. Tidskr., 66, 126 (1954).

(6) P. S. Buckley and H. Hartley, Phil. Mag., 8, 320 (1929).

(7) F. K. Koch, J. Chem. Soc. 1551, (1930).

Continued on next page

(8) A. Macfarlane and H. Hartley, Phil. Mag. 13, 425 (1932).

(9) E. L. Mackor, Rec. Trav. Chim., 70, 457 (1952).

APPENDIX III

SOLUBILITIES OF SOME ELECTROLYTES IN SELECTED NONAQUEOUS SOLVENTS

Notes to the Tables

1. The solubilities listed in the Tables were obtained from Reference (51).

2. All solubilities are expressed as gms. of salt per 100 gms. of solvent, except where noted otherwise.

3. Solubilities are listed for the anhydrous solvents except where noted otherwise.

4. The temperature, in degrees Centigrade, at which the solubility was measured is indicated by the figure in parentheses.

5. ε in Table 1, is the dielectric constant of the solvent at 25°C.

TABLE 1

Solubility
(gms of Salt/100 gms of solution)

Salt	Methanol ϵ = 32.63	Ethanol ϵ = 24.3	Acetone ϵ = 20.7	Ethylene Glycol ϵ = 37.7	Acetonitrile ϵ = 37.5	Nitro Methane ϵ = 35.9
LiCl	43.8(30)	25.1(20)	0.61(37)	11.01(15)	0.14(25)	-
LiBr	140 (25)	72.1(20)	18.20(20)	60 (15)	8.18(25)	-
LiI	343.4(25)	250.8(20)	42.56(18)	38.9 (15)	154 (25)	2.52(25)
$LiNO_3$	-		23.67(20)	-	2.99(23)	-
NaCl	1.33(25)	0.065(25)	3.2×10^5[1] (18)	7.15(25)	2.5×10^4 (25)	-
NaBr	17.36(25)	2.41 (25)	0.008 (25)	35.4 (25)	4.0×10^2 (25)	-
NaI	77.7 (25)	46.02 (25)	40.10 (25)	-	18.43 (25)	0.48(25)
NaSCN	40.04(25)	20.60 (25)	6.85 (19)	-	-	-
$NaNO_3$	0.41(25)	0.036(25)	1.98[3] (25)	-	-	-
KCl	0.43(25)	0.029(25)	Insol. (25)	5.0[5](30)	2.4×10^3(25)	-
KBr	1.69(25)	0.135(25)	0.036[2] (25)	18.0[6](30)	2.4×10^2(25)	-
KI	13.28(25)	1.92 (25)	1.30 (25)	33.6[7](30)	2.11 (25)	0.307(25)
KSCN	-	-	20.75 (22)	-	11.31 (18)	-
KNO_3	0.43(30)	0.40 (30)	0.7[4] (25)	-	-	-
$AgNO_3$	2.84(20)	1.67 (20)	0.5 (20)	49.67(25)	138.2 (25)	

(Continued on next page)

TABLE 1 CONTINUED

Solubility (gms of Salt/100 gms of solution)

Footnotes to Table 1.

[1] gms of salt per 100 gms of saturated solution.

[2] gms of salt per liter of saturated solution.

[3]Solvent contained 10% water.

[4]Solvent contained 12.4% water.

[5]Solvent contained 5% water.

[6]Solvent contained 14% water.

[7]Solvent contained 34% water.

TABLE 2

Solubility
(gms of salt/100 gms of solution)

Salt	Methanol	Ethanol	Acetone	Ethylene Glycol
$CaCl_2$	22.6[1] (20)	20.5[1] (20)	0.0118 (25)	20.6 (25)
$CaBr_2$	56.2 (20)	54.0 (25)	2.74 (25)	-
CaI_2	126.1 (20)	-	88.3 (20)	-
$Ca(NO_3)_2$	144.2 (40)	51.4 (20)	16.8 (20)	-
$SrCl_2 \cdot 6H_2O$	63.3 (6)	3.8 (6)	-	36.4[1] (25)
$SrBr_2$	119.4 (20)	63.9 (20)	0.62 (20)	-
SrI_2	-	4.3[1] (39)	42.0 (20)	-
$Sr(NO_3)_2$	-	0.0074 (25)	-	-
$BaCl_2$	2.18 (15.5)	0.08[2] (30)	-	36.8 (25)
$BaBr_2$	41.9 (20)	4.13 (20)	0.026 (25)	
BaI_2	-	77.0 (20)	-	
$Ba(NO_3)_2$	0.057 (20)	0.0018 (25)	0.005 (25)	

[1] gms of salt per 100 gms of saturated solution.
[2] Solvent contained 2% water.

TABLE 3

Solubility
(gms of salt/100 gms of solution)

Salt	Methanol	Ethanol	Acetone	Ethylene Glycol	Acetonitrile
$CuCl_2$	58.6 (20)	35.7 (20)	2.88 (18)	-	1.57 (18)
$CuBr_2$	-	-	-	-	24.4 (18)
$FeCl_3 \cdot 6H_2O$	143 (15)	51.43(25)	62.9 (18)	-	-
$CoCl_2$	43.6 (25)	54.4 (20)	3.71 (25)	10.7 (25)	4.08 (18)
$CoBr_2$	43.0 (20)	77.1 (20)	65.0 (25)	-	-
$NiCl_2$	37.6[1](5)	10.05(25)	6×10^3(35) n	16.2 (25)	-
$NiBr_2$	35.1 (20)	-	0.81 (20)	-	-
$Ni(NO_3)_2$	-	-	-	7.5 (25)	-
$CdCl_2$	2.15 (20)	1.48 (20)	-	-	-
$CdBr_2$	16.2 (20)	30.0 (20)	1.56 (18)	-	-
CdI_2	206.7 (20)	110.5 (20)	41 (25)	-	-

[1]gms of salt per 100 gms of saturated solution.

APPENDIX IV

WAVELENGTH CALIBRATION* FOR BECKMANN DU SPECTROPHOTOMETER

Wavelength Range mμ	Correction mμ
750-600	+1
600-570	+2
570-530	+3
530-450	+4
450-400	+5

*A didymium filter was used.

APPENDIX V

A. TITRATION CELL COMPARTMENT FOR USE WITH A BECKMANN DU SPECTROPHOTOMETER

A special non-magnetic cell compartment was built for the Beckmann DU spectrophotometer, to accommodate a 65-ml rectangular titration cell and the tip of a buret. It was made from one-half inch plywood. Its outside dimensions were 13 cm long, 14 cm wide and 9.5 cm high. The design of its ends was exactly the same as that of the standard Beckmann cell compartment. One-eighth inch thick felt was glued to the ends so as to prevent light leakage. This cell compartment was held in place in the spectrophotometer by four one-eighth inch diameter brass screws which were 9½" long, the last ½" being threaded. The screws passed through the holes provided in the phototube housing and through four holes, 5/16" diameter, drilled through the special cell compartment.

A lid, 16 cm by 15 cm with a 1-cm over-hang, was made of one-half inch plywood. A hole, 0.7 cm in diameter, was bored in the center of the lid. This hole was countersunk ⅛" by a larger hole, 1.7 cm in diameter. A Silicone-rubber septum, 1.7 cm in diameter and ⅛" thick, fitted into the countersink; the compartment was then light-tight.

To maintain constant temperature inside this cell compartment, two copper tanks, 12.5 cm long by 6.5 cm high by 4 cm wide, were installed on either side of the light

path. The two tanks were connected by ¼" diameter copper tubing, just above the slit opening. Two ¼" diameter pieces of copper tubing, 1½" long were soldered onto the outer sides and near the bottom of each tank. They protruded through holes bored on either side of the cell compartment, near the phototube housing. The holes were made light-tight by sealing with plastic wood.

Water from a constant-temperature bath was circulated at approximately 0.5 liters/min through the two copper tanks, by means of a circulating pump.

B. MEASUREMENT OF THE TEMPERATURE OF THE SOLUTION IN THE TITRATION CELL

The temperature of the water in the constant-temperature bath was controlled by a Micro-Set mercury contact thermoregulator. The temperature of the water could be controlled to ± 0.1°C at 25°C. The temperature of the water was measured with a thermometer which had been calibrated against a standard thermometer certified by the National Bureau of Standards, Washington. At 25°C it had an error of + 0.04 degree. The temperature of the solution in the titration cell was measured by means of a copper-constantan thermocouple. The reference junction of the thermocouple was in ⅛" diameter thin-walled glass tubing, 10 cm long, and sealed at one end. The glass tubing was attached to the calibrated thermometer in the water bath with rubber bands. The copper wire of the

thermocouple was connected to the positive and negative terminals of a sensitive galvonometer. The working end of the thermocouple was led in through the lid of the cell compartment into the solution to be titrated. The sensitivity of the galvonometer was 125 microamps for full-scale deflection. The needle of the galvonometer was adjusted to centre zero, so that positive and negative temperature deviations could be observed. The temperature of the solutions in the titration cell was given by the difference between it and the temperature of the water in the water-bath. When no deflection showed on the galvonometer, the temperature of the solution corresponded to that of the water in the water-bath. Furthermore, by calibrating the galvonometer deflections, the exact temperature of the solution in the titration cell could be measured. The galvonometer was calibrated by observing the deflections caused by dipping the working end of the thermocouple in water. The temperature of the water was varied from 10° to 30°C and from 30° to 60°C. One division of the galvonometer was found to correspond to 0.2°C. It was possible to read the scale of the galvonometer to one-half of a division. Hence, the temperature of the solution could be measured to within ± 0.1°C.

C. TITRATION CELLS

Two types of cells were used for the titrations. One had a capacity of 65 ml and the other a capacity of 3 ml.

Two cells of each type were used. The 65-ml cell was made of glass. The cell had outside dimensions 5.4 cm long by 3 cm wide by 5.5 cm deep. The glass was 2 mm thick. The path length at the top edge of the cells was measured by a cathetometer and found to be 5.005 cm for one cell and 5.008 cm for the other. The path length at the bottom of the cells was measured with precision calipers and was 5.010 cm for both cells. The 3-ml cells were conventional 1-cm rectangular matched silica cells.

D. CELL COVERS

A cover for each cell was designed to prevent solvent evaporation. For the 65-ml cell the 7 cm long by 3.5 cm wide cover was a sandwich of $\frac{1}{8}$" Silicone rubber between two $\frac{1}{8}$" aluminum plates. Two rectangles, 3.5 cm long by 1.5 cm wide, were cut in the centre of the aluminum plates, but not in the Silicone rubber. This "sandwich" was bolted together with four $\frac{1}{8}$" bolts, two at each end. An effective seal between the cover and the cell was made by smearing the top edges of the cell with Silicone grease. The thermocouple wires were passed between the top aluminum plate and the Silicone-rubber septum and then pushed through the rubber to gain access to the solution. The wires were led out of the cell compartment between the lid and the body of the compartment. A similar "sandwich" was constructed for the 3-ml cell. Its dimensions were 1.2 cm wide by 3 cm

long. A ¼" diameter hole was drilled in the aluminum plates, to allow access to the cell, through the Silicone rubber.

APPENDIX VI

MANUAL, CONTROLLED-POTENTIAL ELECTROLYSIS APPARATUS

The following components were used in the construction of a manual, controlled-potential electrolysis apparatus (Section IV A subsection 5).

(a) D.C. Power Supply

A D.C. power supply was obtained from the Eberbach Electro-Analyzer described in Section IV A subsection 4. The voltage was adjusted to 6 volts.

(b) Potential-Measuring Device

The function of this device was to measure the potential of the working electrode (cathode) against the external, reference electrode. A conventional Beckmann pH meter was used as a high-impedance, high-resistance voltmeter.

(c) Ammeter

A variable-range ammeter was constructed from a milliammeter having a range of 0-5 mA. Ranges of 0-500 mA and 0-50 mA were obtained by using shunts. A bypass enabled the ammeter to be used in the 0-5 mA range. The ammeter was switched to the lower ranges as the electrolysis proceeded.

(d) Voltage Adjuster

The function of the voltage adjuster was to vary the total voltage applied to the cell so that the potential of the working electrode remained constant. A rheostat

arranged as a potential divider was used. The rheostat was a tubular type with a ceramic core. It had a resistance of 23 ohms and a current rating of 4.3 amps.

(e) Voltmeter

The voltmeter was used to measure the applied potential. It had a range of 0-10 volts and its scale was calibrated with a standard Weston cell in the conventional manner.

(f) Saturated Calomel Electrode

The cell was made from the conventional chemicals. The physical design was that suggested in (67). The vessel was constructed from a 50-ml test tube. A 6 cm side arm was blown onto it, 3 cm from the top. It was bent at right-angles 2 cm from the joint. The tip of the side arm was drawn to a diameter of about 1 mm and bent upward into a J to prevent mixing of the saturated KCl solution.

As an extra precaution the tip was filled with an agar gel plug. In use the tip of the calomel electrode was placed as close to the working electrode as possible.

(g) Working Electrode and Anode

The working electrode was a cylindrical platinum gauze electrode. It was gold-plated to protect it from such metals as lead, zinc and cadmium. The anode was a platinum rod, 1 mm in diameter and 10 cm long. The electrodes were held in position with a support made by fastening binding posts to a bakelite block.

APPENDIX VII

VACUUM SUBLIMATION APPARATUS

This apparatus was used to purify oxine by vacuum sublimation (see Section IV A subsection 6).

The complete "Quickfit" vacuum sublimation assembly was supplied by Hysil Ltd. It consisted of a sample chamber, a 10.5 cm long cold finger, and adapters for connecting to the vacuum line. When the chamber that was supplied by the manufacturer was in place, the tip of the cold finger was about 11 cm from the surface of the solid sample. It was found that with this arrangement the sublimation took several hours. Use of a shorter chamber reduced the sublimation time without loss of purity of the sublimate.

The shorter chamber was blown from Pyrex tubing fused to a B24 "Quickfit" ground-glass joint. Its length was 7 cm excluding the joint. With this chamber in place, the tip of the cold-finger was 2.5 cm from the surface of the solid to be sublimed. A heating mantle for the sample chamber was constructed by inserting a copper tube, 3 cm in diameter and 7.5 cm long, in a tin can 9 cm in diameter and 7.5 cm high. The copper tube was surrounded by sand. The sample chamber was inserted into the copper tube.

A chromel-alumel thermocouple wire was inserted into the copper tube alongside the sample chamber. The thermocouple was connected to a Fisher "Indicating Pyrometer" which was designed for use with chromel-alumel. Heat was

supplied from a controlled, electric hot plate. The heating rate was 2°C per minute until the temperature at which sublimation took place was reached. The heating rate was then reduced so as to maintain the desired temperature until sublimation was complete.

APPENDIX VIII

COMPARISON OF THE BEHAVIOUR OF DITHIZONE IN DIFFERENT GRADES OF BENZENE

A comparison was made between reagent-grade, spectrophotometric-grade and purified, distilled reagent-grade benzene (Section IV B subsection 1). The following experiments were carried out:

(1) Study of the change of absorbance with time for pure dithizone solutions.

(2) Change of titre with time in the titration of dithizone with standard silver nitrate.

(3) Freezing-point measurements.

(a) Study of the Change of Absorbance with Time for Purified Dithizone Solutions

Dithizone was an excellent reagent with which to compare the purities of the three grades of benzene, because it is very sensitive to impurities in the solvent. It is easily oxidized to diphenylthiocarbadiazone. This oxidation product absorbs more strongly than dithizone at 450 mμ but negligibly at 618 mμ, which are the two absorption maxima of dithizone. A measure of the ratio of the absorbance at 618 mμ to that at 450 mμ, as a function of time, should show the effects of the solvent on the dithizone. The solutions of dithizone were stored in red, low-actinic glassware to eliminate photochemical changes.

Purified dithizone was prepared by the method given in Appendix IX. Solutions of dithiozne having concentrations 2.5×10^{-5} M and 5.0×10^{-4} M were prepared in reagent-grade, spectrophotometric-grade and purified, distilled reagent-grade benzene. Reagent-grade benzene was purified by a conventional procedure. Thus, it was first washed with concentrated sulphuric acid, then with water until the washings were neutral. The benzene was then dried by percolating it through silica gel. Finally it was distilled under a blanket of dry nitrogen. The middle-third fraction boiling at 80.1°C was collected. In addition, solutions of dithizone were prepared and studied in spectrophotometric-grade benzene that had been dried with silica gel, spectrophotometric-grade benzene that had been dried with silica gel and calcium hydride, and distilled reagent-grade benzene that had been dried with calcium hydride. Measurements of the absorbance at 618 mμ and 450 mμ were made over a period of one month, with a Unicam SP500 spectrophotometer. The ratio of the absorbance at 618 mμ to that at 450 mμ is plotted as a function of time in Figure 1 for the 2.5×10^{-5} M dithizone solution. The results obtained are given in Table 1. Table 2 gives the results obtained with the dried benzenes.

The measurements show that spectrophotometric-grade benzene was at least as good as purified, distilled benzene over a period of three weeks. Table 2 shows that the presence of water did not speed up the oxidation of dithizone.

FIGURE 1

COMPARISON OF A_{618}/A_{450} FOR A 2.5×10^{-5} M
DITHIZONE SOLUTION IN SELECTED GRADES OF BENZENE

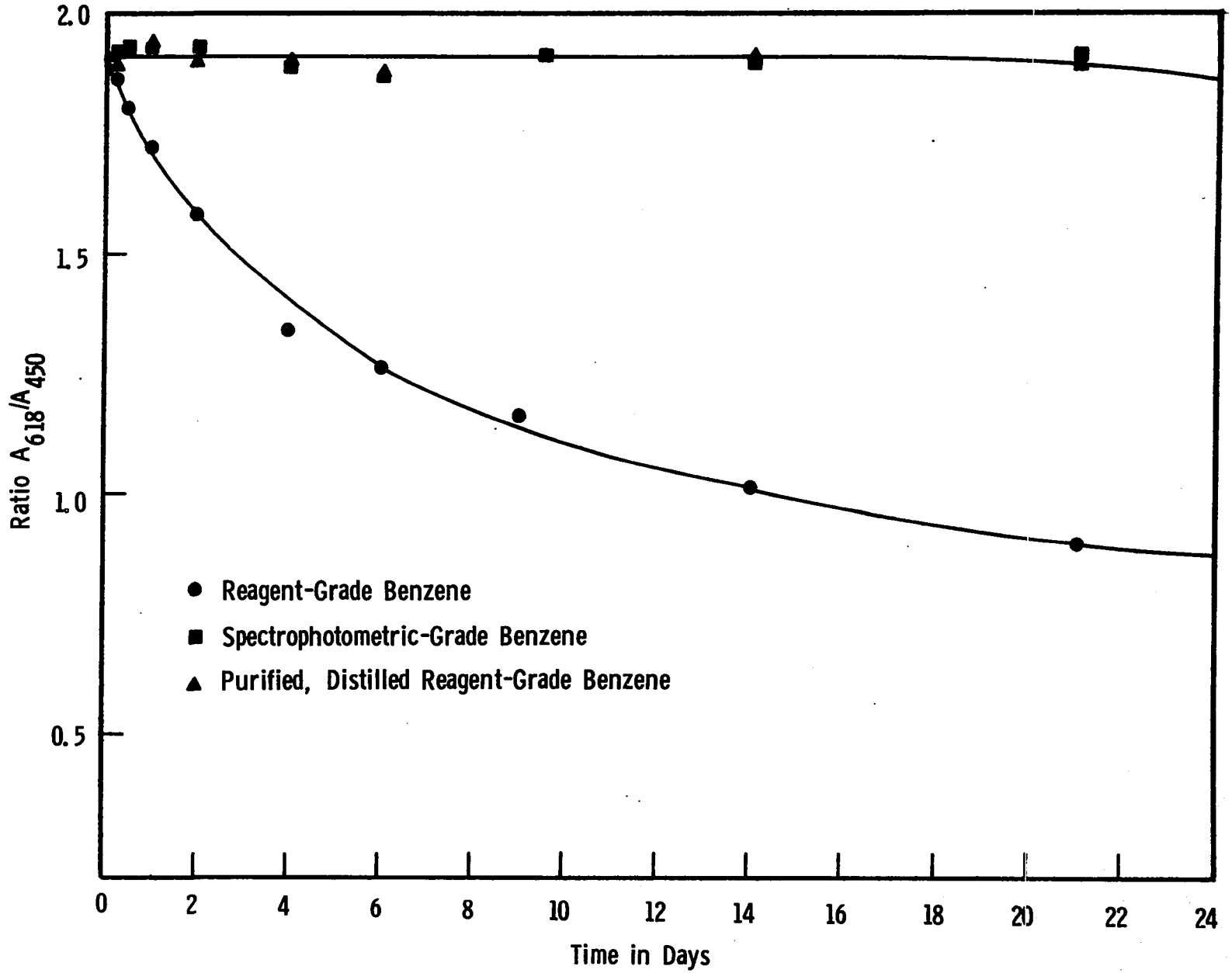

2.0
1.5
1.0
0.5
Ratio A_{618}/A_{450}
Reagent-Grade Benzene
Spectrophotometric-Grade Benzene
Purified, Distilled Reagent-Grade Benzene
0
2
4
6
8
10
12
14
16
18
20
22
24
Time in Days

TABLE 1

THE VARIATION OF THE RATIO A_{618}/A_{450}, WITH TIME, OF $2.5 \pm 0.5 \times 10^{-5}$ M AND $5.0 \pm 0.5 \times 10^{-4}$ M DITHIZONE SOLUTIONS IN SELECTED GRADES OF BENZENE

Time in Days	Reagent-Grade Benzene			Spectrophotometric-Grade Benzene			Purified, Distilled Reagent-Grade Benzene		
	A_{618}	A_{450}	A_{618}/A_{450}	A_{618}	A_{450}	A_{618}/A_{450}	A_{618}	A_{450}	A_{618}/A_{450}
				$2.5 \pm 0.5 \times 10^{-5}$ M Dithizone					
0.042	0.920	0.489	1.88	0.931	0.488	1.91	0.928	0.491	1.89
0.25	0.898	0.483	1.86	0.921	0.488	1.89	0.930	0.484	1.92
0.50	0.892	0.496	1.80	0.925	0.482	1.92	0.935	0.487	1.92
1.0	0.872	0.507	1.72	0.940	0.485	1.94	0.920	0.479	1.92
2.0	0.864	0.545	1.58	0.936	0.493	1.90	0.927	0.491	1.89
4.0	0.850	0.635	1.34	0.918	0.483	1.90	0.920	0.492	1.87
6.0	0.840	0.666	1.26	0.937	0.498	1.88	0.918	0.491	1.91
9.0	0.823	0.710	1.16	0.933	0.498	1.91	0.932	0.491	1.90
14.0	0.801	0.794	1.01	0.924	0.484	1.91	0.921	0.488	1.89
21.0	0.787	0.885	0.89	0.910	0.482	1.89	0.930	0.492	1.89
30.0	--	--	--	0.920	0.495	1.86	0.935	0.484	1.93
				$5.0 \pm 0.5 \times 10^{-4}$ M Dithizone					
0.042	1.626	0.865	1.88	1.638	0.860	1.90	1.645	0.857	1.92
0.25	1.615	0.855	1.89	1.638	0.856	1.91	1.630	0.840	1.94
0.50	1.610	0.851	1.89	1.625	0.869	1.87	1.638	0.860	1.90
1.0	1.602	0.866	1.85	1.630	0.875	1.86	1.630	0.849	1.92
2.0	1.588	0.881	1.80	1.632	0.864	1.89	1.624	0.869	1.87
4.0	1.578	0.950	1.66	1.642	0.855	1.92	1.632	0.874	1.87
6.0	1.560	1.028	1.52	1.640	0.850	1.93	1.638	0.865	1.89
9.0	1.550	1.120	1.38	1.627	0.865	1.88	1.635	0.851	1.92
14.0	1.537	1.300	1.18	1.620	0.852	1.90	1.640	0.862	1.90
21.0	1.518	1.390	1.09	1.630	0.857	1.90	1.630	0.866	1.88
30.0	1.493	1.821	0.82	1.621	0.862	1.88	1.629	0.848	1.92

TABLE 2

THE VARIATION OF THE RATIO A_{618}/A_{450}, WITH TIME, OF A 5.0 $\pm$ 0.5 x 10^{-4} M SOLUTION OF DITHIZONE IN SELECTED PURE GRADES OF BENZENE DRIED WITH DIFFERENT REAGENTS

Time in Days	Spectrophotometric-Grade Benzene dried with Silica Gel			Spectrophotometric-Grade Benzene dried with Silica Gel and Calcium Hydride			Purified, Distilled Benzene dried with Calcium Hydride		
	A_{618}	A_{450}	A_{618}/A_{450}	A_{618}	A_{450}	A_{618}/A_{450}	A_{618}	A_{450}	A_{618}/A_{450}
0.042	1.555	0.831	1.87	1.503	0.791	1.90	1.595	0.840	1.90
0.25	1.561	0.819	1.91	1.491	0.785	1.90	1.590	0.827	1.92
0.50	1.560	0.835	1.87	1.495	0.790	1.89	1.595	0.849	1.88
1.0	1.550	0.815	1.90	1.495	0.807	1.85	1.598	0.850	1.88
2.0	1.547	0.806	1.92	1.495	0.786	1.90	1.590	0.845	1.88
4.0	1.553	0.835	1.86	1.510	0.786	1.92	1.582	0.830	1.91
7.0	1.560	0.825	1.89	1.500	0.785	1.91	1.597	0.830	1.92
14.0	1.542	0.805	1.92	1.510	0.795	1.90	1.590	0.841	1.89
21.0	1.540	0.810	1.90	1.498	0.788	1.90	1.592	0.829	1.92
30.0	1.540	0.819	1.88	1.500	0.802	1.87	1.590	0.841	1.89

No difference between spectrophotometric-grade benzene, undried, dried with silica gel and dried with silica gel and calcium hydried, existed.

(b) The Spectrophotometric Titration of Dithizone Solutions with Standard Silver Nitrate

The oxidation product of dithizone is known not to react with metals. A study of the change of titre in the spectrophotometric titration of dithizone solutions with silver nitrate as a function of time would thus reveal oxidation of dithizone by the benzene. Details of the spectrophotometric titration of dithizone were given in Section IV C subsection 2. The results obtained are given in Table 3. The titre is expressed as found molarity.

There is scatter in the results from day to day but no trend upwards or downwards over a period of four weeks. It was proved that the fluctuations were random by a statistical analysis (103).

(c) Note on Air-Oxidation of Dithizone Solutions

In the experiments carried out with the dried benzenes, the solutions were stored in a dry box under a blanket of dry nitrogen. There was little chance for the benzene solutions of dithizone to be oxidized by oxygen in the atmosphere. Yet the results obtained agree, within experimental error, with those benzene solutions (spectrophotometric-grade and purified, distilled reagent-grade) which had not been dried and had been left in the atmosphere.

TABLE 3

FLUCTUATIONS IN THE FOUND MOLARITY OF A SOLUTION OF DITHIZONE IN SPECTROPHOTOMETRIC-GRADE BENZENE AS A FUNCTION OF TIME

Time in Days	Found Molarity of Dithizone in Spectrophotometric-Grade Benzene* x 10^3
1	1.089
2	1.042
7	1.076
14	1.030
18	1.029
19	1.033
21	1.040
25	1.053
27	1.043
32	1.053

*Mean of five titrations.

Therefore it is reasonable to assume that the changes in the ratio of A_{618}/A_{450} were produced by impurities in the solvent only.

(d) Freezing Point Measurements

Freezing point measurements were made on the spectrophotometric-grade benzene and compared both with the purified, distilled reagent-grade benzene, and with the accepted literature value. In addition, the freezing point of a sample of spectrophotometric-grade benzene dried with silica gel was measured.

The freezing point was obtained in the conventional manner by plotting the temperature of the benzene against time. The temperature at which the curve became horizontal was taken as the freezing point. The thermometer used was calibrated against a National Bureau of Standards, Washington standardized thermometer*. The conventional stem corrections were also applied. The freezing points were determined from liquid to solid and solid to liquid.

The freezing points obtained are given in Table 4. The purified, distilled reagent-grade benzene is slightly lower than the literature value. This is to be expected since the literature value was obtained from a sample of benzene that was of extraordinarily high purity. The freezing point of the undried spectrophotometric-grade benzene was lower

*This thermometer was generously loaned to the author by Professor A. S. Ross, McGill University.

TABLE 4

THE FREEZING POINTS OF SELECTED GRADES OF BENZENE

Spectrophotometric-Grade Benzene	Purified, Distilled, Reagent-Grade Benzene	Spectrophotometric-Grade Benzene dried with Silica Gel	Literature* Value
5.39 ± 0.05°C	5.44 ± 0.05°C	5.44 ± 0.05°C	5.493 ± 0.01°C

*International Critical Tables, 1st Ed., Vol. IV (1928). (122)

than that of the purified, distilled reagent-grade. However, after drying the spectrophotometric-grade benzene with silica gel, its freezing point was the same as that of the purified benzene, with experimental error.

APPENDIX IX

METHOD FOR THE PURIFICATION OF DITHIZONE

Purified dithizone solutions were required for use as titrant in the spectrophotometric titrations (Section IV D, 1(c)), determination of its absorptivity (Section IV C, 5(a)), and for the study of its reactions with metal chelates (Section IV C, 6). The method of purification used is as follows.

All operations in the purification method must be carried out in a darkened room. Weigh out 2.0 gms of impure dithizone and dissolve in one litre of purified chloroform*. Extract the dithizone into the aqueous phase with 500 ml of 5% purified ammonia solution**. Separate the aqueous phase into a 1-litre beaker and discard the chloroform layer. Neutralize the aqueous solution by the dropwise addition of a solution containing 1 volume saturated aqueous SO_2 solution and 5 volumes concentrated HCl. Transfer the solution to a clean separatory funnel and reextract the dithizone into one litre of purified chloroform. Repeat the above procedure four times. Wash the final extract of chloroform with ten 200-ml portions of a mixture of 1 volume saturated aqueous solution of SO_2 plus 99 volumes of water.

---

*See Section IV B subsection 2 for method of purification.

**Five ml of purified, concentrated ammonia solution in 95 ml of ion-exchanged water.

After washing, filter the chloroform layer through three thicknesses of filter paper into a two-litre beaker. Renew the filter paper if necessary.

Transfer the chloroform solution into a dry box which has previously been flushed with nitrogen. The dry box must be in a darkened room. To remove oxygen from the nitrogen pass it through a gas-washing bottle containing a saturated, aqueous solution of SO_2, a water wash, an acetone-dry ice trap, and finally a liquid-air trap. Allow the chloroform to evaporate to one-half its volume in the dry box with the exhaust gases vented to a fume-hood. Then add an equal volume of carbon tetrachloride and evaporate to a volume of 200 ml. Remove from the dry box and cool in an ice-bath. Filter the crystals of dithizone onto a fritted-glass filter in a darkened room. Wash the crystals with three 20-ml portions of ice-cold carbon tetrachloride and allow them to dry in the dry box under a stream of dry nitrogen. Finally dry the dithizone under vacuum over potassium hydroxide for two weeks.

APPENDIX X

PROCEDURE FOR THE PURIFICATION OF OXINE*

(a) Recrystallization

Prepare a saturated solution of commercial reagent-grade oxine in absolute ethanol. Allow the solution to stand in the dark for 24 hours. The ethanol will then have evaporated to about one-half of its original volume (this helps to produce an adequate crop of crystals). Filter the crystals onto a fritted-glass filter. Wash them with three portions of ice-cold ethanol. Repeat the crystallization. Filter and wash the crystals as before, and allow them to dry in a stream of dry nitrogen. Grind the crystals to a fine powder in a clean mortar, before the vacuum sublimation.

(b) Vacuum Sublimation

An apparatus for vacuum sublimation is described in Appendix VII. Weigh out 0.5 gm of the recrystallized oxine into the sample chamber. Insert the cold finger and set the apparatus up in the sand bath, as described in Appendix VII. Evacuate the sample chamber and continue pumping until all the sample has sublimed. Raise the temperature of the sand-bath at the rate of 2°C per minute. When the temperature has reached 100°C reduce the heating rate so as to maintain this temperature. When all the oxine has sublimed, remove the sand bath and allow the apparatus to cool, still

*For Section IV B subsection 6.

under vacuum. After cooling, clamp the outlet to the vacuum pump, and shut off the pump. Slowly release the vacuum in the apparatus. Carefully remove the cold finger, making sure it does not touch the sides of the sample chamber, particularly at the joint where there is vacuum grease. Scrape the sublimed oxine into a weighing bottle and dry it under vacuum over "Drierite", for one week. Repeat the above procedure with new batches, until enough oxine for use is obtained.

APPENDIX XI

PROCEDURE FOR THE PREPARATION OF METAL OXINATES* (88)

Transfer a sufficient quantity of the pure metal solution to a 400-ml beaker. Add the buffer recommended in Table 1 for the precipitation of the particular metal oxinate. Dilute the solution to 200 ± 5 ml, whereupon it will then be at the correct pH; then heat it to 70-80°C. With rapid stirring, add dropwise a 5% solution of purified oxine in ethanol, until precipitation is complete. Avoid an unnecessary excess of oxine. Digest the precipitate for three hours on a steam bath, with occasional stirring. Allow the solution to cool, and let it stand for four hours. Filter the precipitate of metal oxinate onto a fritted-glass filter of medium porosity. Wash it with ten 20-ml portions of hot water, then with several 20-ml portions of cold water, in order to remove excess oxine.

Redissolve the precipitate in 100 ± 2 ml of 2N HCl. Heat the solution to 70-80°C, and reprecipitate the metal oxinate by adjusting to the prescribed pH. In most cases this involves neutralizing with concentrated ammonia to a pH of about 1 and then adding sodium acetate in order to achieve the correct pH. Allow the mixture to digest as before. Filter and wash by the same procedure as for the first precipitation. Dry the metal oxinates at the temperatures recommended in Table 2.

---

*For Section IV B subsection 8.

TABLE 1

pH RANGE FOR THE PRECIPITATION OF METAL OXINATES

Metal Oxinate	pH Range		Reference
$PbOx_2$	8.44-12.28	ammonia-ammonium acetate buffer	1
$ZnOx_2$	4.58-7.0	acetate buffer	2
$CdOx_2$	5.66-6.58	acetate buffer	3
$CuOx_2$	3.36-4.55	acetate buffer	4
$AgOx \cdot HOx$	See this Appendix		6
$InOx_3$	2.5-3.0	acetic acid-acetate buffer	5
$NiOx_2$	4.33-6.25	acetate buffer	4
$CoOx_2$	4.27-6.16	acetate buffer	4

1. Z. Karaoglanov & B. Sagortschev, Z. Anal. Chem., 81, 275 (1930).
2. R. Berg, Z. Anal. Chem., 71, 175 (1927).
3. H. R. Fleck, Analyst, 62, 378 (1937).
4. H. R. Fleck, & A. M. Ward, Analyst, 58, 388 (1933).
5. W. Geilmann & F. W. Wrigge, Z. anorg. Chem., 209, 129 (1932).
6. F. Hein & H. Regler, Naturwissenschaften, 23, 320 (1935).

TABLE 2

RECOMMENDED DRYING TEMPERATURES FOR THE METAL OXINATES

Metal Oxinate	Drying Temperature ± 5°C	Reference
$PbOx_2$	105°C	1
$ZnOx_2$	140°C	2,3
$CdOx_2$	130°C	3
$CuOx_2$	105°C	4
$AgOx \cdot HOx$	Vacuum dried Decomposes at 80°C	7
$InOx_3$	120°C	6
$NiOx_2$	130°C	5
$CoOx_2$	125°C	5

1. C. Duval, Anál. Chim. Acta., 4, 168 (1950).
2. M. de Clerq & C. Duval, Anal. Chim. Acta., 5, 288 (1951).
3. R. Berg, Z. Anal. Chem. 71, 321 (1927).
4. R. Berg, Z. Anal. Chem. 70, 341 (1927).
5. R. Berg, Z. Anal. Chem. 76, 191 (1929).
6. W. Geilmann, & F. W. Wrigge, Z. Anorg. Chem., 209, 129 (1932).
7. F. Hein & H. Regler, Naturwissenschaften, 23, 320 (1935).

A different procedure is used to prepare silver oxinate. Silver forms two oxinates. The first is a white crystalline material, assigned the formula $Ag(C_9H_6NOH)_2NO_3$ by Hein and Regler, as stated in (88). From this the yellow chelate, $Ag(C_9H_6NO)\cdot C_9H_6NOH$, is prepared.

Perform all operations in a darkened room. Dissolve 2.0 gms of $AgNO_3$ in 75 ± 5 ml of absolute ethanol. Prepare a separate solution containing 3.0 ± 0.1 gm of oxine dissolved in 45 ± 5 ml of ethanol. Run the $AgNO_3$ solution as a fine stream into the oxine solution. After a few moments, white flakes of the first complex are precipitated. Filter these crystals onto a fritted-glass filter and wash them with ice-cold ethanol.

Dissolve the white material in 40 ± 2 ml of water plus 12 ± 1 ml of 1:1 H_2SO_4. Filter the resulting yellow solution, and treat the filtrate with concentrated ammonia until it is just alkaline. Stir the precipitate for one-half hour in the dark, then filter it onto a fritted-glass filter, wash it with water, ethanol and finally with absolute ether. Redissolve the precipitate in concentrated ammonia. Place the solution in a vacuum desiccator and connect the outlet to a water aspirator. Evaporate until no fumes of ammonia can be detected. Filter the crystals, wash them with water, ethanol and absolute ether. Dry them for 24 hours over concentrated sulphuric acid. Store the crystals in the dark.

APPENDIX XII

APPROXIMATE SOLUBILITIES OF METAL DITHIZONATES AND METAL OXINATES IN CHLOROFORM, CARBON TETRACHLORIDE AND BENZENE

Very limited data on the solubilities of metal oxinates and metal dithizonates in nonaqueous solvents are available in the literature. In the present work, saturated solutions of the metal chelates in benzene were prepared as stock solutions for use. The metal concentration was then determined as a means of standardizing these solutions. The concentrations found for these solutions are given in Table 1. Cupric, zinc and indium dithizonates were all relatively soluble in benzene and saturated solutions were not prepared. Therefore the values given in the Table are preceded by > to indicate that the solubility is greater than the concentration of the stock solution that was prepared. No account of temperature has been taken.

The Table also lists estimates of the solubilities of those metal chelates in carbon tetrachloride and chloroform for which there was no data. The estimates were made from the upper concentration limit quoted for the colorimetric determination of the particular metal in reference 5 of the Table.

In general, the solubility increases in the order (see ref. 5 of the Table):

$$CCl_4 < C_6H_6 < CHCl_3$$

TABLE 1

APPROXIMATE SOLUBILITIES OF METAL DITHIZONATES AND METAL OXINATES IN CHLOROFORM, CARBON TETRACHLORIDE AND BENZENE

Metal Oxinate	Solvent	Approximate Solubility	Reference
$PbOx_2$	Benzene	5×10^{-5} M	This work
	Chloroform	2×10^{-4} M	1
$CuOx_2$	Benzene	2×10^{-4} M	This work
	Chloroform	10^{-3} M	1
$InOx_3$	Benzene	2×10^{-3} M	This work
	Chloroform	0.24 M**	2
$CdOx_2$*	Benzene	3.0×10^{-4} M	This work
$ZnOx_2$**	Benzene	3.5×10^{-4} M	This work
AgOx·HOx	Benzene	10^{-6} M	This work

Metal Dithizonate	Solvent	Approximate Solubility	Reference
$Pb(HDz)_2$	Benzene	5×10^{-5} M	This work
	Carbon Tetrachloride	5.7×10^{-6} M**	3
	Chloroform	2×10^{-4} M	This work
$Cu(HDz)_2$	Benzene	$> 10^{-3}$ M	This work
	Carbon Tetrachloride	5.5×10^{-4} M**	4
	Chloroform	$> 5 \times 10^{-3}$	This work
CuDz	Benzene	$> 10^{-3}$ M	This work
	Carbon Tetrachloride	10^{-3} M	4
$In(HDz)_3$	Benzene	$> 10^{-3}$ M	This work
	Carbon Tetrachloride	10^{-4} M	5
	Chloroform	$> 10^{-3}$ M	This work
$Zn(HDz)_2$	Benzene	$> 10^{-3}$ M	This work
	Carbon Tetrachloride	10^{-4} M	5
	Chloroform	$> 10^{-3}$ M	This work
$Cd(HDz)_2$	Benzene	2×10^{-5} M	This work
	Carbon Tetrachloride	10^{-5} M	5
	Chloroform	6×10^{-5} M	This work

Continued on next page

TABLE 1 CONTINUED

APPROXIMATE SOLUBILITIES OF METAL DITHIZONATES AND METAL OXINATES IN CHLOROFORM, CARBON TETRACHLORIDE AND BENZENE

Metal Dithizonate	Solvent	Approximate Solubility	Reference
AgHDz	Benzene	5×10^{-5} M	This work
	Carbon Tetrachloride	10^{-5} M	5
	Chloroform	$> 10^{-4}$ M	This work
Ag_2Dz	Benzene	10^{-6} M	This work

*The hydrates $CdOx_2 \cdot 2H_2O$ and $ZnOx_2 \cdot 2H_2O$ are insoluble in benzene and chloroform.

**These are not approximate values.

REFERENCES

1. G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", Wiley, New York (1957).

2. R. LaCroix, Anal. Chim. Acta., 1, 260 (1947).

3. O. B. Mathre and E. B. Sandell, Talanta, 11, 295 (1964).

4. R. W. Geiger and E. B. Sandell, Anal. Chim. Acta., 8, 197 (1953).

5. E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience Publ., Inc., New York (1959).

APPENDIX XIII

PROCEDURE FOR THE PREPARATION OF METAL DITHIZONATES*

Perform all operations in a darkened room.

Transfer an aliquot of purified aqueous metal solution to a 2-litre separatory funnel such that the chloroform layer will be almost saturated with the metal dithizonate after extraction**. (This may be calculated from the approximate solubilities given in Appendix XII). Dilute the aqueous layer to 500 ml, then adjust its pH to the value recommended in Table 1.

All reagents used are to be purified before use. As an extra precaution, their solutions are to be shaken with a little dithizone solution in order to remove any reacting metals.

Prepare a purified $1.0 \pm 0.5 \times 10^{-3}$ M solution of dithizone in purified chloroform. Add an aliquot of the dithizone solution to the aqueous solution in the separatory funnel such that 95 ± 2% of the free metal in the aqueous phase will be extracted as metal dithizonate into the chloroform layer. Dilute the resulting chloroform layer to one litre. Shake the two layers for ten minutes.

---

*For Section IV B subsection 9.

**Usually several batches will have to be made, in order to obtain a sufficient quantity of the metal dithizonate.

TABLE 1

AQUEOUS-SOLUTION CONDITIONS FOR THE PREPARATION OF METAL DITHIZONATES BY EXTRACTION INTO CHLOROFORM

Metal Dithizonate	Conditions for Aqueous Phase	Reference
$Cu(HDz)_2$	0.1 N HCl	1
CuDz	1 M $CuCl_2$ in neutral solution - deficiency of H_2Dz	1
$Zn(HDz)_2$	pH = 8.3 citrate buffer	2
$Pb(HDz)_2$	pH = 10 ammonia solution	3
$Cd(HDz)_2$	5% NaOH	4
AgHDz	0.5 N H_2SO_4	5
$In(HDz)_3$	pH = 8.5 ammonia solution	6

1. R. W. Geiger & E. B. Sandell, Anal. Chim. Acta., 8, 197 (1953).

2. J. Cholak, D. M. Hubbard & R. E. Burkey, Ind. Eng. Chem. Anal. Ed. 15, 754 (1943).

3. O. B. Mathre & E. B. Sandell, Talanta 11, 295 (1964).

4. H. Fischer & G. Leopoldi, Mikrochim. Acta 1, 30 (1937).

5. H. Fischer, G. Leopoldi & H. von Uslar, Z. Anal. Chem. 101, 1 (1935).

6. I. May & J. I. Hoffmann, J. Wash. Acad. Sci. 38, 329 (1948).

Separate and discard the aqueous layer. Wash the chloroform solution with three 200-ml portions of purified 1:100 ammonia solution*, followed by enough water washings to render the aqueous phase neutral. For those metal dithizonates that are extracted from acid solution, omit the ammonia washings. With these solutions careful addition of dithizone will ensure that none remains in excess in the chloroform phase.

Filter the washed chloroform solution through three thicknesses of filter paper, into a three-litre beaker. Transfer the beaker to a dry box contained in a darkened room. The dry box must have been previously flushed with dry nitrogen. The nitrogen is freed from oxygen by a process described in Appendix IX. Evaporate the chloroform to one-half its original volume, venting the vapours to a fume-hood, and then add an equal volume of purified carbon tetrachloride. Evaporate the resulting solution to 200 ± 10 ml. Remove the beaker from the dry box and cool the solution in an ice-bath. Filter the crystals onto a fritted-glass filter, and wash them with three, 20-ml portions of ice-cold carbon tetrachloride. Allow the crystals to dry under dry nitrogen. Finally dry the crystals under vacuum over KOH for two weeks. Store the crystals in a tightly sealed container in the dark. Stored in this way the crystals are stable.

---

*Washing with ammonia solution removes any excess dithizone that may be present in the chloroform layer.

APPENDIX XIV

METHOD FOR THE DECOMPOSITION OF THE ORGANIC MATTER IN METAL CHELATES*

K. Ueno et. al. (193) studied several oxidizing mixtures for the complete decomposition of the organic matter in metal chelates. They recommended a 3:1 mixture of concentrated HNO_3:concentrated $HClO_4$. However, such a mixture, when heated in the presence of organic matter must be used with extreme caution. A safer mixture, which is almost as good and studied by the above authors, is a 1:1 mixture of concentrated HNO_3 and 30% (by volume) hydrogen peroxide. This mixture is used unless otherwise stated.

Allow the nonaqueous solution of the metal chelate to evaporate to dryness in a 100-ml beaker. To the residue of the metal chelate, carefully add 4 ml of the 1:1 oxidizing mixture to the covered beaker. This is done by adding first 2.0 ml of concentrated HNO_3, then 2.0 ml of 30% hydrogen peroxide. Heat the solution on a hot-plate until vigorous chemical action has ceased. Remove the beaker to a steam bath and evaporate the solution to moist dryness. The residue is then ready for further treatment by other reagents.

The metal oxinates were found to be easily oxidized; only one treatment was needed. However, the metal dithizonates were less easily oxidized. In general, after only one

---

*For Section IV B subsections 8 and 9.

oxidation a black residue remained. Analyses of this residue for the metal showed that the dithizonate was incompletely oxidized. It was found that at least three oxidations were needed; four are recommended as an extra precaution. When zinc is to be determined polarographically, the sodium stannate present as a stabilizer in the 30% hydrogen peroxide interferes in the analysis. However, the zinc chelates may be oxidized by four oxidations with aqua regia. Indium dithizonate was never completely oxidized by the 1:1 oxidizing mixture. Therefore, for indium dithizonate 4 ml of the 1:1 mixture are added twice, followed by the addition of 2.0 ml of concentrated sulphuric acid. The solution is evaporated to strong fumes of SO_3. Complete oxidation of the indium dithizonate takes place.

In all cases, care must be taken not to evaporate the aqueous solution beyond moist dryness; otherwise the metal-salt residue may be partially volatilized. This is particularly important when handling indium, lead and zinc salts because their salts are relatively volatile.

APPENDIX XV

COLORIMETRIC DETERMINATION OF THE OXINATE RADICAL IN A METAL OXINATE*

Oxine and its metal chelates dissolve readily in 0.1-N HCl, due to the formation of the H_2Ox^+ ion. This ion has absorption maxima at 358 mμ (a ∿ 1660) and 252 mμ (a ∿ 43,000) (190). The colorimetric analysis is based on this property, and the procedure recommended below is based on the method proposed by Deterding and Harding (194) for the determination of magnesium oxinate.

Weigh out five 0.1 gm samples of metal oxinate into 100-ml red, low-actinic volumetric flasks. Add purified 0.1-N HCl to the mark. Accurately dilute 5 ml of this solution to 100 ml with 0.1-N HCl. Measure the absorbance in 1-cm cells at 358 mμ, using purified 0.1-N HCl as a blank.

Prepare a standard oxine solution by dissolving 0.146 gm of purified oxine into a 100-ml red, low-actinic volumetric flask and diluting to the mark with 0.1-N HCl. This solution is known to be stable for several days. Accurately dilute this 0.01-M solution with 0.1-N HCl to give 10 standard solutions having a concentration range from 10^{-3} M to 4×10^{-5} M. Measure the absorbance of each solution in 1-cm cells against a blank of 0.1-N HCl.

Beer's Law was found to be obeyed. Therefore the equation of the straight-line calibration curve was calcu-

*For Section IV B subsection 8.

lated by least squares and used to obtain the concentration of oxinate ion in the metal oxinate solution. For optinum accuracy, the calibration curve must be measured at the same time as the measurements on the samples for analysis.

APPENDIX XVI

STANDARD METAL SOLUTIONS

Pure metal solutions were required for the preparation of metal oxinates, metal dithizonates, and standard solutions of metals for the standardization methods. (Section IV B subsections 8 and 9.)

(a) Lead Nitrate

The lead nitrate used was "Analar" reagent grade. It was recrystallized three times from 0.01-N HNO_3 solution and vacuum dried over KOH (75). Determination of the lead content of a sample of lead nitrate by the chromate method gave the theoretical value. The lead nitrate was used as a primary standard. Standard solutions were prepared from accurately weighed amounts of the dried salt.

(b) Zinc Metal

Fisher analytical-grade zinc metal was used. A solution of a weighed amount was electrolyzed at constant potential using the apparatus described in Appendix VI. The solution was first electrolyzed at a potential of -1.15 volts v's the saturated calomel electrode using a gold-plated platinum gauze cathode, according to the method described in (67). At a potential of -1.15 volts any copper, lead and cadmium present as impurity would have plated out. After electrolysis, the platinum electrode was dipped in 1:1 hydrochloric acid, dried and weighed. The solution was then electrolyzed at

-1.50 volts vs' the saturated calomel electrode. When the current had reached zero, the electrode was removed, washed, dried and weighed. The weight of zinc was calculated. The zinc was then dissolved in a calibrated volume of pure 2 N/HCl to give a standard solution of pure zinc metal.

(c) Cadmium Metal

"Analar" analytical-grade cadmium metal was used. A solution of weighed amount of the metal was electrolyzed at constant potential as described under "Zinc Metal". The solution was first electrolyzed at -0.60 volts vs' the saturated calomel electrode. At this potential any lead and copper present as impurity would have plated out. The platinum electrode was removed and dipped in 1:1 hydrochloric acid. It was dried and weighed. The cadmium in the solution was then plated out at -1.15 volts vs' the saturated calomel electrode. After the current had reached zero, the electrode was removed, washed, dried and weighed. The weight of cadmium was calculated. The cadmium was then dissolved in a calibrated volume of 2 N/HCl, to give a standard solution of pure cadmium metal.

(d) Copper Metal

Pure electrolytic-grade copper metal supplied by British Drug Houses Ltd. was used. This grade of copper is recognized as a primary standard (86). Standard solutions were prepared for accurately weighed amounts of the pure metal.

To prepare a standard copper solution for the standardization of sodium diethyldithiocarbamate solutions and for the determination of oxine solutions, 0.127 gm of pure copper metal was weighed into a 100-ml beaker. The copper was dissolved in 1:1 nitric acid and the solution evaporated to moist dryness. The residue was taken up with 5 ml of water and the solution was evaporated as near to dryness as possible without forming basic insoluble copper salts. The residue was then taken up in absolute ethanol, quantitatively transferred to a calibrated volumetric flask and made up to the mark. The desired concentration was then obtained by dilution of the stock, standard solution with ethanol.

(e) Indium Metal

"Analar" analytical-grade indium metal was used. An accurately weighed amount of the metal was dissolved in 1:1 HCl and the indium precipitated as In_2O_3 (86). The gravimetric determination gave the theoretical value. Standard solutions were prepared from accurately weighed amounts of the pure metal.

(f) Silver Nitrate

Reagent-grade silver nitrate supplied by the Nichols Chemical Co. was recrystallized twice from water. The crystals were dried first at 110 ± 5°C for four hours, and for a further 15 minutes at its melting point of 225°C. The silver nitrate thus dried can be used as a primary standard. Standard solutions of 8.0×10^{-3} M silver nitrate

for the standardization of dithizone were prepared in absolute methanol from accurately weighed amounts of the dried salt. A 1:20 methanol-benzene solution of 4.0×10^{-4} M $AgNO_3$ was prepared by diluting 5 ml of the stock methanol solution to 100 ml with benzene. These solutions were stored in red, low-actinic glassware.

Standard solutions of $AgNO_3$ for other applications were prepared from accurately weighed amounts of the dried salt.

(g) Cobalt Sulphate

"Analar" reagent-grade cobalt sulphate heptahydrate was recrystallized three times from ethanol solution, then dried at 450 ± 5°C. Five, 0.5-gm samples were dissolved in 100 ml of 1:1 ammonia and electrolyzed (88). Calculated for Co in $CoSO_4$ is 38.02 found 38.04 ± 0.03.

Five 0.15-gm samples of the cobalt sulphate were dissolved in 25 ml of water and 0.4 ml of concentrated hydrochloric acid added. The solution was diluted to 200 ml and the sulphate determined by the conventional method with barium chloride. Calculated for SO_4 in $CoSO_4$ 61.98 found 61.96 ± 0.09. The cobalt sulphate was therefore 100% pure.

Standard solutions of cobalt sulphate were prepared from accurately weighed amounts of the dried salt.

(h) Nickel Ammonium Sulphate

"Analar" reagent-grade nickel ammonium sulphate hexahydrate was recrystallized three times from water. Five, 1.0-gm samples of the hexahydrate were dissolved in 100 ml of water and the nickel precipitated as the dimethylglyoximate. Calculated for Ni in $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$ 14.86 found 14.87 ± 0.06.

The sulphate in nickel ammonium sulphate was determined by the conventional method of precipitation with barium chloride. Five, 0.2-gm samples were taken for the analysis. Calculated for SO_4 in $NiSO_4(NH_4)_2SO_4 \cdot 6H_2O$ 48.63 found 48.60 ± 0.09. The nickel ammonium sulphate was thus 99.99% pure.

Standard nickel solutions were prepared from accurately weighed amounts of nickel ammonium sulphate hexahydrate.

APPENDIX XVII

REVERSION TECHNIQUE (101, 103)

This technique is used to prepare a fresh, pure, standard solution of dithizone solution by reverting a standard concentration of metal dithizonate in benzene with an aqueous acid solution (see Section IV C sub-section 5(a)).

The procedure with lead and zinc dithizonates is as follows:

Six concentrations of dithizone, each in triplicate, covering the concentration range 10^{-4} M to 10^{-6} M are ultimately prepared from each metal. Transfer aliquots of 5 x 10^{-4} M purified lead nitrate or zinc chloride solution to red, low-actinic 125-ml separatory funnels. The size of the aliquots should give, after reversion and ultimate dilution to 50 ml, the required concentration of dithizone. Add 5 ± 0.1 ml of purified 1M NH_3/1M NH_4Cl buffer to each lead solution, and 5 ± 0.1 ml of purified ammonium acetate adjusted to pH 8 with purified ammonia to each zinc solution. Make up the aqueous phase to 50 ± 2 ml with water. Add aliquots of purified 10^{-4} M dithizone solution in benzene to each separatory funnel. The size of the aliquots should result in an excess of dithizone in the aqueous phase after extraction (visible by the brown colour imparted to the aqueous phase). Make up the benzene layer to 30 ± 2 ml with benzene. Shake the

solutions for five minutes. Separate the aqueous phase and wash the benzene solution of metal dithizonate with three 5-ml portions of purified 1:100 ammonia.

Without removing the benzene layer from the separatory funnel, add 10 ml of 0.1-N HCl containing 1% of an aqueous, saturated solution of SO_2 to each separatory funnel. Shake the solutions for five minutes. Quantitatively transfer each aqueous phase to 50-ml beakers. Wash the dithizone solutions with small portions of 1:100 HCl containing a few drops of saturated SO_2 solution. Add the washings to the beakers. Then transfer each benzene solution of dithizone to red, low-actinic 50-ml volumetric flasks. Wash each separatory funnel with small portions of benzene and add the washings to the volumetric flasks. Make up each volumetric flask to the mark with benzene. Measure the spectral transmission curves of the dithizone solutions from 750 mμ to 350 mμ on the Perkin Elmer Model 350 spectrophotometer (see Section IV A subsection 2).

Evaporate the aqueous solutions to moist dryness on a steam bath. Quantitatively transfer the lead solutions to 25-ml volumetric flasks with 0.1-N HCl. Quantitatively transfer the zinc solutions to 25-ml volumetric flasks with 1M NH_3/1M NH_4Cl buffer. Determine the concentrations of lead and zinc polarographically by the conventional procedure.

Calculate the concentration of the dithizone solutions in benzene from the found concentrations of lead and zinc. Then calculate at 5 mμ intervals the absorptivities of dithizone from the concentration, path length and absorbance.

APPENDIX XVIII

TABLES OF VALUES FOR THE MOLAR ABSORPTIVITY OF DITHIZONE IN BENZENE AT 25°C AS A FUNCTION OF WAVELENGTH

TABLE 1

MOLAR ABSORPTIVITY OF DITHIZONE IN BENZENE AT 25°C FOR THE VISIBLE REGION

λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4}
700	0.10	0.15	0.04
690	0.19	0.17	0.04
680	0.38	0.49	0.07
670	0.70	0.27	0.05
660	1.24	1.00	0.10
650	1.94	1.46	0.12
640	2.67	2.91	0.17
630	3.23	1.21	0.11
625	3.41	0.81	0.09
620	3.46	0.55	0.07
615	3.47	0.51	0.07
610	3.40	0.70	0.08
600	3.10	1.41	0.12
590	2.74	2.06	0.14
580	2.38	2.56	0.16
570	1.98	2.49	0.16
560	1.54	0.99	0.10
550	1.19	0.80	0.09
540	0.19	0.25	0.05
530	0.74	0.36	0.06
520	0.60	0.19	0.04
515	0.54	0.12	0.04
510	0.51	0.09	0.03
505	0.53	0.09	0.03
500	0.61	0.18	0.04
490	1.07	1.01	0.10
480	1.36	0.85	0.09
470	1.56	0.64	0.08
460	1.75	0.29	0.05
455	1.80	0.10	0.03
450	1.83	0.14	0.04
445	1.84	0.15	0.04
440	1.82	0.23	0.05
435	1.76	0.28	0.05
430	1.67	0.33	0.06
420	1.45	0.49	0.07
410	1.19	0.52	0.07

a is the average of 81 samples.

TABLE 2

MOLAR ABSORPTIVITY OF DITHIZONE IN BENZENE AT 25°C

λ mμ	a x 10^{-3}	S^2 x 10^{-4}	S x 10^{-3}
400	9.10	33.6	0.58
390	6.70	23.2	0.48
380	4.80	16.0	0.40
375	3.90	26.0	0.51
370	3.50	9.1	0.30
365	3.70	3.8	0.19
360	4.10	10.6	0.33
350	5.44	17.6	0.42
345	6.06	12.5	0.35
340	6.67	15.9	0.40
335	7.10	17.0	0.41
330	7.31	17.0	0.41
327.5	7.35	17.0	0.41
325	7.35	17.0	0.41
322.5	7.29	17.0	0.41
320	7.25	18.8	0.43
317.5	7.13	20.5	0.45
315	7.06	21.2	0.46
312.5	7.00	20.0	0.45
310	7.06	15.5	0.40
307.5	7.23	10.4	0.32
305	7.52	3.2	0.18
300	8.17	7.8	0.28
295	8.20	12.2	0.35
290	8.06	13.4	0.37
285	8.00	5.3	0.23
280	7.88	4.4	0.4

a is the mean of 18 samples.

APPENDIX XIX

TABLES OF VALUES FOR THE MOLAR ABSORPTIVITY OF OXINE IN BENZENE AT 25°C AS A FUNCTION OF WAVELENGTH

MOLAR ABSORPTIVITY OF OXINE IN BENZENE AT 25°C

λ mμ	a x 10^{-3}	S^2 x 10^{-2}	S x 10^{-3}
360	0.08	1.00	0.01
355	0.23	9.13	0.03
350	0.55	23.3	0.05
345	0.97	49.4	0.07
340	1.41	66.2	0.08
335	1.81	49.0	0.07
330	2.15	44.4	0.07
325	2.34	24.8	0.05
320	2.44	34.2	0.06
317.5	2.48	25.1	0.05
315	2.50	27.9	0.05
312.5	2.50	27.7	0.05
310	2.49	25.4	0.05
307.5	2.45	23.3	0.05
305	2.41	26.5	0.05
300	2.24	30.7	0.06
295	1.99	40.8	0.06
290	1.74	49.4	0.07
285	1.53	47.5	0.07
280	1.28	36.2	0.06
275	1.11	33.6	0.06

a is the mean of 24 samples.

APPENDIX XX

TABLES OF VALUES FOR THE MOLAR ABSORPTIVITY OF THE METAL DITHIZONATES IN BENZENE AT 25°C AS A FUNCTION OF WAVELENGTH

TABLE 1

MOLAR ABSORPTIVITY OF LEAD DITHIZONATE
IN BENZENE AT 25°C

λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4}
600	0.15	0.58	0.08
590	0.28	0.53	0.07
580	0.61	0.46	0.07
570	1.26	2.51	0.16
560	2.38	3.70	0.19
550	3.87	5.60	0.24
540	5.24	2.35	0.15
530	6.14	3.83	0.20
525	6.34	1.00	0.10
520	6.47	0.87	0.09
515	6.47	0.78	0.09
510	6.32	0.78	0.09
505	6.10	0.78	0.09
500	5.83	0.95	0.10
490	5.07	2.38	0.15
480	4.16	2.39	0.15
470	3.32	2.27	0.15
460	2.57	2.29	0.15
450	1.98	1.99	0.14
440	1.54	1.00	0.10
430	1.18	1.00	0.10
420	0.92	0.43	0.06
410	0.77	0.19	0.04
405	0.75	0.17	0.04
400	0.76	0.08	0.03
395	0.81	0.09	0.03
390	0.86	0.19	0.04
380	1.04	0.33	0.06
370	1.23	0.46	0.07
360	1.36	0.29	0.05
350	1.43	0.42	0.06

a is the mean of 48 samples.

TABLE 2

MOLAR ABSORPTIVITY OF CUPRIC PRIMARY DITHIZONATE IN BENZENE AT 25°C

λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4}
650	0.83	0.16	0.04
640	0.94	0.25	0.05
630	1.09	0.33	0.06
620	1.24	0.85	0.09
610	1.59	0.61	0.08
600	1.98	1.40	0.12
590	2.53	1.12	0.11
580	3.10	1.14	0.11
570	3.58	1.05	0.10
565	3.78	0.99	0.10
560	3.94	0.80	0.09
555	4.04	0.89	0.09
550	4.10	0.77	0.09
545	4.11	0.79	0.09
540	4.06	0.98	0.10
535	3.99	0.54	0.07
530	3.91	0.74	0.09
520	3.68	0.53	0.07
510	3.46	0.81	0.09
500	3.27	0.70	0.08
490	3.02	0.90	0.09
480	2.83	0.87	0.09
470	2.67	0.50	0.07
460	2.58	0.35	0.06
450	2.50	0.32	0.06
440	2.38	0.21	0.05
430	2.26	0.24	0.05
420	2.16	0.19	0.04
410	2.09	0.23	0.05
400	2.07	0.29	0.05
390	1.95	0.27	0.05
380	1.82	0.25	0.05
370	1.66	0.18	0.04
360	1.53	0.18	0.04
350	1.42	0.17	0.04

a is the mean of 36 samples.

TABLE 3

MOLAR ABSORPTIVITY OF SECONDARY COPPER DITHIZONATE IN BENZENE AT 25°C

λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4}
650	0.68	0.30	0.05
625	0.68	0.27	0.06
600	0.68	0.32	0.06
575	0.68	0.26	0.05
570	0.69	0.35	0.06
560	0.71	0.39	0.06
550	0.76	0.44	0.07
540	0.84	0.39	0.06
530	0.96	0.33	0.06
520	1.11	0.31	0.06
510	1.29	0.22	0.05
500	1.48	0.18	0.04
490	1.70	0.20	0.04
480	1.91	0.16	0.04
470	2.10	0.22	0.05
460	2.22	0.33	0.06
455	2.27	0.37	0.06
450	2.29	0.39	0.06
445	2.30	0.41	0.06
440	2.30	0.42	0.06
435	2.28	0.40	0.06
430	2.25	0.33	0.06
420	2.12	0.16	0.04
410	1.93	0.11	0.03
400	1.71	0.06	0.02
390	1.46	0.11	0.03
380	1.22	0.15	0.04
370	1.02	0.25	0.05
360	0.86	0.36	0.06
350	0.78	0.45	0.07

a is the mean of 36 samples.

TABLE 4

MOLAR ABSORPTIVITY OF INDIUM DITHIZONATE IN BENZENE AT 25°C

λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4}
600	0.26	0.27	0.05
590	0.40	0.29	0.05
580	0.79	0.54	0.07
570	1.72	2.95	0.17
560	3.29	6.90	0.26
550	5.45	5.40	0.23
540	7.54	4.82	0.22
530	9.08	5.34	0.23
520	9.96	4.25	0.21
515	10.22	4.01	0.20
510	10.31	3.89	0.20
505	10.39	3.61	0.19
500	10.26	4.14	0.20
495	10.05	4.54	0.21
490	9.78	5.65	0.24
480	8.89	5.19	0.23
470	7.80	4.92	0.22
460	6.71	6.33	0.25
450	5.61	4.26	0.21
440	4.51	4.07	0.20
430	3.58	3.94	0.20
420	2.86	3.44	0.18
410	2.32	1.74	0.13
400	2.02	1.11	0.10
390	1.75	0.66	0.08
380	1.68	0.37	0.06
370	1.67	0.12	0.03
360	1.69	0.10	0.03
350	1.77	0.33	0.06

a is the mean of 72 samples.

TABLE 5

MOLAR ABSORPTIVITY OF ZINC DITHIZONATE
IN BENZENE AT 25°C

λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4}
600	0.08	0.93	0.10
590	0.27	2.60	0.16
580	0.84	5.49	0.23
570	2.31	4.51	0.21
560	4.93	5.91	0.24
550	7.62	4.37	0.21
540	9.11	3.22	0.18
535	9.42	4.85	0.22
530	9.55	4.10	0.20
525	9.54	4.21	0.20
520	9.32	5.42	0.23
515	9.05	5.84	0.24
510	8.63	5.03	0.22
500	7.38	4.80	0.22
490	5.89	2.63	0.16
480	4.42	1.95	0.14
470	3.23	2.25	0.15
460	2.27	0.99	0.10
450	1.48	0.89	0.09
440	0.97	0.68	0.08
430	0.63	0.27	0.05
420	0.52	0.48	0.07
410	0.52	0.17	0.04
405	0.55	0.09	0.03
400	0.62	0.16	0.04
390	0.82	0.26	0.05
380	0.99	0.30	0.05
370	1.08	0.49	0.07
360	1.10	0.87	0.09
350	1.10	0.28	0.05

a is the mean of 60 samples.

TABLE 6

MOLAR ABSORPTIVITY OF CADMIUM DITHIZONATE IN BENZENE AT 25°C

λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4}
590	0.16	0.67	0.08
580	0.36	0.40	0.06
570	0.76	1.35	0.12
560	1.56	3.11	0.18
550	3.24	3.69	0.19
540	5.47	3.50	0.19
530	7.07	2.67	0.16
525	7.51	3.03	0.17
520	7.79	2.14	0.15
515	7.93	2.98	0.17
510	7.95	3.75	0.19
505	7.71	2.66	0.16
500	7.43	2.65	0.16
495	7.00	2.79	0.17
490	6.59	1.88	0.14
480	5.31	2.46	0.16
470	4.06	3.00	0.17
460	3.14	3.37	0.18
450	2.28	3.10	0.18
440	1.60	1.30	0.11
430	1.16	1.50	0.12
420	0.88	0.68	0.08
410	0.72	0.59	0.08
400	0.64	0.39	0.06
390	0.80	0.41	0.06
380	1.00	0.88	0.09
370	1.12	0.77	0.09
360	1.22	0.60	0.08
350	1.25	0.50	0.07

a is the mean of 42 samples.

TABLE 7

MOLAR ABSORPTIVITY OF SILVER DITHIZONATE IN BENZENE AT 25°C

λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4}
590	0.01	0.10	0.03
580	0.04	0.10	0.03
570	0.06	0.10	0.03
560	0.10	0.10	0.03
550	0.17	0.21	0.04
540	0.31	0.69	0.08
530	0.53	2.04	0.14
520	0.94	2.62	0.16
510	1.47	1.10	0.10
500	2.02	0.94	0.10
490	2.38	0.99	0.10
480	2.62	0.99	0.10
475	2.69	0.94	0.10
470	2.76	0.90	0.09
465	2.79	0.90	0.09
460	2.79	0.90	0.09
455	2.74	0.90	0.09
450	2.64	0.90	0.09
445	2.48	0.93	0.10
440	2.28	1.20	0.11
430	1.83	0.89	0.09
420	1.42	1.35	0.12
410	1.00	1.06	0.10
400	0.73	1.80	0.13
390	0.54	0.60	0.08
380	0.43	0.33	0.06
370	0.39	0.17	0.04
360	0.38	0.08	0.03
350	0.43	0.15	0.04

a is the mean of 21 samples.

APPENDIX XXI

WAVELENGTH OF MAXIMUM ABSORPTION IN THE VISIBLE REGION OF SOME METAL DITHIZONATES IN BENZENE, CHLOROFORM AND CARBON TETRACHLORIDE

Metal Dithizonate	Solvent	λ Max mμ	Absorptivity x 10^{-4}	Reference
$Pb(HDz)_2$	Benzene	517	6.47	this investigation
	Chloroform	510	6.30, 6.59	1, this work
	Carbon tetrachloride	520	6.63	2
$Zn(HDz)_2$	Benzene	528	9.55	this work
	Chloroform	530	9.81	this work
	Carbon tetrachloride	535	9.2	3
$Cd(HDz)_2$	Benzene	512	7.99	this work
	Chloroform	518	8.56, 8.75	4, this work
	Carbon tetrachloride	520	8.8	4
$Cu(HDz)_2$	Benzene	545	4.10	this work
	Chloroform	545	4.42	this work
	Carbon tetrachloride	545	4.50	5
CuDz	Benzene	442	2.30	this work
	Chloroform	-	-	-
	Carbon tetrachloride	445	2.27	5
AgHDz	Benzene	463	2.79	this work
	Chloroform	465	2.9, 2.87	6, this work
	Carbon tetrachloride	462	2.99	7
$In(HDz)_3$	Benzene	505	10.39	this work
	Chloroform	505	10.54	this work
	Carbon tetrachloride	510	11.9	8

Continued on next page

WAVELENGTH OF MAXIMUM ABSORPTION IN THE VISIBLE REGION
OF SOME METAL DITHIZONATES IN BENZENE, CHLOROFORM AND CARBON TETRACHLORIDE

REFERENCES

1. L. J. Snyder, Anal. Chem., 19, 684 (1947).

2. O. B. Mathre & E. B. Sandell, Talanta, 11, 295 (1964).

3. S. S. Cooper & M. L. Sullivan, Anal. Chem., 23, 613 (1951).

4. G. Iwantscheff, "Das Dithizon und seine Anwendung in der Mikro und Spurenanalyse", published by Verlag Chemie (1958).

5. R. W. Geiger & E. B. Sandell, Anal. Chim. Acta., 8, 197 (1953).

6. A. Crouquet, These licence (1953) [reviewed in "Spectrophotometric Data for Colorimetric Analysis" I.U.P.A.C. published by Butterworths, London (1963)].

7. H. Irving & R. S. Ramakrishna, Analyst, 85, 860 (1960).

8. I. May & J. I. Hoffmann, J. Wash. Acad. Sci., 38, 329 (1948).

APPENDIX XXII

TABLES OF VALUES FOR THE MOLAR ABSORPTIVITY OF THE METAL OXINATES IN BENZENE AT 25°C AS A FUNCTION OF WAVELENGTH

TABLE 1

MOLAR ABSORPTIVITY OF LEAD OXINATE IN BENZENE AT 25°C

λ mμ	a x 10^{-3}	S^2 x 10^{-4}	S x 10^{-3}
500	0.04	0.02	0.01
490	0.09	0.02	0.01
480	0.24	0.11	0.03
470	0.54	0.13	0.03
460	1.05	0.80	0.09
450	1.74	3.39	0.18
440	2.56	6.50	0.25
430	3.40	5.51	0.15
420	4.10	1.96	0.14
415	4.36	2.01	0.14
410	4.54	1.85	0.14
405	4.59	1.93	0.14
400	4.53	2.07	0.14
395	4.36	2.37	0.15
390	4.14	2.62	0.16
380	3.51	1.02	0.10
370	2.81	0.11	0.03
365	2.51	0.27	0.05
360	2.30	0.29	0.05
355	2.48	0.06	0.02
350	2.77	0.39	0.06
345	3.63	0.42	0.06
340	4.63	1.39	0.12
335	5.15	3.53	0.19
330	5.46	3.92	0.20
325	5.72	4.40	0.21
322.5	5.76	1.13	0.11
320	5.76	2.28	0.15
317.5	5.72	2.25	0.15
315	5.67	2.16	0.15
310	5.60	0.35	0.06
305	5.48	0.84	0.09
300	5.36	1.48	0.12
297.5	5.32	1.48	0.12
295	5.29	1.54	0.12
292.5	5.35	2.18	0.15
290	5.43	1.06	0.10
285	6.15	2.89	0.17
280	7.53	13.76	0.37

a is the mean of 19 samples.

TABLE 2

MOLAR ABSORPTIVITY OF CUPRIC OXINATE
IN BENZENE AT 25°C

λ mμ	a x 10^{-3}	S^2 x 10^{-4}	S x 10^{-3}
500	0.07	0.07	0.03
490	0.10	0.11	0.03
480	0.19	0.18	0.04
470	0.56	1.21	0.11
460	1.65	4.04	0.20
450	3.35	3.10	0.18
440	4.89	2.79	0.17
430	5.69	3.03	0.17
425	5.88	3.01	0.17
420	5.90	3.35	0.18
415	5.76	3.30	0.18
410	5.47	2.69	0.16
400	4.75	1.41	0.12
390	3.90	4.45	0.21
380	3.01	3.88	0.20
370	2.29	1.90	0.14
360	1.68	0.63	0.08
355	1.45	0.20	0.04
350	1.32	0.13	0.03
347.5	1.31	0.05	0.26
345	1.46	0.05	0.26
340	2.36	0.06	0.37
337.5	2.64	0.06	0.39
335	2.44	0.06	0.40
332.5	2.18	0.07	0.49
330	2.13	0.11	1.12
327.5	2.17	0.09	0.81
325	2.27	0.09	0.86
322.5	2.42	0.04	0.14
320	2.44	0.04	0.14
317.5	2.37	0.02	0.04
315	2.34	0.03	0.10
312.5	2.37	0.04	0.17
310	2.49	0.04	0.19
305	2.74	0.06	0.30
300	3.04	0.08	0.66
295	3.49	0.10	1.01
290	4.11	0.19	3.76
285	5.95	0.41	16.66

a is the mean of 25 samples.

TABLE 3

MOLAR ABSORPTIVITY OF INDIUM OXINATE
IN BENZENE AT 25°C

λ mμ	a x 10^{-3}	S^2 x 10^{-4}	S x 10^{-3}
470	0.17	0.02	0.01
460	0.45	0.14	0.04
450	1.15	1.09	0.10
440	2.22	0.67	0.08
430	3.42	1.16	0.11
420	4.48	2.47	0.16
415	4.89	2.58	0.16
410	5.17	2.54	0.16
405	5.36	2.80	0.17
400	5.41	2.94	0.17
395	5.38	3.29	0.18
390	5.19	2.82	0.17
380	4.52	1.22	0.11
370	3.65	1.22	0.11
360	2.80	1.47	0.12
350	2.19	0.64	0.08
347.5	2.12	0.53	0.07
345	2.13	0.42	0.06
342.5	2.40	0.55	0.07
340	2.81	0.31	0.06
337.5	3.29	0.38	0.06
335	3.39	0.44	0.07
332.5	3.20	0.37	0.06
330	2.95	0.21	0.04
327.5	2.86	0.48	0.07
325	2.85	0.52	0.07
322.5	2.85	0.50	0.07
320	2.82	0.39	0.05
317.5	2.61	0.25	0.05
315	2.38	0.25	0.05
310	2.05	0.25	0.05
305	1.78	0.20	0.04
300	1.54	0.12	0.03
295	1.30	0.21	0.04
292.5	1.22	0.14	0.04
290	1.23	0.09	0.03
287.5	1.40	0.11	0.03
285	1.78	0.12	0.03
282.5	2.60	0.12	0.03
280	5.31	0.34	0.06

a is the mean of 37 samples.

TABLE 4

MOLAR ABSORPTIVITY OF ZINC OXINATE IN BENZENE AT 25°C

λ mμ	a x 10^{-3}	S^2 x 10^{-4}	S x 10^{-3}
490	0.02	0.01	0.01
480	0.10	0.12	0.03
470	0.20	0.41	0.06
460	0.38	0.37	0.06
450	0.71	0.51	0.07
440	1.11	0.53	0.07
430	1.61	2.02	0.14
420	2.12	4.71	0.22
410	2.72	1.21	0.11
400	3.44	1.60	0.13
390	4.00	1.17	0.11
385	4.18	1.78	0.13
380	4.24	1.01	0.10
375	4.27	1.99	0.14
370	4.21	1.72	0.13
365	4.01	2.30	0.15
360	3.77	2.66	0.16
355	3.57	1.82	0.14
350	3.60	1.56	0.12
347.5	3.66	1.23	0.11
345	3.74	0.85	0.09
342.5	3.87	2.66	0.13
340	3.87	3.28	0.18
337.5	3.67	1.11	0.11
335	3.52	0.49	0.07
332.5	3.43	0.29	0.05
330	3.37	0.24	0.05
325	3.14	0.44	0.07
320	2.89	0.10	0.03
315	2.61	0.53	0.07
310	2.44	1.02	0.10
305	2.24	0.14	0.04
302.5	2.21	0.08	0.03
300	2.19	0.17	0.04
297.5	2.19	0.05	0.02
295	2.24	0.23	0.05
292.5	2.44	0.51	0.07
290	2.69	1.39	0.12
287.5	3.00	1.96	0.14
285	3.49	1.20	0.11

a is the mean of 22 samples.

TABLE 5

MOLAR ABSORPTIVITY OF CADMIUM OXINATE
IN BENZENE AT 25°C

λ mμ	a x 10^{-3}	S^2 x 10^{-4}	S x 10^{-3}
470	0.07	0.10	0.03
460	0.12	0.11	0.03
450	0.20	0.18	0.04
440	0.35	0.13	0.04
430	0.55	0.50	0.07
420	0.88	1.42	0.12
410	1.29	1.49	0.12
400	1.74	1.21	0.11
390	2.09	0.99	0.10
385	2.19	0.85	0.09
380	2.27	1.09	0.10
375	2.31	0.65	0.08
370	2.27	0.69	0.08
365	2.18	0.59	0.08
360	2.04	0.57	0.08
350	1.91	1.61	0.13
345	1.92	1.31	0.11
340	1.91	0.20	0.04
335	1.90	0.30	0.06
330	1.82	0.39	0.06
325	1.70	0.36	0.06
320	1.63	0.50	0.07
315	1.53	0.13	0.04
310	1.42	0.18	0.04
305	1.34	0.10	0.03
300	1.31	0.08	0.03
297.5	1.32	0.27	0.05
295	1.33	0.09	0.03
292.5	1.40	0.11	0.03
290	1.47	0.69	0.08
287.5	1.62	0.88	0.09
285	1.79	1.30	0.11

a is the mean of 16 samples.

APPENDIX XXIII

WAVELENGTH OF MAXIMUM ABSORPTION IN THE VISIBLE REGION OF SOME METAL OXINATES IN BENZENE AND CHLOROFORM

Metal Oxinate	Solvent	λ Max mμ	Absorptivity x 10^{-3}	Reference
$PbOx_2$	Benzene	405	4.59	This work
	Chloroform	-	-	
$ZnOx_2$	Benzene	375	4.27	This work
	Chloroform	378	4.45	1
$CdOx_2$	Benzene	375	2.31	This work
	Chloroform	-	-	
$CuOx_2$	Benzene	423	5.90	This work
	Chloroform	410	5.2	2
$InOx_3$	Benzene	400	5.41	This work
	Chloroform	395	6.67	3
$NiOx_2$	Benzene	465,380	-	This work
	Chloroform	455,395	4.9 (at 395 mμ)	2
$CoOx_2$	Benzene	410	-	This work
	Chloroform	420	7.8	2

1. K. Sone, J. Am. Chem. Soc., 75, 5207 (1953).

2. T. Moeller, Ind. Eng. Chem., Anal. Ed., 15, 346 (1943).

3. T. Moeller, Ind. Eng. Chem., Anal. Ed., 15, 270 (1943).

APPENDIX XXIV

PREPARATION OF SOLUTIONS FOR THE STUDY OF REACTIONS OF LEAD, COPPER AND INDIUM OXINATES IN BENZENE

These solutions were prepared for the determination of relevant equilibrium constants in the study of the reactions of metal oxinates with dithizone in benzene (see Section IV C subsection 6 for a description of the reactions studied and Section IV D subsection 3 for the use of the results in the calculation of equilibrium constants).

All solutions described below were prepared in a darkened room and stored in red, low-actinic glassware. Where this glassware was not available, the vessels were covered with black, adhesive tape. Unless otherwise stated, all solutions were allowed to stand for one week before the absorbance of the solutions was measured.

Replicates of 5 solutions of the same concentration of reactants were prepared at intervals in a series of solutions. They were usually at the beginning, middle and end of the series.

Undried, spectrophotometric-grade benzene will be referred to as wet benzene; benzene dried with silica gel will be referred to as dried benzene; benzene dried with calcium hydride will be referred to as dry benzene

1. The Lead System*

(a) Reaction of Lead Oxinate with Dithizone

Sets of continuous-variations solutions at 10^{-5} M total

* All solutions were prepared in benzene and dried benzene

concentration of reactants were prepared. Similar sets were prepared in which a constant concentration of oxine, 100-fold in excess with respect to the total molarity of reactants, was present in each solution. Replicates of five solutions were prepared for the solutions containing 7.5×10^{-6} M, 5.0×10^{-6} M and 2.5×10^{-6} M $PbOx_2$.

A series of solutions was prepared in which the normal concentrations of $PbOx_2$ and H_2Dz were exactly equivalent. The initial molar concentrations of $PbOx_2$ were 5×10^{-5} M, 2.5×10^{-5} M, 10^{-5} M, 5×10^{-6} M, 2.5×10^{-6} M, 10^{-6} M and 5×10^{-7} M. The concentration of dithizone added to these solutions was double those of $PbOx_2$.

(b) Reaction of Lead Oxinate with Lead Dithizonate

The following method was used to prepare solutions for studying this reaction: A mixture of solid lead oxinate and lead dithizonate was dissolved in dried benzene in a dry box, and stirred vigorously for four hours. The resulting solution was filtered and stored in red, low-actinic glass volumetric flasks. The solution was standardized by extracting 25-ml aliquots with 0.1-N HCl. The lead in the aqueous phase was determined polarographically. The dithizone in the benzene phase was made up exactly to 50 ml, and the concentration determined by spectrophotometric titration with silver nitrate. The lead analysis gave the total concentration of lead in the solution, the dithizone analysis gave the total concentration of dithizonate radical.

It did not represent the total lead dithizonate present in the solution, which would have been the case if no reaction with lead oxinate had taken place.

Solutions were prepared by taking 20, 15, 10 and 5-ml aliquots of the stock solution of the mixture in 50-ml beakers. To one set of these aliquots, 5, 10, 15 and 20-ml aliquots of a 5×10^{-5} M standardized lead oxinate solution were added, respectively. To another set, the same volumes of a 5×10^{-5} M standardized lead dithizonate solution were added. Thus a series of eight solutions were prepared, four in which $PbOx_2$ was in excess and four in which $Pb(HDz)_2$ was in excess. To bring about reaction the above solutions were evaporated in the dark in a dry box, together with an extra solution, a 25-ml aliquot of the stock solution. After evaporation each residue was transferred quantitatively to a 25-ml volumetric flask and stored in the dark for one week.

The stock solution was diluted ten-fold and a similar series of solutions was prepared, evaporated and rediluted as described above, in 50-ml volumetric flasks. The volumes of the aliquots were, of course, doubled. Solutions of lead oxinate and lead dithizonate which had been diluted ten-fold were added to provide the required excess of each reactant.

(c) <u>Reaction of Lead Oxinate and Lead Dithizonate in Dried Benzene, in the Presence of Excess Free Oxine</u>

After the absorbances of the solutions prepared under

subsection (b) and had been measured, they were used as stock solutions for the reaction with oxine. Accurately weighed 100-mg amounts of dried oxine were weighed into nine, 10-ml volumetric flasks. Each portion of oxine was dissolved in one of the solutions prepared above, at the higher concentration, and made up to the mark with the solution. For the solutions which had been diluted ten-fold, it was not possible to accurately weigh out an amount of oxine. Thus a standard solution of oxine of the appropriate concentration was prepared. Nine aliquots of this solution, such that the final concentration of excess free oxine would be $10^{-3} \pm 0.1$ M, were delivered into 25-ml volumetric flasks. The benzene was evaporated. The residue of oxine was then dissolved in the solutions prepared above. The solutions were allowed to stand for one week, in the dark.

(d) Reaction of Lead Dithizonate with Dithizone in Dried Benzene

A series of ratio solutions in which the molar ratio of $(Pb(HDz)_2)_i : (H_2Dz)_i$ was 10:1, 5:1, 2:1, 1:1, 1:2, 1:5, 1:10, 1:20, 1:30, 1:40 and 1:50 were prepared. The constant initial concentration of $Pb(HDz)_2$ was 10^{-5} M. A similar series was prepared in which the constant initial concentration of $Pb(HDz)_2$ was 2×10^{-5} M. The last two ratios were omitted for this series. Replicates of five solutions were prepared for the 5:1, 1:1 and 1:30 ratios.

(e) Reaction of Lead Dithizonate with Oxine in Dried Benzene

Ratio solutions, in which the molar ratio of $(Pb(HDz)_2)_i$: $(HOx)_i$ was 1:5, 1:10, 1:20, 1:25, 1:40, 1:100, 1:200, 1:300 and 1:500 were prepared. Four sets of solutions were prepared which contained initial concentrations of $Pb(HDz)_2$ of 4×10^{-5}, 2×10^{-5}, 4×10^{-6} and 2×10^{-6} M.

2. The Copper System

(a) Reaction of Cupric Oxinate with Dithizone in Wet and Dried Benzene

Continuous-variations solutions at 10^{-4} M and 10^{-5} M total concentration of reactants were prepared in wet and dried benzene. A similar set of solutions was prepared in which there was initial free oxine in excess. The initial concentration of free oxine was 100-fold with respect to the initial concentration of $CuOx_2$.

(b) Reaction of Secondary Cupric Dithizonate with Dithizone in Wet and Dried Benzene

Continuous-variations solutions at 10^{-4} M total concentration of reactants were prepared in wet and dry benzene. A series of solutions was also prepared which contained an equal concentration, with respect to the CuDz concentration, of $Cu(HDz)_2$ in excess. The ratio of $(CuDz)_i$: $(Cu(HDz)_2)_i$ was the same in every solution. The total copper concentration was 2×10^{-4} M, 10^{-4} M, 5×10^{-5} M, 2×10^{-5} M, 5×10^{-6} M and 10^{-6} M in the series of solutions. Replicates of three solutions were prepared for the 2×10^{-4} M, 2×10^{-5} M and 10^{-6} M total copper concentrations.

(c) Reaction of Secondary Cupric Dithizonate with Oxine

Continuous-variations solutions at 10^{-4} M total concentration of reactants were prepared in dried benzene. Replicates of five solutions were prepared for the solutions containing 7.5×10^{-5} M, 5.0×10^{-5} M and 2.5×10^{-5} M CuDz.

(d) Reaction of Primary Cupric Dithizonate with Dithizone in Dry Benzene

Ratio solutions in which the initial molar ratio of $(Cu(HDz)_2)_i : (H_2Dz)_i$ was varied from 10:1, 5:1, 1:10 and 1:20 dry benzene. The constant initial concentration of $Cu(HDz)_2$ was varied from 5×10^{-4} to 5×10^{-6} in 2.5 unit steps for each ratio. A series of solutions, in four sets of five, in which the initial $Cu(HDz)_2$ concentration was 10^{-4} M, 5×10^{-5} M, 10^{-5} M, 5×10^{-6} M and 10^{-6} M was also prepared. In the first set, the initial molar ratio of $(Cu(HDz)_2)$: $(H_2Dz)_i$ was 1:1, the second 1:2, the third 1:4 and the fourth 1:10.

(e) Reaction of Primary Cupric Dithizonate with Cupric Oxinate

A series of solutions, in which the total copper concentration was 1.5×10^{-4} M, 10^{-4} M, 5×10^{-5} M and 5×10^{-6} M, were prepared in wet benzene. In these solutions, two solutions were prepared at each concentration. In one of them the initial molar ratio of $(CuOx_2)_i : (Cu(HDz)_2)_i$ was 1.4:1 and the other in which the initial molar ratio of $(CuOx_2)_i : (Cu(HDz)_2)_i$ was 1:1.4.

3. The Indium System

(a) Reaction of Indium Oxinate with Dithizone

Continuous-Variation solutions at a total concentration of reactants of 10^{-5} M were prepared in benzene. Three sets of solutions were prepared. In one set, the initial free oxine concentration in excess was zero. In the second set, there was an initial tenfold excess, with respect to the total concentration of reactants, of free oxine present in the solutions, and in the third the free oxine was 50-fold in excess. Replicates of five solutions were prepared for the solutions which contained 7.5×10^{-6} M, 5.0×10^{-6} M and 2.5×10^{-6} M $InOx_3$.

Ratio solutions in which the initial molar ratio of $(InOx_3)_i : (H_2Dz)_i$ was 10:1, 5:1, 3:1, 2:1, 1:1, 1:3, 1:5, 1:10, 1:20, 1:30, 1:40, 1:50 and 1:60 were prepared. Replicates of five solutions were prepared for the 3:1, 1:3 and 1:30 ratios. The constant initial concentration of $InOx_3$ was 10^{-5} M. A similar set of solutions was prepared, in which the initial free oxine concentration was 50-fold with respect to the initial molar concentration of $InOx_3$.

(b) Reaction of Indium Dithizonate with Oxine

Continuous-Variation solutions were prepared at a total concentration of reactants of 10^{-4} M in benzene. Replicates of five solutions were prepared for those solutions which contained 7.5×10^{-5} M, 5.0×10^{-5} M and 2.5×10^{-5} M $In(HDz)_3$.

(c) Reaction of Indium Dithizonate and Indium Oxinate in Dried Benzene

A similar stock solution as that prepared for the study of the similar reaction in the lead system was prepared. The same procedure for the preparation of the solutions and standardizations as that used for the lead system was followed. Solutions diluted ten-fold were not prepared.

(d) Reaction of Indium Dithizonate and Dithizone in Wet and Dried Benzene

Ratio solutions in which the initial molar ratios of $(In(HDz)_3)_i : (H_2Dz)_i$ was 10:1, 5:1, 2:1, 1:1, 1:2, 1:5, 1:10, 1:20, 1:30, 1:40 and 1:50 were prepared in wet and dried benzene. The constant initial concentration of $In(HDz)_3$ was 10^{-5} M. Replicates of five solutions were prepared for the 5:1, 1:1 and 1:30 ratios.

APPENDIX XXV

TABLE 1(a)

PARAMETERS USED IN TESTING FOR HOMOGENEITY OF VARIANCES FOR DIFFERENT METHODS OF END-POINT DETERMINATION, IN THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE

Molar Ratio $(HOx)_i : (CuOx_2)_i$	$Si^2 \times 10^6$				$fiSi^2 \times 10^6$			
	From Visual Inspection		From Least Squares Method		From Visual Inspection		From Least Squares Method	
$(CuOx_2)_i$ = 0.3463 μeq.	618 mμ	545 mμ	618 mμ	545 mμ	618 mμ	545 mμ	618 mμ	545 mμ
0	31.30	57.80	29.02	16.99	156.5	289.0	145.1	85.0
10.7	0.75	11.05	8.20	2.46	3.8	55.2	41.0	12.3
21.3	6.24	43.40	19.25	14.08	31.2	217.0	96.2	70.4
42.6	2.25	24.60	8.71	29.02	11.2	123.0	43.6	145.1
85.3	54.40	1.56	12.39	25.90	272.0	7.8	62.0	129.5
106.6	5.08	35.34	16.07	41.63	25.4	176.7	80.4	208.2
TOTALS					500.1	868.7	468.3	650.5
$\bar{S}^2 \times 10^6$					16.67	28.96	15.61	21.68
$\log \bar{S}^2$					-16.7781	-16.5382	-16.8066	-16.6639
$\frac{1}{k}\sum_{i=1}^{k} \log Si^2$					-17.1734	-16.7375	-16.8500	-16.7892
B*					25.2	12.8	2.78	8.05

TABLE 1(a) CONTINUED

PARAMETERS USED IN TESTING FOR HOMOGENEITY OF VARIANCES FOR DIFFERENT METHODS OF END-POINT DETERMINATION, IN THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE

log Si^2			
From Visual Inspection		From Least Squares Method	
618 mμ	545 mμ	618 mμ	545 mμ
-16.5045	-16.2381	-16.5373	-16.7697
-18.1249	-16.9567	-17.0862	-17.6091
-17.2048	-16.3625	-16.7156	-16.8515
-17.6478	-16.6091	-17.0600	-16.5373
-16.2644	-17.8069	-16.9070	-16.5867
-17.2941	-16.4517	-16.7941	-16.3806
-103.0405	-100.4250	-101.1002	-100.7349

*$\chi^2_{0.05}(5) = 11.1$

TABLE 1(b)

SAMPLE CALCULATION IN THE TEST FOR HOMOGENEITY OF VARIANCES, IN THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE

λ = 545 mμ from Visual Inspection

$$\bar{S}^2 = \frac{\sum_{i=1}^{k} f_i S_i^2}{f} = 28.96 \times 10^{-6}$$

$$\log \bar{S}^2 = -16.5382$$

$$\frac{1}{k}\sum_{i=1}^{k} \log S_i^2 = -16.7375$$

$$B = \frac{2.303}{C} k f_o \left(\log \bar{S}^2 - \frac{1}{k}\sum_{i=1}^{k} \log S_i^2\right)$$

$B \approx \chi^2$ with k-1 degrees of freedom

f_o = 5 (5 replicate determinations)

k = 6 (six different initial oxine concentrations in excess)

$$C = 1 + \frac{k + 1}{3Kf_o} = 1.0778$$

$\therefore B = 12.8 > \chi^2_{0.05}(5) = 11.1$

The hypothesis of homogeneity of variances is rejected.

TABLE 2

ANALYTICAL DATA FOR THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE

(a) λ = 618 mμ

Molar Ratio $(HOx)_i : (CuOx_2)_i$	0		10.7	21.3	42.6		85.3	106.6	
μeq. $CuOx_2$ Found	0.3443	0.03416	0.3471	0.3539	0.3510	0.03441	0.3551	0.3720	0.03542
	0.3531	0.03466	0.3443	0.3471	0.3539	0.03416	0.3551	0.3619	0.03517
	0.3430	0.03416	0.3500	0.3471	0.3471	0.03517	0.3603	0.3648	0.03718
	0.3417	0.03416	0.3500	0.3539	0.3529	0.03668	0.3617	0.3632	0.03718
	0.3388	0.03642	0.3443	0.3443	0.3481	0.03492	0.3539	0.3675	0.03718
Total μeq. Found	1.7209	0.17356	1.7357	1.7463	1.7530	0.17534	1.7861	1.8294	0.18213
Mean μeq. Found	0.3442	0.03471	0.3471	0.3493	0.3506	0.03507	0.3572	0.3659	0.03643
μeq. $CuOx_2$ Taken	0.3463	0.03463	0.3463	0.3463	0.3463	0.03463	0.3463	0.3463	0.03463
% Error in Mean	-0.61	+0.23	+0.23	+0.87	+1.24	+1.27	+3.14	+5.66	+5.20
$S^2 \times 10^6$	29.02	0.89	8.20	19.25	8.71	0.97	12.39	16.07	0.96
$S \times 10^3$	5.39	0.94	2.86	4.39	2.95	0.99	3.52	4.01	0.98

TABLE 2 CONTINUED

ANALYTICAL DATA FOR THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE

(b) λ = 545 mμ

Molar Ratio $(HOx)_i : (CuOx_2)_i$	0		10.7	21.3	42.6		85.3	106.6	
μeq. $CuOx_2$ Found	0.3474	0.03466	0.3480	0.3571	0.3608	0.03818	0.3761	0.3727	0.03668
	0.3548	0.03517	0.3522	0.3531	0.3510	0.03517	0.3698	0.3802	0.03718
	0.3490	0.03466	0.3510	0.3480	0.3660	0.03617	0.3671	0.3841	0.03793
	0.3448	0.03592	0.3493	0.3571	0.3614	0.03617	0.3771	0.3699	0.03894
	0.3448	0.03416	0.3510	0.3531	0.3614	0.03517	0.3660	0.3699	0.03718
Total μeq. Found	1.7408	0.17457	1.7515	1.7684	1.8006	0.18086	1.8561	1.8768	0.18791
Mean μeq. Found	0.3482	0.03491	0.3503	0.3537	0.3602	0.03617	0.3712	0.3754	0.03758
μeq. $CuOx_2$ Taken	0.3463	0.03463	0.3463	0.3463	0.3463	0.03463	0.3463	0.3463	0.03463
% Error in Mean	+0.55	+0.81	+1.18	+2.14	+4.00	+4.44	+7.16	+8.40	+8.50
$S^2 \times 10^6$	16.99	0.44	2.46	14.08	29.02	1.51	25.90	41.63	0.92
$S \times 10^3$	4.12	0.67	1.57	3.75	5.39	1.23	5.09	6.45	0.96

TABLE 3

ANALYSIS VARIANCE ON THE DATA FROM THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE AT 618 mμ AND 545 mμ

$CuOx_2$ taken = 0.3463 μeq.

m = 2 k = 6 n = 5

Source	Sums of Squares x 10^5	Degrees of Freedom	Variances x 10^6	F[1]
Rows[2]	82.73597	1	$S_4^2 = 827.3497$	$S_4^2/S_2^2 = 18.2$
Columns[3]	451.8211	5	$S_3^2 = 904.6422$	$S_3^2/S_2^2 = 19.9$
Interaction	22.73098	5	$S_2^2 = 45.46195$	$S_2^2/S_1^2 = 2.42$
Replicates[4]	90.19151	48	$S_1^2 = 18.78990$	
Sum	647.4786	59		

Components of Population Variances

$\sigma_R^2 \simeq S_1^2 = 18.79 \times 10^{-6}$

$\sigma_I^2 \simeq (S_2^2 - \sigma_R^2)/n = 5.33 \times 10^{-6}$

$\sigma_{HOx}^2 \simeq S_3^2/mn - (n\sigma_I^2 + \sigma_R^2)/mn = 85.9 \times 10^{-6}$

$\sigma_\lambda^2 \simeq S_4^2/kn - (n\sigma_I^2 + \sigma_R^2)/kn = 26.06 \times 10^{-6}$

[1] $F_{0.05}(5,48) = 2.41$ $F_{0.05}(5,5) = 5.05$ $F_{0.05}(1,5) = 6.61$
[2] Rows refers to the two different wavelengths 618 mμ and 545 mμ (m = 2).
[3] Columns refers to the different concentrations of initial free oxine (k = 6).
[4] No. of parallel determinations (n = 5).

TABLE 4

VERIFICATION OF THE LINEARITY OF THE REGRESSION LINES OF THE CORRECTION CURVES AT 618 mμ AND 505 mμ FOR THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE

Regression Equations: 618 mμ $E = 5.19 \times 10^{-2} R - 0.55$
545 mμ $E = 7.51 \times 10^{-2} R + 0.55$

Molar Ratio $(HOx)_i : (CuOx_2)_i$ R	% Error E		Calc. % Error E		95% Confidence Limits			
	618 mμ	545 mμ	618 mμ	545 mμ	618 mμ		545 mμ	
0	-0.61	0.55	-0.55	0.55	-2.40	1.29	-0.01	1.12
10.7	0.23	1.18	0	1.35	-1.78	1.78	0.80	1.90
21.3	0.87	2.14	0.55	2.15	-1.18	2.29	1.62	2.68
42.6	1.24	4.00	1.66	3.76	-0.03	3.36	3.23	4.28
85.3	3.14	7.06	3.88	6.96	2.06	5.70	6.40	7.52
106.6	5.66	8.40	4.99	8.56	3.01	6.96	7.95	9.17

$n = 5 \quad m = 6$

$$S_2^2 = \frac{n}{(m-2)} \Sigma (\bar{E} - E)^2$$

618 mμ

$\Sigma(\bar{E} - E)^2 = 1.4185$

$S_2^2 = 1.773$

$S_R^2 = 0.766$

$F = \frac{1.773}{0.766} = 2.32$

$2.32 < F_{0.05}\ (4,24) = 4.22$

∴ Graph is linear

545 mμ

$\Sigma(\bar{E} - E)^2 = 0.1212$

$S_2^2 = 0.1515$

$S_R^2 = 1.83$

$F = \frac{0.1515}{1.83} = 0.083$

$0.083 < F_{0.05}\ (4,24) = 4.22$

∴ Graph is linear

TABLE 5

TEST OF SIGNIFICANCE FOR THE DIFFERENCE IN THE ANGULAR COEFFICIENTS OF THE CORRECTION CURVES AT 618 mμ AND 545 mμ FOR THE TITRATION OF COPPER OXINATE WITH DITHIZONE IN BENZENE

REGRESSION EQUATIONS

545 mμ: $E_1 = 7.51 \times 10^{-2} R + 0.55$ 618 mμ: $E_2 = 5.19 \times 10^{-2} R - 0.55$

$m = 6$ $n = 5$

F-test on the Variances of the Angular Coefficients

545 mμ: $So_1^2 = 3.44 \times 10^{-2}$ degrees of freedom = 4
618 m : $So_2^2 = 0.33$ degrees of freedom = 4
$F = 9.6 < F_{0.05}\ (4,4) = 6.39$

∴ Variances differ significantly

t-test for the significance of the difference in the Angular Coefficients

$$t = \frac{b_1 - b_2}{\sqrt{\left[\left(\frac{So_1^2}{D_1}\right) + \left(\frac{So_2^2}{D_2}\right)\right]}}$$

$$D1 = D2 = \Sigma(R^2 - m\bar{R}^2) = 9189.63$$

$$So_1^2/D = 3.75 \times 10^{-6} \qquad So_2^2/D = 3.60 \times 10^{-5}$$

Degrees of freedom = m - 2 = 4

$$t = 3.67$$

$$3.67 > t_{0.05}\ (4) = 2.13$$

∴ Angular Coefficients are significantly different

APPENDIX XXVI

TABLE 1

ANALYTICAL DATA FOR THE TITRATION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 505 mμ

Molar Ratio $(HOx)_i : (InOx_3)_i$	0		5.1	10.2		20.4	
μeq. $InOx_3$ Found	0.1157	0.01165	0.1365	0.1396	0.01481	0.1361	0.01383
	0.1125	0.01187	0.1302	0.1386	0.01394	0.1416	0.01361
	0.1188	0.01241	0.1292	0.1375	0.01394	0.1416	0.01481
	0.1188	0.01165	0.1323	0.1375	0.01394	0.1481	0.01470
	0.1230	0.01176	0.1262	0.1344	0.01307	0.1405	0.01492
Total μeq. Found	0.5888	0.05934	0.6564	0.6876	0.06970	0.7079	0.07187
Mean μeq. Found	0.1178	0.01187	0.1313	0.1375	0.01394	0.1416	0.01437
μeq. $InOx_3$ Taken	0.2656	0.02656	0.2656	0.2656	0.02656	0.2656	0.02656
% Error in Mean	-55.5	-54.8	-50.6	-48.3	-47.6	-46.7	-45.8
$S^2 \times 10^6$	15.38	0.100	10.82	3.76	0.370	18.43	0.369
$S \times 10^3$	3.92	0.32	3.29	1.94	0.61	4.29	0.61

(Continued on next page)

TABLE 1 CONTINUED

ANALYTICAL DATA FOR THE TITRATION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 505 mμ

Molar Ratio $(HOx)_i : (InOx_3)_i$	30.6	50.9	
μeq. $InOx_3$ Found	0.1459	0.1438	0.01503
	0.1416	0.1500	0.01546
	0.1492	0.1459	0.01503
	0.1448	0.1490	0.01470
	0.1481	0.1573	0.01546
Total μeq. Found	0.7296	0.7460	0.07568
Mean μeq. Found	0.1459	0.1492	0.01514
μeq. $InOx_3$ Taken	0.2656	0.2656	0.02656
% Error in Mean	-45.0	-43.9	-43.1
$S^2 \times 10^6$	8.86	26.58	0.106
$S \times 10^3$	2.98	5.15	0.32

TABLE 2

ANALYSIS OF VARIANCE ON THE DATA FROM THE TITRATION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE AT 505 mμ

$InOx_3$ taken = 0.2656 μeq.

m = 6 n = 5

Source	Sums of Squares x 10^5	Degrees of Freedom	Variances x 10^6	F[1]
Columns[2]	326.1	5	$S_2^2 = 65.2$	$S_2^2/S_1^2 = 46.7$
Replicates[3]	33.5	24	$S_1^2 = 1.40$	
Sum	359.6	29		

Components of Population Variances

$\sigma_R^2 \approx S_1^2 = 1.40 \times 10^6$

$\sigma_{HOx}^2 \approx S_2^2/n - \sigma_R^2/n = 128 \times 10^6$

[1] $F_{0.05}$ (5,24) = 2.62
[2] Columns refers to the different concentrations of initial free oxine (m = 6).
[3] No. of parallel determinations (n = 5).

TABLE 3

VERIFICATION OF THE LINEARITY OF THE REGRESSION LINE OF THE CORRECTION CURVE AT 505 mμ FOR THE TITRATION OF INDIUM OXINATE WITH DITHIZONE IN BENZENE

REGRESSION EQUATION: $E = 6.86 \log R - 55.4$

Molar Ratio $(HOx)_i : (InOx_3)_i$ R	% Error E	Calc. % Error $\bar{E}$	95 Percent Confidence Limits	
0	-55.5	-55.4	-56.2	-54.6
5.1	-50.6	-50.5	-51.3	-49.9
10.2	-48.3	-48.5	-49.2	-47.9
20.4	-46.7	-46.5	-47.1	-45.8
30.6	-45.0	-45.3	-46.0	-44.6
50.9	-43.9	-43.8	-44.5	-43.0

$$n = 5 \qquad m = 6$$

$$S_2^2 = \frac{n}{(m-2)} \Sigma(\bar{E} - E)^2$$

$$\Sigma(\bar{E} - E)^2 = 0.19$$

$$S_2^2 = 0.317$$

$$S_R^2 = 1.92$$

$$F = \frac{0.317}{1.92} = 0.16 < F_{0.05}\ (3,20) = 3.10$$

$\therefore$ Graph is linear

APPENDIX XXVII

NOTES TO APPENDIX XXVII

Unless otherwise stated, all data are for benzene solutions in undried, spectrophotometric-grade benzene at 25°C where "dry" benzene is specified, it refers to benzene dried with calcium hydride.

SET A - Continuous variations solution for the reaction of secondary copper dithizonate with oxine.

SET B - Ratio solutions for the reaction of primary copper dithizonate with copper oxinate.

SET C - Ratio solutions for the reaction of secondary copper dithizonate with dithizone.

SET D - Continuous variations solutions for the reaction of copper oxinate with dithizone.

SET E - Continuous variations solutions for the reaction of copper oxinate with dithizone, when the solutions contained initial free oxine, onehundredfold in excess with respect to the initial concentration of copper oxinate.

SET G - Ratio solutions for the formation of adducts of dithizone with primary copper dithizonate both in dry benzene.

SET H - Continuous variations solutions for the reaction of secondary copper dithizonate with dithizone.

SET I - Continuous variations solutions for the reaction of secondary copper dithizonate with dithizone both in dry benzene.

SET J - Ratio solutions for the determination of the absorptivity of $Cu(HDz)_2 \cdot H_2Dz$ in dry benzene.

SET K - Ratio solutions for the determination of the absorptivity of $Cu(HDz)_2 \cdot 2H_2Dz$ in dry benzene.

An * beside a particular solution number indicates that the solution was prepared in replicates of five and the given value of the absorbance is the mean of the absorbances of the replicates.

A range of path lengths was used, but all absorbance values have been calculated to a 1-cm path, except where stated otherwise.

TABLE 1

ANALYTICAL DATA FOR SET A

Molarity of stock CuDz solution in benzene = 3.243×10^{-4} M
Molarity of stock HOx solution in benzene = 9.944×10^{-4} M
Volume of solution = 25 ML
Total concentration of reactants = 10^{-4} M

Solution Number	(CuDz) Taken M x 10^5	(HOx) Taken M x 10^5	Initial Mole Fraction HOx
CJA- 1	10.26	0	0
2	9.755	0.517	0.05
3	9.236	0.994	0.10
4	8.717	1.512	0.15
5	8.211	1.989	0.20
6	7.705	2.506	0.25
7	7.186	2.983	0.29
8	6.668	3.500	0.34
9	6.162	3.978	0.39
10	5.643	4.495	0.44
11	5.124	5.012	0.49
12	4.618	5.489	0.54
13	4.099	6.006	0.59
14	3.593	6.484	0.64
15	3.074	7.001	0.70
16	2.568	7.478	0.74
17	2.050	7.995	0.80
18	1.544	8.512	0.85
19	1.025	8.989	0.90
20	0.519	9.506	0.95
21	0	9.984	1.00

TABLE 2

EXPERIMENTAL ABSORBANCES FOR SET A

b = 1 cm

Solution Number	Wavelength, mμ								
	618	575	545	525	500	475	442	425	400
CJA- 1	0.698	0.698	0.811	1.067	1.519	2.073	2.36	2.25	1.755
2	0.665	0.701	0.819	1.050	1.457	1.959	2.23	2.11	1.662
3	0.625	0.698	0.819	1.022	1.380	1.828	2.07	1.970	1.550
4	0.564	0.667	0.786	0.956	1.256	1.630	1.845	1.757	1.379
5	0.544	0.676	0.802	0.953	1.221	1.559	1.762	1.678	1.332
6	0.508	0.674	0.802	0.927	1.151	1.437	1.616	1.542	1.232
7	0.458	0.638	0.762	0.863	1.045	1.281	1.435	1.371	1.101
8	0.441	0.645	0.773	0.860	1.016	1.218	1.365	1.304	1.053
9	0.406	0.623	0.749	0.818	0.945	1.111	1.240	1.187	0.964
10	0.369	0.591	0.712	0.766	0.865	0.999	1.114	1.068	0.872
11	0.337	0.568	0.688	0.725	0.796	0.897	0.993	0.952	0.782
12	0.297	0.522	0.633	0.658	0.707	0.781	0.862	0.828	0.684
13	0.276	0.493	0.597	0.618	0.659	0.722	0.796	0.764	0.634
14	0.241	0.447	0.543	0.556	0.581	0.625	0.687	0.661	0.552
15	0.198	0.376	0.457	0.464	0.480	0.510	0.559	0.537	0.451
16	0.163	0.323	0.394	0.395	0.400	0.414	0.450	0.435	0.367
17	0.132	0.270	0.330	0.326	0.325	0.328	0.360	0.346	0.294
18	0.099	0.207	0.253	0.254	0.245	0.246	0.267	0.257	0.220
19	0.064	0.140	0.172	0.167	0.161	0.159	0.171	0.165	0.142
20	0.033	0.073	0.089	0.087	0.083	0.081	0.088	0.086	0.074
21	0	0	0	0	0	0	0	0	0

TABLE 3

ANALYTICAL DATA FOR SET B

Molarity of stock $CuOx_2$ solution in benzene = 1.551×10^{-4} M

Molarity of stock $Cu(HDz)_2$ solution in benzene = 6.664×10^{-4} M

Volume of solution = 25 ML

Solution Number	$(CuOx_2)_i$ Taken M x 10^5	$(Cu(HDz)_2)_i$ Taken M x 10^5	$(Cu)_T$ Taken M x 10^5	$(HDz)_T$ Taken M x 10^5
CRB- 1	9.306	6.664	15.97	13.33
2	6.204	8.886	15.09	17.77
3	6.204	4.446	10.65	8.892
4	3.102	6.664	9.767	1.333
5	3.102	2.222	5.324	4.444
6	1.861	3.332	5.193	6.664
7	"	"	"	"
8	"	"	"	"
9	0.3102	6.665	0.9767	1.333
10	"	"	"	"
11	"	"	"	"
12	0.1861	3.332	0.5193	0.6664
13	"	"	"	"
14	"	"	"	"

TABLE 4

EXPERIMENTAL ABSORBANCES FOR SET B

b = 1 cm

Solution Number	Wavelength, mμ								
	618	575	545	525	500	475	442	425	400
CRB- 1	0.893	1.720	2.10	2.12	2.17	2.28	2.60	2.53	2.12
2	0.990	2.01	2.45	2.44	2.44	2.49	2.68	2.57	2.18
3	0.505	1.400	1.719	1.680	1.636	1.625	1.775	1.72	1.471
4	0.860	1.820	2.23	2.20	2.16	2.17	2.17	2.04	1.75
5	0.259	0.362	0.433	0.490	0.592	0.724	0.874	0.855	0.687
6	0.496	1.060	1.296	1.269	1.234	1.222	1.211	1.136	0.981
7	0.459	0.971	1.186	1.165	1.138	1.133	1.128	1.059	0.912
8	0.465	1.001	1.224	1.197	1.160	1.145	1.135	1.065	0.919
9	0.0668	0.0916	0.1084	0.1234	0.1508	0.1848	0.2036	0.1930	0.1548
10	0.0769	0.1138	0.1361	0.1527	0.1824	0.2212	0.2418	0.2290	0.1844
11	0.0704	0.0970	0.1158	0.1319	0.1605	0.1976	0.2176	0.2064	0.1654
12	0.0370	0.0448	0.0531	0.0638	0.0828	0.1066	0.1192	0.1131	0.0896
13	0.0382	0.0458	0.0543	0.0654	0.0853	0.1101	0.1232	0.1169	0.0926
14	0.0358	0.0436	0.0517	0.0618	0.0799	0.1025	0.1144	0.1085	0.0861

TABLE 5

ANALYTICAL DATA FOR SET C

Molarity of stock solution of CuDz in benzene = 3.160×10^{-4} M
Molarity of stock solution of $Cu(HDz)_2$ in benzene = 5.003×10^{-4} M
Molarity of stock solution of H_2Dz in benzene = 1.029×10^{-3} M
Volume of solution = 25 ML

Solution Number		$(CuDz)_i$ Taken M x 10^5	$(Cu(HDz)_2)_i$ Taken M x 10^6	(H_2Dz) Taken M x 10^6	$(Cu)_T$ Taken M x 10^5	$(HDz)_T$ Taken M x 10^5
CRC-	1	10.36	99.8	95.06	20.35	39.83
	2	7.774	99.81	76.08	17.76	35.34
	3	"	"	"	"	"
	4	"	"	"	"	"
	5	5.183	49.91	47.53	10.17	19.92
	6	2.591	24.95	23.77	5.086	9.958
	7	1.036	9.981	9.506	2.035	3.983
	8	"	"	"	"	"
	9	"	"	"	"	"
	10	0.7774	9.981	7.605	1.776	3.534
	11	0.5183	4.991	4.753	1.017	1.992
	12	0.2591	2.495	2.377	0.5086	0.9958
	13	0.1036	0.9981	0.9506	0.2035	0.3983
	14	0.07774	0.9981	0.7605	0.1776	0.3534
	15	"	"	"	"	"
	16	"	"	"	"	"

TABLE 6

EXPERIMENTAL ABSORBANCES FOR SET C

b = 1 cm

Solution Number		Wavelength, mμ								
		618	575	545	525	500	475	442	425	400
CRL-	1	2.50	6.46	7.96	7.40	6.51	5.63	4.60	4.64	4.28
	2	2.24	5.93	7.30	6.75	5.84	4.95	4.34	4.00	3.73
	3	2.22	5.86	7.22	6.67	5.78	4.90	4.31	3.97	3.70
	4	2.22	5.86	7.22	6.68	5.79	4.92	4.32	3.98	3.71
	5	1.188	3.06	3.77	3.51	3.09	2.68	2.39	2.21	2.03
	6	0.622	1.617	1.99	1.844	1.61	1.382	1.225	1.134	1.045
	7	0.257	0.656	0.804	0.743	0.647	0.554	0.491	0.452	0.418
	8	0.253	0.646	0.793	0.738	0.650	0.564	0.504	0.466	0.428
	9	0.256	0.656	0.806	0.745	0.649	0.555	0.491	0.453	0.419
	10	0.244	0.555	0.663	0.608	0.526	0.457	0.407	0.373	0.341
	11	0.1334	0.3192	0.3918	0.3712	0.3388	0.3098	0.2878	0.2670	0.2392
	12	0.0683	0.1631	0.1973	0.1822	0.1590	0.1383	0.1237	0.1138	0.1042
	13	0.0296	0.0662	0.0790	0.0728	0.0637	0.0563	0.0508	0.0467	0.0424
	14	0.0252	0.0566	0.0677	0.0628	0.0554	0.0494	0.0450	0.0414	0.0374
	15	0.0265	0.0580	0.0690	0.0637	0.0560	0.0499	0.0454	0.0417	0.0376
	16	0.0263	0.0599	0.0710	0.0667	0.0589	0.0524	0.0476	0.0438	0.0396

TABLE 7

ANALYTICAL DATA FOR SET D

Concentration of stock H_2Dz solution in benzene = 1.551×10^{-4} M
Concentration of stock $CuOx_2$ solution in benzene = 8.79×10^{-5} M
Volume of solution = 50 ML
Total concentration of reactants = 10^{-5} M

Solution Number	$CuOx_2$ Taken M x 10^6	H_2Dz Taken M x 10^6	Initial Mole Fraction H_2Dz	Solution Number	$CuOx_2$ Taken M x 10^6	H_2Dz Taken M x 10^6	Initial Mole Fraction H_2Dz
CJD- 1	10.24	0	0	CJD- 11	5.118	5.348	0.533
2	9.728	0.597	0.058	12	4.610	5.945	0.583
3	9.220	1.174	0.113	13	4.101	6.522	0.631
4	8.711	1.450	0.167	14	3.592	7.119	0.680
5	8.202	2.048	0.222	15	3.084	8.196	0.727
6	7.694	2.524	0.275	16	2.543	8.293	0.776
7	7.185	3.021	0.329	17	2.035	9.369	0.822
8	6.644	3.598	0.381	18	1.526	9.766	0.867
9	6.136	4.195	0.433	19	1.017	10.04	0.912
10	5.627	4.972	0.484	20	0.509	10.62	0.956
				21	0	11.22	1.000

TABLE 8

EXPERIMENTAL ABSORBANCES FOR SET D

b = 5 cm

Solution Number	Wavelength, mμ			Solution Number	Wavelength, mμ		
	618	545	445		618	545	445
CJD- 1	0	0	0.214	CJD- 11*	0.164	0.314	0.528
2	0.020	0.022	0.270	12	0.186	0.462	0.488
3	0.040	0.042	0.306	13	0.216	0.686	0.472
4	0.052	0.058	0.334	14	0.270	0.838	0.484
5	0.074	0.080	0.384	15	0.472	0.850	0.564
6*	0.090	0.098	0.418	16*	0.706	0.824	0.636
7	0.102	0.112	0.450	17	0.882	0.792	0.686
8	0.120	0.134	0.488	18	1.256	0.770	0.824
9	0.136	0.164	0.524	19	1.438	0.736	0.888
10	0.155	0.210	0.544	20	1.690	0.698	0.968
				21	2.032	0.670	1.066

* Average of five replicates.

TABLE 9

ANALYTICAL DATA FOR SET E

Molarity of stock $CuOx_2$ solution in benzene = 1.558×10^{-4} M
Molarity of stock H_2Dz solution in benzene = 1.108×10^{-4} M
Molarity of stock HOx solution in benzene = 4.972×10^{-3} M
Volume of solution = 50 ML
Total concentration of reactants ($(CuOx_2)_i + (H_2Dz)_i$) = 10^{-5} M

Solution Number		$(CuOx_2)$ Taken M x 10^6	(H_2Dz) Taken M x 10^6	(HOx) Taken M x 10^4	Initial Mole Fraction H_2Dz	Solution Number		$(CuOx_2)$ Taken M x 10^6	(H_2Dz) Taken M x 10^6	(HOx) Taken M x 10^4	Initial Mole Fraction H_2Dz
CJE-	1	10.03	0	9.944	0	CJE-	11	5.017	6.293	4.293	0.556
	2	9.536	0.620	9.447	0.061		12	4.518	6.936	4.475	0.606
	3	9.037	1.263	8.950	0.123		13	4.020	7.557	3.978	0.653
	4	8.538	1.584	8.452	0.181		14	3.521	8.199	3.480	0.700
	5	8.040	2.126	7.955	0.239		15	3.023	8.320	2.983	0.745
	6	7.541	2.647	7.458	0.294		16	2.493	9.493	2.486	0.791
	7	7.043	3.289	6.961	0.350		17	1.994	10.08	1.989	0.835
	8	6.513	3.910	6.464	0.404		18	1.496	10.72	1.492	0.878
	9	6.014	4.552	5.966	0.456		19	0.997	11.35	0.994	0.919
	10	5.516	5.173	5.469	0.507		20	0.499	11.97	0.497	0.960
							21	0	12.61	0	1.000

TABLE 10

EXPERIMENTAL ABSORBANCES FOR SET E

b = 5 cm

Solution Number	Wavelength, mμ			Solution Number	Wavelength, mμ		
	618	545	445		618	545	445
CJE- 1	0.	0	0.232	CJE- 11*	0.178	0.610	0.400
2	0.012	0.048	0.240	12	0.192	0.686	0.425
3	0.032	0.103	0.254	13	0.216	0.758	0.446
4	0.046	0.152	0.266	14	0.378	0.832	0.498
5	0.064	0.204	0.278	15	0.612	0.838	0.598
6*	0.076	0.248	0.286	16*	0.814	0.805	0.687
7	0.102	0.310	0.302	17	1.126	0.776	0.782
8	0.122	0.375	0.322	18	1.418	0.744	0.874
9	0.132	0.455	0.345	19	1.686	0.714	0.961
10	0.160	0.538	0.370	20	1.978	0.682	1.046
				21	2.19	0.656	1.128

* Average of five replicates.

TABLE 11

ANALYTICAL DATA FOR SET G

Molarity of stock $Cu(HDz)_2$ solution in benzene = 4.990×10^{-4} M
Molarity of stock H_2Dz solution in dry benzene = 1.321×10^{-3} M
Volume of solution = 10 ML

Solution Number	Approximate Molar Ratio $(H_2Dz)_i:(Cu(HDz)_2)_i$	$(Cu(HDz)_2)$ Taken M x 10^6	(H_2Dz) Taken M x 10^5	$(HDz)_T$ Taken M x 10^5
CRG- 1	1:1	99.81	10.57	30.53
2	"	49.91	5.285	15.27
3	"	9.981	1.057	3.053
4	"	4.991	0.5285	1.527
5	"	0.9981	0.1057	0.3053
6	2:1	99.81	21.14	41.10
7	"	49.91	10.57	20.55
8	"	9.981	2.114	4.110
9	"	4.991	1.057	2.055
10	"	0.9981	0.2114	0.4110
11	4:1	99.81	42.28	62.24
12	"	49.91	21.14	31.12
13	"	9.981	4.228	6.224
14	"	4.991	2.114	3.112
15	"	0.9981	0.4228	0.6224
16	10:1	99.81	105.7	125.6
17	"	49.91	52.85	62.83
18	"	9.981	10.57	12.56
19	"	4.991	5.285	6.283
20	"	0.9981	1.057	1.256

TABLE 12

EXPERIMENTAL ABSORBANCES FOR SET T

b = 1 cm

Solution Number		Wavelength, mμ								
		618	575	545	525	500	475	445	425	400
CRG-	1	5.58	6.65	6.50	5.46	4.60	4.91	5.32	4.63	3.52
	2	2.78	3.33	3.26	2.76	2.33	2.46	2.65	2.31	1.78
	3*	0.423	0.552	0.559	0.488	0.415	0.417	0.431	0.376	0.301
	4	0.2534	0.3050	0.2960	0.2566	0.2194	0.2280	0.2384	0.2088	0.1630
	5	0.0499	0.0580	0.0549	0.0474	0.0409	0.0438	0.0452	0.0399	0.0311
	6	11.43	11.09	9.67	6.99	5.71	7.92	9.42	8.21	5.57
	7	5.04	4.92	4.27	3.26	2.71	3.53	4.09	3.56	2.47
	8*	0.903	0.892	0.771	0.627	0.531	0.644	0.723	0.629	0.449
	9	0.478	0.455	0.328	0.311	0.265	0.329	0.369	0.320	0.228
	10	0.0864	0.0828	0.0691	0.0574	0.0497	0.0605	0.0662	0.0578	0.0418
	11	19.93	15.14	12.87	8.76	7.21	11.76	14.40	12.52	8.04
	12	9.36	7.89	6.07	4.20	3.47	5.55	6.75	5.87	3.79
	13*	1.722	1.420	1.051	0.788	0.672	0.999	1.184	1.024	0.676
	14	0.762	0.638	0.475	0.371	0.319	0.452	0.525	0.454	0.304
	15	0.1568	0.1276	0.0920	0.0725	0.0633	0.0906	0.1044	0.0905	0,0607
	16	-	-	20.00	13.07	11.09	-	-	-	14.04
	17	-	15.02	9.66	6.40	5.46	10.37	12.88	11.14	6.82
	18*	4.12	2.98	1.882	1.273	1.098	2.06	2.54	2.19	1.346
	19	2.80	1.932	1.131	0.768	0.676	1.326	1.639	1.413	0.856
	20	0.3888	0.2758	0.1678	0.1202	0.1062	0.1904	0.2314	0.1992	0.1234

* Average of five replicates.

TABLE 13

ANALYTICAL DATA FOR SETS H AND I

Molarity of CuDz solution in benzene = 5.137×10^{-4} M
Molarity of H_2Dz solution in benzene = 5.235×10^{-4} M
Molarity of CuDz solution in "dry" benzene = 4.881×10^{-4} M
Molarity of H_2Dz solution in "dry" benzene = 5.007×10^{-4} M
Volume of solution = 25 ML
Total concentration of reactants = 10^{-4} M

	SET H				SET I		
	Benzene				"Dry" Benzene		
Solution Number	(CuDz) Taken moles/litre M x 10^5	(H_2Dz) Taken moles/litre M x 10^5	Initial Mole Fraction H_2Dz	Solution Number	(CuDz) Taken moles/litre x 10^5	(H_2Dz) Taken moles/litre x 10^5	Initial Mole Fraction H_2Dz
CJH- 1	10.17	0	0	CJI- 1	10.00	0	0
2	9.017	1.007	0.102	2	9.000	1.001	0.100
3	8.019	2.004	0.203	3	8.000	2.003	0.200
4	7.092	3.008	0.304	4	7.000	3.004	0.300
5	6.064	4.008	0.404	5	6.000	4.006	0.400
6	5.037	5.005	0.505	6	5.000	5.007	0.500
7	4.010	6.002	0.604	7	4.000	6.008	0.600
8	3.082	7.001	0.704	8	3.000	7.010	0.700
9	2.055	8.002	0.803	9	2.000	8.011	0.800
10	1.017	9.003	0.902	10	1.000	9.013	0.900
11	0	10.07	1.000	11	0	10.01	1.000

TABLE 14

EXPERIMENTAL ABSORBANCES FOR SETS H AND I

b = 1 cm

Solution Number		Wavelength, mμ 618	545	445	Solution Number		Wavelength, mμ 618	545	445
		Benzene					"Dry" Benzene		
CJH-	1	0.69	0.74	2.27	CJI-	1	0.68	0.828	2.28
	2	0.67	1.012	2.11		2	0.68	1.066	2.07
	3	0.66	1.270	1.908		3	0.64	1.295	1.870
	4	0.64	1.523	1.674		4	0.630	1.532	1.702
	5	0.66	1.775	1.456		5	0.690	1.794	1.433
	6	0.67	1.932	1.322		6	0.76	2.04	1.360
	7	1.29	1.948	1.310		7	1.35	2.11	1.479
	8	1.86	1.729	1.436		8	2.09	2.12	1.762
	9	2.44	1.618	1.572		9	2.63	1.951	1.970
	10	3.03	1.350	1.758		10	3.08	1.528	2.01
	11	3.63	1.009	1.880		11	3.51	1.045	1.82

TABLE 15

ANALYTICAL DATA FOR SET J

Molarity of stock $Cu(HDz)_2$ solution in dry benzene = 8.060×10^{-4} M

Molarity of stock H_2Dz solution in dry benzene = 1.195×10^{-4} M

Solution Number	Approximate Molar Ratio $(Cu(HDz)_2)_i : (H_2Dz)_i$	$(Cu(HDz)_2)$ Taken M x 10^5	(H_2Dz) Taken M x 10^6
CRJ- 1	10:1	48.35	47.80
2	"	24.18	23.90
3	"	9.670	9.56
4	"	7.253	7.13
5	"	4.835	4.78
6	"	2.418	2.39
7	"	0.9760	0.956
8	"	0.7253	0.713
9	"	0.4835	0.478
10	5:1	2.418	4.78
11	"	0.9670	1.912
12	"	0.7253	1.434
13	"	0.4835	0.956
14	"	0.2418	0.478

TABLE 16

EXPERIMENTAL ABSORBANCES FOR SET J

b = 1 cm

Solution Number		Wavelength, mμ								
		618	575	545	525	500	475	450	425	400
CRJ-	1	7.94	17.6	-	19.16	16.54	14.26	12.92	11.76	10.68
	2	3.99	8.84	10.55	9.62	8.30	7.16	6.55	5.89	5.34
	3	1.58	3.52	4.21	3.84	3.31	2.86	2.58	2.34	2.13
	4	1.17	2.61	3.10	2.87	2.44	2.11	1.89	1.74	1.59
	5	0.792	1.754	2.09	1.916	1.661	1.423	1.287	1.169	1.062
	6	0.385	0.888	1.056	0.968	0.714	0.647	0.587	0.535	
	7	0.1548	0.353	0.421	0.3808	0.3274	0.2856	0.2588	0.2348	0.2138
	8	0.1178	0.2608	0.3118	0.2826	0.2472	0.2118	0.1910	0.1742	0.1580
	9	0.0784	0.1734	0.207	0.1910	0.1646	0.1420	0.1264	0.1152	0.1052
	10	0.478	0.936	1.088	0.980	0.842	0.743	0.705	0.638	0.568
	11	0.197	0.383	0.444	0.402	0.345	0.305	0.286	0.257	0.229
	12	0.1438	0.2816	0.3280	0.2924	0.2546	0.2238	0.2090	0.1886	0.1684
	13	0.0988	0.1970	0.2260	0.2104	0.1740	0.1554	0.1442	0.1278	0.1134
	14	0.0498	0.0961	0.1112	0.1007	0.0869	0.0769	0.0720	0.0646	0,0564

TABLE 17

ANALYTICAL DATA FOR SET K

Molarity of stock $Cu(HDz)_2$ solution in dry benzene = 8.060×10^{-4} M
Molarity of stock (H_2Dz) solution in dry benzene = 1.195×10^{-4} M

Solution Number	Approximate Molar Ratio $(H_2Dz)_i:(Cu(HDz)_2)_i$	$(Cu(HDz)_2)$ Taken$_6$ M x 10^6	(H_2Dz) Taken$_5$ M x 10^5	(HDz) Taken$_5$ M x 10^5
CRK- 1	10:1	48.35	47.80	57.47
2	"	24.18	23.90	28.74
3	"	9.760	9.56	11.51
4	"	4.835	4.78	5.747
5	"	0.9760	0.956	1.151
6	20:1	48.35	95.6	105.3
7	"	24.18	47.8	52.64
8	"	9.760	19.12	21.07
9	"	4.835	9.56	10.53
10	"	0.9760	1.912	2.107

TABLE 18

EXPERIMENTAL ABSORBANCES FOR SET K

b = 1 cm

Solution Number		Wavelength, mμ								
		618	575	545	500	500	475	450	425	400
CRK-	1	19.25	14.20	9.18	6.16	5.32	9.92	12.29	10.56	6.47
	2	9.46	6.91	4.46	3.01	2.57	4.72	5.84	5.10	3.14
	3	3.70	2.70	1.69	1.18	1.01	1.86	2.29	1.98	1.22
	4	1.800	1.298	0.809	0.573	0.500	0.901	1.096	0.937	0.587
	5	0.3712	0.271	0.1718	0.1190	0.1056	0.1882	0.2310	0.1986	0.1226
	6	-	-	14.37	9.41	8.25	17.05	-	18.34	10.95
	7	17.90	12.18	7.09	4.61	4.04	8.36	10.46	9.04	5.38
	8	7.06	4.80	2.76	1.82	1.61	3.28	4.08	3.52	2.11
	9	3.50	2.37	1.345	0.902	0.794	1.622	2.02	1.734	1.037
	10	0.686	0.460	0.257	0.176	0.1572	0.3152	0.3896	0.3352	0.2014

TABLE 19

MOLAR ABSORPTIVITY OF $Cu(HDz)_2.H_2Dz$ IN DRY BENZENE AT 25°C

λ mμ	ā x 10^4	S^2 x 10^6	S x 10^4 d.f. = 13	λ mμ	ā x 10^4	S^2 x 10^6	S x 10^4 d.f. = 13
650	2.76	2.77	0.17	525	5.57	15.1	0.39
640	3.63	3.01	0.17	520	5.30	14.13	0.38
630	4.58	3.20	0.18	510	4.83	7.41	0.27
618	5.16	3.20	0.18	500	4.71	5.06	0.22
610	5.45	3.20	0.18	490	4.74	6.93	0.26
600	5.75	5.93	0.25	480	4.80	5.00	0.22
590	6.01	8.81	0.30	475	4.74	5.20	0.23
580	6.26	7.64	0.28	470	4.83	8.81	0.30
575	6.42	10.0	0.32	460	5.00	7.23	0.27
570	6.55	10.33	0.32	450	5.05	9.50	0.31
560	6.76	10.08	0.32	440	4.88	5.00	0.22
550	6.55	9.77	0.31	430	4.60	3.38	0.18
545	6.40	9.56	0.31	425	4.37	2.58	0.16
540	6.21	10.19	0.32	420	4.15	1.97	0.14
530	5.80	12.85	0.36	410	3.76	2.36	0.15
				400	3.41	1.41	0.12

ā is the mean of 14 samples.

TABLE 20

SYSTEM OF QUADRATIC EQUATIONS FOR SET K USED TO CALCULATE THE ABSORPTIVITY OF $Cu(HDz)_2 . 2H_2Dz, a_{6,545}$

Wavelength = 545 mμ
Absorptivity of $Cu(HDz)_2 . H_2Dz$ = 6.40×10^4
Absorptivity of H_2Dz = 1.04×10^4
Path length = 1 cm

System of Equations	$a_6 \times 10^{-4}$ Litre mole cm^{-1}
CRK-1 to CRK-5	
$5.698 \times 10^{-9} a_6^2 - 1.110 \times 10^{-3} a_6 + 52.08 = 0$	11.61
$2.231 \times 10^{-9} a_6^2 - 4.387 \times 10^{-4} a_6 + 20.69 = 0$	11.81
$7.591 \times 10^{-10} a_6^2 - 1.496 \times 10^{-4} a_6 - 7.064 = 0$	11.87
$4.032 \times 10^{-10} a_6^2 - 7.519 \times 10^{-5} a_6 + 3.414 = 0$	10.83
$3.280 \times 10^{-10} a_6^2 - 6.560 \times 10^{-5} a_6 + 3.124 = 0$	12.18
$1.328 \times 10^{-10} a_6^2 - 2.660 \times 10^{-5} a_6 + 1.266 = 0$	11.24
$9.850 \times 10^{-11} a_6^2 - 1.778 \times 10^{-5} a_6 + 0.786 = 0$	10.29
$8.306 \times 10^{-12} a_6^2 - 1.6708 \times 10^{-6} a_6 + 7.942 \times 10^{-2} = 0$	12.41
$1.536 \times 10^{-11} a_6^2 - 2.584 \times 10^{-6} a_6 + 0.108 = 0$	9.18
$3.726 \times 10^{-12} a_6^2 - 5.948 \times 10^{-7} a_6 + 2.367 \times 10^{-2} = 0$	9.43

Mean value of a_6 = 11.65×10^4
Variance = 3.26×10^8
Std. Deviation = 1.80×10^4 (for 4 degrees of freedom).

(Continued on next page)

TABLE 20 CONTINUED

SYSTEM OF QUADRATIC EQUATIONS FOR SET K USED TO CALCULATE THE ABSORPTIVITY OF $Cu(HDz)_2 \cdot 2H_2Dz$, $a_{6,545}$

System of Equations	$a_6 \times 10^{-4}$ Litre mole cm^{-1}
CRK-6 to CRK- 10	
$1.597 \times 10^{-8} a_6^2 - 3.099 \times 10^{-3} a_6 + 143.7 = 0$	12.04
$7.648 \times 10^{-9} a_6^2 - 1.487 \times 10^{-3} a_6 + 69.00 = 0$	11.78
$3.214 \times 10^{-9} a_6^2 - 6.230 \times 10^{-4} a_6 + 28.85 = 0$	13.33
$2.236 \times 10^{-10} a_6^2 - 4.331 \times 10^{-5} a_6 + 2.004 = 0$	11.22
$1.267 \times 10^{-9} a_6^2 - 2.472 \times 10^{-4} a_6 + 11.49 = 0$	11.86
$6.438 \times 10^{-10} a_6^2 - 1.246 \times 10^{-4} a_6 + 5.763 = 0$	11.72
$4.946 \times 10^{-11} a_6^2 - 9.563 \times 10^{-6} a_6 + 0.4417 = 0$	11.71
$5.322 \times 10^{-11} a_6^2 - 1.009 \times 10^{-5} a_6 + 0.4599 = 0$	11.36
$5.937 \times 10^{-12} a_6^2 - 1.133 \times 10^{-6} a_6 + 5.177 \times 10^{-2} = 0$	11.50
$9.391 \times 10^{-13} a_6^2 - 1.806 \times 10^{-7} a_6 + 8.286 \times 10^{-3} = 0$	10.08

Mean value of a_6 = 11.75×10^4
Variance = 1.47×10^8
Std. Deviation = 1.21×10^4 (for 4 degrees of freedom).

$F = \frac{3.26 \times 10^8}{1.47 \times 10^8} = 2.20 \quad F_{0.05}(4,4) = 6.39$

Pooled variance = 2.36×10^8

$t = 0.21 \quad t_{0.05}(18) = 0.69$

Grand Mean = 11.70×10^4

TABLE 21

MOLAR ABSORPTIVITY OF $Cu(HDz)_2 \cdot 2H_2Dz$
IN DRY BENZENE AT 25°C

λ mμ	$a \times 10^{-4}$	$s^2 \times 10^{-6}$	$S \times 10^{-4}$ d.f. = 8	λ mμ	$a \times 10^{-4}$	$s^2 \times 10^{-6}$	$S \times 10^{-4}$ d.f. = 8
650	9.08	23.5	0.48	525	7.64	186.8	1.37
640	12.91	20.6	0.45	520	6.95	237.1	1.54
630	12.63	41.4	0.64	510	6.29	234.5	1.53
618	13.14	56.1	0.75	500	6.00	170.2	1.30
610	15.26	87.4	0.93	490	6.22	169.4	1.30
603	16.60	95.9	0.98				
600	16.52	81.0	0.90	480	7.50	189.5	1.38
590	15.10	197.8	1.41	475	8.80	219.6	1.48
580	13.62	198.9	1.41	470	9.23	204.9	1.43
575	12.98	211.3	1.45	460	9.97	245.0	1.56
570	12.40	220.1	1.48	450	11.40	229.7	1.52
560	11.78	231.9	1.52	440	11.21	243.0	1.56
550	11.75	236.9	1.54	430	10.55	204.5	1.43
545	11.70	236.0	1.54	425	10.00	198.7	1.41
540	11.22	252.6	1.59	420	9.45	196.0	1.40
530	8.53	207.9	1.44	410	8.10	194.4	1.39
				400	6.56	193.3	1.39

a is the mean of 10 samples.

APPENDIX XXVIII

COMMENTS ON THE TABLES OF APPENDIX XXVIII

SET C refers to continuous variations solutions for the reaction of indium oxinate with dithizone in benzene at 25°C.

SET A is the same as SET C except that each solution contained initial free oxine which approximately was fiftyfold in excess with respect to the total concentration of reactants.

SET D is the same as SET C except that each solution contained initial free oxine which approximately was tenfold in excess with respect to the total concentration of reactants.

SET B refers to continuous variations solutions for the reaction of indium dithizonate with oxine in benzene at 25°C.

SET RI refers to a set of Ratio solutions for the reaction of indium oxinate with dithizone in benzene at 25°C.

SET RIH is the same as SET RI except that each solution contained initial free oxine which was approximately fiftyfold in excess with respect to the initial concentration of indium oxinate.

An * beside a particular solution number indicates that the solution was prepared in replicates of five and the given value of the absorbance is the mean of the absorbances of five replicates.

A range of pathlengths was used, but all absorbance values have been calculated to a 1-cm path, except where stated otherwise.

TABLE 1

ANALYTICAL DATA FOR SET A

Molarity of stock solution of $InOx_3$ in benzene = 1.417×10^{-4} M
Molarity of stock solution of H_2Dz in benzene = 1.040×10^{-4} M
Molarity of stock solution of HOx in benzene = 2.622×10^{-3} M
Molarity of HOx in each solution = 5.244×10^{-4} M
Total concentration of reactants = 10^{-5} M
Volume of solution = 50 ML

Solution Number	$(InOx_3)_i$ Taken M x 10^6	$(H_2Dz)_i$ Taken M x 10^6	Initial Mole Fraction H_2Dz	Absorbance Pathlength = 5 cm 618 mμ	505 mμ
JIA- 1	10.00	0	0	0	0
2	9.494	0.499	0.050	0.070	0.014
3	9.012	0.998	0.100	0.012	0.100
4	8.502	1.498	0.150	0.118	0.136
5	7.992	1.997	0.200	0.148	0.152
6*	7.510	2.496	0.250	0.168	0.215
7	7.000	2.995	0.300	0.286	0.254
8	6.490	3.494	0.350	0.340	0.282
9	6.008	3.994	0.400	0.410	0.322
10	5.498	4.493	0.450	0.470	0.330
11*	4.988	4.992	0.500	0.566	0.360
12	4.506	5.491	0.549	0.655	0.370
13	3.996	5.990	0.600	0.735	0.380
14	3.486	6.490	0.651	0.832	0.395
15	3.004	6.989	0.699	0.930	0.394
16*	2.494	7.509	0.751	1.044	0.388
17	2.012	8.008	0.799	1.148	0.378

(Continued on next page)

TABLE 1 CONTINUED

ANALYTICAL DATA FOR SET A

Solution Number	$(InOx_3)_i$ Taken M x 10^6	(H_2Dz) Taken M x 10^6	Initial Mole Fraction H_2Dz	Absorbance Pathlength = 5 cm 618 mμ	505 mμ
JIA- 18	1.502	8.507	0.850	1.250	0.364
19	0.992	0.006	0.901	1.392	0.329
20	0.510	9.506	0.949	1.520	0.283
21	0	10.00	1.000	1.682	0.246

* These particular solutions were prepared in replicates of 5, and the absorbances are the mean value.

TABLE 12

ANALYTICAL DATA FOR SET B

Molarity of stock solution of $In(HDz)_3$ = 4.565×10^{-4} M
Molarity of stock solution of HOx = 5.244×10^{-4} M
Total concentration of reactants = 10^{-4} M
Volume of solution = 25 ML

Solution Number	$(In(HDz)_3)_i$ Taken M x 10^5	(HOx) Taken M x 10^5	Initial Mole Fraction HOx	Absorbance Pathlength = 1 cm 618 mμ	505 mμ	450 mμ
JZB- 1	9.988	0	0	0	10.34	5.55
2	9.495	0.503	0.050	0.022	5.46	3.75
3	9.002	1.007	0.101	0.159	8.25	4.44
4	8.509	1.489	0.149	0.216	7.65	4.14
5	7.998	1.993	0.200	0.325	7.42	4.08
6*	7.487	2.496	0.250	0.400	6.93	3.85
7	6.994	3.000	0.300	0.511	6.58	3.72
8	6.500	3.503	0.350	0.524	5.95	3.38
9	6.008	4.006	0.400	0.585	5.48	3.15
10	5.496	4.489	0.450	0.612	4.94	2.87
11*	5.003	4.992	0.500	0.640	4.44	2.62
12	4.492	5.496	0.550	0.652	3.91	2.34
13	3.999	5.999	0.600	0.654	3.40	2.07
14	3.506	6.502	0.650	0.646	2.91	1.802
15	2.995	6.985	0.700	0.639	2.43	1.546
16*	2.502	7.488	0.750	0.607	1.96	1.281
17	1.990	7.992	0.801	0.549	1.488	0.999
18	1.744	8.244	0.825	0.520	1.259	0.872
19	1.497	8.495	0.850	0.488	1.048	0.747
20	1.251	8.747	0.875	0.445	0.839	0.620

(Continued on next page)

TABLE 2 CONTINUED

ANALYTICAL DATA FOR SET B

Solution Number	$(In(HDz)_3)_i$ Taken M x 10^5	(HOx) Taken M x 10^5	Initial Mole Fraction HOx	Absorbance Pathlength = 1 cm 618 mμ	505 mμ	450mμ
JZB- 21	1.004	8.999	0.900	0.399	0.642	0.498
22	0.740	9.250	0.926	0.273	0.395	0.498
23	0.403	9.502	0.951	0.156	0.202	0.1650
24	0.246	9.754	0.975	0.106	0.089	0.0893
25	0	9.985	1.000	0	0	0

* These particular solutions were prepared in replicates of 5, and the absorbances are the mean values.

TABLE 3

ANALYTICAL DATA FOR SET C

Molarity of stock solution of $InOx_3$ = 7.084×10^{-5} M
Molarity of stock solution of H_2Dz = 5.200×10^{-5} M
Total concentration of reactants = 10^{-5} M
Volume of solution = 25 ML

Solution Number		$(InOx_3)_i$ Taken M x 10^6	$(H_2Dz)_i$ Taken M x 10^6	Initial Mole Fraction H_2Dz	Absorbance Pathlength = 5 cm 618 mμ	505 mμ
JIC-	1	10.00	0	0	-	0
	2	9.494	0.499	0.050	-	0.074
	3	9.012	0.998	0.100	-	0.172
	4	8.502	1.498	0.150	-	0.252
	5	7.992	1.997	0.200	-	0.345
	6	7.510	2.496	0.249	0.010	0.437
	7	7.000	2.995	0.300	0.012	0.532
	8	6.490	3.494	0.350	0.016	0.614
	9	6.008	3.994	0.399	0.026	0.690
	10	5.498	4.493	0.450	0.048	0.765
	11	4.988	4.992	0.500	0.062	0.822
	12	4.506	5.491	0.549	0.105	0.847
	13	3.996	5.990	0.600	0.155	0.898
	14	3.486	6.490	0.651	0.178	0.885
	15	3.004	6.989	0.699	0.360	0.844
	16	2.494	7.509	0.751	0.524	0.780
	17	2.012	8.008	0.799	0.758	0.706
	18	1.502	8.507	0.850	0.983	0.596
	19	0.992	9.006	0.901	1.150	0.468
	20	0.510	9.506	0.949	1.463	0.367
	21	0	10.00	1.000	1.688	0.252

TABLE 4

ANALYTICAL DATA FOR SET D

Molarity of stock solution of $InOx_3$ in benzene = 1.417×10^{-4} M
Molarity of stock solution of H_2Dz in benzene = 1.040×10^{-4} M
Molarity of stock solution of HOx in benzene = 2.622×10^{-3} M
Molarity of HOx in each solution = 1.049×10^{-4} M
Total concentration of reactants = 10^{-5} M
Volume of solution = 50 ML

Solution Number		$(InOx_3)_i$ Taken M x 10^6	$(H_2Dz)_i$ Taken M x 10^6	Initial Mole Fraction H_2Dz	Absorbance Pathlength = 5 cm 618 mμ	505 mμ
JID-	1	10.00	0	0	0	0
	2	9.494	0.499	0.050	0.008	0.048
	3	9.012	0.998	0.100	0.012	0.084
	4	8.502	1.498	0.150	0.046	0.190
	5	7.992	1.997	0.200	0.064	0.262
	6*	7.510	2.496	0.250	0.098	0.340
	7	7.000	2.995	0.300	0.134	0.398
	8	6.490	3.494	0.350	0.142	0.454
	9	6.008	3.994	0.400	0.206	0.487
	10	5.498	4.493	0.450	0.266	0.546
	11*	4.988	4.992	0.500	0.296	0.564
	12	4.506	5.491	0.549	0.398	0.592
	13	3.996	5.990	0.600	0.432	0.586
	14	3.486	6.490	0.651	0.576	0.602
	15	3.004	6.989	0.699	0.690	0.592
	16*	2.494	7.509	0.751	0.842	0.560
	17	2.012	8.008	0.799	0.924	0.550
	18	1.502	8.507	0.850	1.132	9.472
	19	0.998	9.006	0.901	1.302	0.402
	20	0.510	9.506	0.949	1.480	0.332
	21	0	10.00	1.00	1.682	0.252

* These particular solutions were in replicates of 5, and the absorbances are the mean values.

TABLE 5

CALCULATED EQUILIBRIUM CONCENTRATIONS OF SPECIES PRESENT IN SOLUTIONS OF SET B

$K_1^1 = 0.01086$ $K_2^1 = 0.143$ $K_3^1 = 0.300$

Solution Number	Equilibrium Concentration M x 10^5					
	$[InOx_3]$	$[InOx_2(HDz)]$	$[InOx(HDz)_2]$	$[In(HDz)_3]$	[HOx]	$[H_2Dz]$
JZB- 1	0	0	0		0	0
2	0.0046	0.3727	2.309	6.809	0.2671	0.2363
3	0.0042	0.3466	2.172	6.479	0.5313	0.4755
4	0.0038	0.3194	2.032	6.154	0.7804	0.7089
5	0.0036	0.3036	1.919	5.772	1.047	0.9452
6	0.0034	0.2929	1.818	5.372	1.323	1.173
7	0.0033	0.2702	1.690	5.030	1.584	1.415
8	0.0040	0.2970	1.680	4.520	1.938	1.565
9	0.0049	0.3261	1.659	4.018	2.320	1.686
10	0.0058	0.3496	1.610	3.530	2.708	1.781
11	0.0071	0.3809	1.563	3.052	3.148	1.844
12	0.0086	0.4099	1.491	2.582	3.617	1.879
13	0.0103	0.4352	1.402	2.151	4.109	1.890
14	0.0122	0.4564	1.293	1.744	4.629	1.873
15	0.0140	0.4612	1.151	1.368	5.149	1.836
16	0.0167	0.4686	1.000	1.016	5.739	1.749
17	0.0199	0.4630	0.8186	0.6889	6.381	1.611
18	0.0222	0.4587	0.7220	0.5410	6.731	1.513
19	0.0244	0.4453	0.6186	0.4091	7.089	1.406
20	0.0267	0.4332	0.5092	0.2916	7.464	1.282
21	0.0363	0.4261	0.3803	0.1616	7.981	1.017
22	0.0460	0.3812	0.2402	0.0720	8.487	0.7637
23	0.0584	0.2978	0.1155	0.0213	9.004	0.4986
24	0.0610	0.1535	0.0294	0.0027	9.494	0.2594
25	0	0	0	0	9.984	0

TABLE 6

CALCULATED EQUILIBRIUM CONCENTRATIONS OF SPECIES PRESENT IN THE SOLUTIONS OF SET A

$K_1 = 92.0$ $K_2 = 7.00$ $K_3 = 3.33$

Solution Number		Equilibrium Concentration M x 10^6					
		$[InOx_3]$	$[InOx_2(HDz)]$	$[InOx(HDz)_2]$	$[In(HDz)_3]$	[HOx]	$[H_2Dz]$
JIA-	1	10.00	0	0	0	524.4	0
	2	9.190	0.3090	0	0	524.7	0.1915
	3	8.401	0.5958	0.00319	0	525.0	0.404
	4	7.635	0.8582	0.00733	0	525.3	0.641
	5	6.893	1.092	0.0132	0	525.5	0.9045
	6	6.180	1.297	0.0216	0.00154	525.7	1.198
	7	5.499	1.469	0.0298	0.00286	525.9	1.525
	8	4.852	1.603	0.0403	0.00475	526.0	1.887
	9	4.243	1.698	0.0516	0.00738	526.1	2.286
	10	3.673	1.752	0.0635	0.011	526.2	2.725
	11	3.146	1.764	0.0752	0.0151	526.2	3.204
	12	2.660	1.734	0.0889	0.02005	526.2	3.724
	13	2.217	1.663	0.0949	0.0255	526.1	4.286
	14	1.815	1.553	0.101	0.031	526.0	4.887
	15	1.480	1.403	0.0989	0.0332	526.0	5.356
	16	1.153	1.214	0.0971	0.0366	525.9	6.010
	17	0.862	1.011	0.0896	0.0379	525.7	6.695
	18	0.609	0.779	0.0757	0.0366	525.6	7.297
	19	0.379	0.533	0.0518	0.0311	525.4	8.023
	20	0.176	0.273	0.0322	0.0189	525.1	8.847
	21	0	0	0	0	524.4	10.00

TABLE 7

CALCULATED EQUILIBRIUM CONCENTRATIONS OF SPECIES PRESENT IN THE SOLUTIONS OF SET C

K_1 = 92.0 K_2 = 7.00 K_3 = 3.33

Solution Number	Equilibrium Concentration M x 10^6					
	$[InOx_3]$	$[InOx_2(HDz)]$	$[InOx(HDz)_2]$	$[In(HDz)_3]$	[HOx]	$[H_2Dz]$
JIC- 1	10.00	0	0	0	0	0
2	3.906	5.072	0.5007	0.0233	0.4931	0.0069
3	3.179	5.150	0.6342	0.0368	0.9827	0.0173
4	2.688	5.045	0.7195	0.0484	1.470	0.0300
5	2.248	4.883	0.8062	0.0627	1.954	0.0461
6	1.790	4.689	0.9338	0.0877	2.431	0.0692
7	1.510	4.410	0.9788	0.1024	2.908	0.0922
8	0.9846	4.057	1.270	0.1876	3.350	0.1499
9	0.8338	3.711	1.355	0.2000	3.818	0.1844
10	0.5444	3.211	1.440	0.3043	4.229	0.2709
11	0.3228	2.609	1.603	0.4644	4.596	0.4035
12	0.1807	1.992	1.669	0.6590	4.912	0.5879
13	0.0818	1.328	1.638	0.9527	5.101	0.8991
14	0.0291	0.7395	1.429	1.302	5.088	1.406
15	0.0091	0.3616	1.087	1.542	4.896	2.104
16	0.0024	0.1524	0.7240	1.621	4.468	3.032
17	0	0.0466	0.3922	1.557	3.631	4.369
18	0	0.0136	0.1931	1.293	2.806	5.694
19	0	0.0030	0.0766	0.920	1.940	7.060
20	0	0	0.0188	0.481	0.985	8.415
21	0	0	0	0	0	10.00

TABLE 8

CALCULATED EQUILIBRIUM CONCENTRATIONS OF SPECIES PRESENT IN THE SOLUTION OF SET D

$K_1 = 92.0$ $K_2 = 7.00$ $K_3 = 3.33$

Solution Number	Equilibrium Concentrations M x 10^6					
	$[InOx_3]$	$[InOx_2(HDz)]$	$[InOx(HDz)_2]$	$[In(HDz)_3]$	[HOx]	$[H_2Dz]$
JID- 1	10.00	0	0	0	104.9	0
2	8.664	0.8300	0.0061	0	105.3	0.1095
3	7.542	1.437	0.0309	0	105.7	0.2190
4	6.580	1.879	0.0407	0	106.1	0.3285
5	5.778	2.160	0.0614	0	106.5	0.4323
6	5.038	2.376	0.0853	0.0015	106.8	0.5475
7	4.288	2.591	0.1189	0.0026	107.2	0.7032
8	3.599	2.738	0.1582	0.0043	107.5	0.8876
9	2.943	2.841	0.2085	0.0072	107.8	1.130
10	2.341	2.878	0.2688	0.0118	108.0	1.441
11	1.797	2.842	0.3417	0.0194	108.0	1.856
12	1.430	2.667	0.3778	0.0252	108.2	2.190
13	1.079	2.460	0.4265	0.0349	108.5	2.680
14	0.7793	2.201	0.4723	0.0478	108.1	3.314
15	0.5513	1.893	0.4942	0.0609	107.9	4.023
16	0.3824	1.562	0.4847	0.0709	107.6	4.772
17	0.2532	1.222	0.4479	0.0774	107.3	5.620
18	0.1577	0.887	0.3789	0.0763	106.9	6.524
19	0.0873	0.567	0.2801	0.0652	106.4	7.504
20	0.0364	0.270	0.1525	0.0406	105.9	8.530
21	0	0	0	0	104.9	10.00

TABLE 9

ANALYTICAL DATA FOR RATIO SOLUTIONS OF SETS RI AND RIH

Molarity of stock solution of $InOx_3$ = 1.672×10^{-4} M
Molarity of stock solution of HOx = 2.622×10^{-3} M
Molarity of stock solution of H_2Dz = 1.04×10^{-3} M
Molarity of HOx in each RIH solution = 5.244×10^{-4} M
Volume of solution = 25 ML

Solution Number	$(InOx_3)_i$ Taken mole/litre	$(H_2Dz)_T$ Taken moles/litre	Approximate Ratio $(H_2Dz)_T/(InOx_3)_T$
RI, RIH- 1	1.134×10^{-5}	1.040×10^{-6}	1:11
2	"	2.080×10^{-6}	1:5
3*	"	3.452×10^{-6}	1:3
4	"	5.200×10^{-6}	1:2
5	1.063×10^{-5}	5.200×10^{-5}	5:1
6	"	1.040×10^{-4}	10:1
7	"	2.080×10^{-4}	20:1
8*	"	3.120×10^{-4}	30:1
9	"	4.169×10^{-4}	40:1
10	"	5.200×10^{-4}	50:1
11	"	6.240×10^{-4}	60:1

* Prepared in replicates of 5.

TABLE 10

CALCULATED EQUILIBRIUM CONCENTRATIONS OF SPECIES PRESENT IN THE SOLUTIONS OF SET RI

$K_1 = 92.0$ $K_2 = 7.0$ $K_3 = 3.33$

Solution Number	Equilibrium Concentration M					
	$[InOx_3]$	$[InOx_2(HDz)]$	$[InOx(HDz)_2]$	$[In(HDz)_3]$	[HOx]	$[H_2Dz]$
RI- 1	1.030×10^{-5}	1.040×10^{-6}	-	-	1.040×10^{-6}	-
2	9.260×10^{-6}	2.080×10^{-6}	-	-	2.080×10^{-6}	-
3	8.004×10^{-6}	3.235×10^{-6}	9.939×10^{-8}	1.452×10^{-9}	3.437×10^{-6}	1.508×10^{-8}
4	6.446×10^{-6}	4.634×10^{-6}	2.532×10^{-7}	6.579×10^{-9}	5.160×10^{-6}	4.027×10^{-8}
5	5.902×10^{-9}	4.562×10^{-7}	2.680×10^{-6}	7.488×10^{-6}	2.827×10^{-6}	2.373×10^{-5}
6	3.154×10^{-10}	6.977×10^{-8}	1.173×10^{-6}	9.386×10^{-6}	3.057×10^{-6}	7.343×10^{-5}
7	2.611×10^{-11}	1.357×10^{-8}	5.363×10^{-7}	1.008×10^{-5}	3.130×10^{-6}	1.767×10^{-4}
8	6.796×10^{-12}	5.569×10^{-9}	3.469×10^{-7}	1.028×10^{-5}	3.152×10^{-6}	2.805×10^{-4}
9	2.688×10^{-12}	3.010×10^{-9}	2.562×10^{-7}	1.037×10^{-5}	3.162×10^{-6}	3.844×10^{-4}
10	1.325×10^{-12}	1.881×10^{-9}	2.030×10^{-7}	1.042×10^{-5}	3.167×10^{-6}	4.883×10^{-4}
11	7.477×10^{-13}	1.286×10^{-9}	1.682×10^{-7}	1.046×10^{-5}	3.171×10^{-6}	5.923×10^{-4}

TABLE 11

CALCULATED EQUILIBRIUM CONCENTRATIONS AT 25°C OF SPECIES PRESENT IN THE SOLUTIONS OF SET RIH

$K_1 = 92.0$ $K_2 = 7.0$ $K_3 = 3.33$

Solution Number	Equilibrium Concentration M					
	$[InOx_3]$	$[InOx_2(HDz)]$	$[InOx(HDz)_2]$	$[In(HDz)_3]$	[HOx]	$[H_2Dz]$
RIH- 1	1.066×10^{-5}	6.734×10^{-7}	3.233×10^{-9}	7.382×10^{-12}	5.251×10^{-4}	3.601×10^{-7}
2	1.002×10^{-5}	1.308×10^{-6}	1.299×10^{-8}	6.132×10^{-11}	5.257×10^{-4}	7.455×10^{-7}
3	9.218×10^{-6}	2.086×10^{-6}	3.589×10^{-8}	2.936×10^{-10}	5.266×10^{-4}	1.294×10^{-6}
4	8.282×10^{-6}	2.976×10^{-6}	8.128×10^{-8}	1.056×10^{-9}	5.275×10^{-4}	2.058×10^{-6}
5	9.294×10^{-7}	6.030×10^{-6}	2.973×10^{-6}	6.975×10^{-7}	5.385×10^{-4}	3.793×10^{-5}
6	2.701×10^{-7}	3.889×10^{-6}	4.256×10^{-6}	2.215×10^{-6}	5.434×10^{-4}	8.496×10^{-5}
7	5.730×10^{-8}	1.770×10^{-6}	4.158×10^{-6}	4.645×10^{-6}	5.484×10^{-4}	1.840×10^{-4}
8	2.037×10^{-8}	9.732×10^{-7}	3.533×10^{-6}	6.103×10^{-6}	5.507×10^{-4}	2.856×10^{-4}
9	9.388×10^{-9}	6.083×10^{-7}	2.995×10^{-6}	7.017×10^{-6}	5.520×10^{-4}	3.884×10^{-4}
10	5.059×10^{-9}	4.142×10^{-7}	2.578×10^{-6}	7.633×10^{-6}	5.529×10^{-4}	4.915×10^{-4}
11	3.026×10^{-9}	2.996×10^{-7}	2.255×10^{-6}	8.072×10^{-6}	5.534×10^{-4}	5.950×10^{-4}

TABLE 12

ABSORBANCES AT SELECTED WAVELENGTHS FOR SETS RI AND RIH

Solution Number		Wavelength, mμ Pathlength = 1 cm							
		618	570	540	510	500	470	440	410
RI-	1	-	0.0017	0.0167	0.0297	0.0304	0.0217	0.0328	0.0604
	2	-	0.0036	0.0336	0.0595	0.0609	0.0418	0.0407	0.0625
	3*	0.0005	0.0068	0.0561	0.0991	0.1013	0.0684	0.0516	0.0672
	4	0.0014	0.0119	0.0854	0.1499	0.1529	0.1030	0.0664	0.0709
	5	0.823	0.642	0.898	1.086	1.103	1.088	0.849	0.516
	6	2.55	1.634	1.426	1.423	1.490	1.934	1.793	1.591
	7	6.13	3.68	2.39	1.98	2.15	3.57	3.68	2.35
	8*	9.73	5.74	3.34	2.51	2.79	5.19	5.58	3.58
	9	13.34	7.79	4.29	3.05	3.43	6.82	7.47	4.82
	10	16.94	9.85	5.24	3.58	4.06	8.44	9.36	6.06
	11	20.00	11.91	6.18	4.11	4.70	10.06	11.26	7.29
RIH-	1	0.0125	0.0082	0.0142	0.0212	0.0221	0.0205	0.0367	0.0641
	2	0.0259	0.0169	0.0282	0.0420	0.0436	0.0391	0.0486	0.0698
	3*	0.0449	0.0293	0.0466	0.0685	0.0712	0.0635	0.0648	0.0780
	4	0.0714	0.0465	0.0698	0.1009	0.1049	0.0945	0.0864	0.0893
	5	1.316	0.820	0.617	0.637	0.675	0.900	0.864	0.577
	6	2.95	1.794	1.178	1.058	1.140	1.771	1.802	1.181
	7	6.38	3.79	2.22	1.747	1.925	3.46	3.69	2.40
	8*	9.91	5.82	3.22	2.35	2.63	5.12	5.58	3.62
	9	13.48	7.86	4.20	2.92	3.30	6.76	7.47	4.85
	10	17.06	9.90	5.16	3.48	3.96	8.39	9.37	6.08
	11	20.00	11.96	6.12	4.03	4.62	10.02	11.26	7.32

* Average of 5 replicates.

TABLE 13

MOLAR ABSORPTIVITY OF $InOx_2(HDz)_2$ IN BENZENE AT 25°C

λ mμ	a x 10^{-4}	s^2 x 10^{-6}	S^2x 10^{46} d.f. = 21	λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4} d.f. = 21
600	0.03	0.09	0.03	500	2.92	4.03	0.20
590	0.06	0.01	0.01	490	2.73	3.23	0.18
580	0.10	0.25	0.05	480	2.40	0.67	0.08
570	0.15	0.85	0.09	470	1.92	0.33	0.06
560	0.45	0.81	0.09	460	1.52	0.69	0.08
550	0.93	5.83	0.24	450	1.22	1.09	0.10
540	1.60	3.26	0.18	440	0.95	0.18	0.04
530	2.15	3.26	0.18	430	0.80	0.08	0.03
520	2.58	8.91	0.30	420	0.74	0.08	0.03
510	2.85	8.27	0.29	410	0.88	0.13	0.04
505	2.89	8.27	0.29	400	0.65	0.05	0.02

a is the mean of 22 samples.

TABLE 14

MOLAR ABSORPTIVITY OF $InOx_2(HDz)$ IN BENZENE AT 25°C

λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4} d.f. = 21	λ mμ	a x 10^{-4}	S^2 x 10^{-6}	S x 10^{-4} d.f. = 21
600	0.03	0.09	0.03	490	2.73	3.23	0.18
590	0.06	0.01	0.01	480	2.40	0.67	0.08
580	0.10	0.25	0.05	470	1.92	0.33	0.06
570	0.15	0.85	0.09	460	1.52	0.69	0.08
560	0.45	0.81	0.09	450	1.22	1.09	0.10
550	0.93	5.8	0.24	440	0.95	0.18	0.04
540	1.60	3.26	0.18	430	0.80	0.08	0.03
530	2.5	3.26	0.18	420	0.74	0.08	0.03
520	2.58	9.91	0.30	410	0.68	0.13	0.04
510	2.85	8.37	0.39	400	0.65	0.05	0.02
505	2.89	8.27	0.29				
500	2.92	4003	0.20				

a is the mean of 22 samples.

Comparison of B_1 and B_2

Coefficient of X^2

The value of t is given by

$$t = \frac{|B_1 - B_2|}{\sqrt{(So_1^2/D_1) + (So_2^2/D_2)}}$$

where

$$S\overset{2}{o}_1 = \sum_{i=1}^{11} \frac{(yi - Yi)^2}{m - 2} \quad m = 11$$

$$= 12{,}853 \times 10^{-5}$$

$S\overset{2}{o} = 0$ (there was no deviation about the curve for $K_1 = 92$ because the absorbnaces (Y) were calculated, not experimental points).

$$D_1 = D_2 = (\Sigma X^2) - m\overline{X}^2 = 1.1176$$

$$\therefore t = \frac{0.521 - 0.513}{\sqrt{11.500 \times 10^{-5}}} = 0.75 < t_{0.05}(9) = 2.26$$

The coefficients are not significantly different.

Coefficient of X^5

$$So_1^2 = 12.853 \times 10^{-5}$$

$$D = 0.11825$$

$$t = \frac{-10.742 + 12.693}{\sqrt{10.87 \times 10^{-4}}} = 58.8 < t_{0.05}(9) = 2.62$$

The coefficients are significantly different.

APPENDIX XXIX

NOTES TO APPENDIX XXIX

All the analytical data are for benzene solutions at 25°C.

SET A1) Ratio solutions for the reactions of lead oxinate
SET A2) with lead dithizonate.

SET B1) Ratio solutions for the formation of the adduct
SET B2) PbOxHDz.HOx

SET C Ratio solutions for the formation of the adduct $Pb(HDz)_2.HOx$

SET D Ratio solutions for the formation of the adduct $Pb(HDz)_2.H_2Dz$

SET E1) Ratio solutions for the reaction of the mixed
SET E2) chelate with dithizone.
SET E2 contained initial free oxine, onehundred-fold in excess with respect to the initial concentration of lead oxinate.

SET F1) Continuous variations solutions for the reaction
SET F2) of lead oxinate with dithizone.
SET F2 contained initial free oxine, onehundred-fold in excess with respect to the total concentration of reactants.

TABLE 1

ANALYTICAL DATA FOR SETS A1 AND A2*

Molarity of stock mixture of $PbOx_2$ and $Pb(HDz)_2$ in benzene; $(Pb)_T = 2.008 \times 10^{-4}$ M; $(HDz)_T = 1.297 \times 10^{-4}$ M

Molarity of stock $PbOx_2$ solution in benzene $= 2.025 \times 10^{-5}$ M

Molarity of stock $Pb(HDz)_2$ solution in benzene $= 6.025 \times 10^{-5}$ M

Volume of solution = 50 ML

Solution Number	$(Pb)_T$ M $\times 10^4$	$(HDz)_T$ M $\times 10^4$	Solution Number	$(Pb)_T$ M $\times 10^5$	$(HDz)_T$ M $\times 10^5$
PRA1- 1	0.8836	1.223	PRA2- 1	0.8836	1.223
2	1.165	1.242	2**	1.165	1.242
3	1.446	1.260	3	1.446	1.260
4	1.707	1.239	4	1.707	1.239
5	0.5635	0.2594	5	0.5635	0.2594
6**	0.9246	0.5188	6**	0.9246	0.5188
7	1.286	0.7882	7	1.286	0.7882
8	1.647	1.038	8	1.647	1.038
9**	2.008	1.297	9**	2.008	1.297

* See Appendix XXIV 1(b) for the method of preparation of these solutions.
** Prepared in replicates of five.

TABLE 2

ABSORBANCES FOR SETS A1 AND A2

PATHLENGTH = 1 cm

Solution Number	Wavelength, mμ							
	575	550	517	500	475	445	425	400
PRA1- 1	0.421	1.953	3.68	3.47	2.32	1.238	0.638	0.446
2*	0.342	1.626	3.50	3.43	2.40	1.284	0.662	0.451
3	0.314	1.511	3.46	3.45	2.46	1.330	0.737	0.530
4	0.303	1.462	3.39	3.39	2.43	1.338	0.827	0.642
5	0.054	0.285	0.703	0.703	0.504	0.291	0.245	0.221
6*	0.126	0.607	1.416	1.418	1.026	0.582	0.424	0.362
7	0.192	0.926	2.15	2.15	1.554	0.872	0.600	0.497
8	0.253	1.221	2.84	2.84	2.04	1.144	0.774	0.635
9*	0.316	1.524	3.54	3.54	2.55	1.424	0.947	0.770
PRA2- 1	0.0420	0.1954	0.3682	0.3466	0.2322	0.1238	0.0636	0.0442
2*	0.0344	0.1626	0.3502	0.3434	0.2400	0.1283	0.0652	0.0352
3	0.0318	0.1526	0.3472	0.3454	0.2458	0.1330	0.0742	0.0536
4	0.0322	0.1546	0.3566	0.3564	0.2548	0.1396	0.0740	0.0638
5	0.0062	0.0300	0.0706	0.0708	0.0517	0.0302	0.0250	0.0226
6*	0.0124	0.0602	0.1411	0.1416	0.1027	0.0583	0.0423	0.0360
7	0.0190	0.0914	0.2144	0.2152	0.1555	0.0872	0.0598	0.0494
8	0.0250	0.1204	0.2822	0.2834	0.2046	0.1144	0.0770	0.0630
9*	0.0310	0.1504	0.3528	0.3540	0.2554	0.1424	0.0952	0.0762

* Average of 5 replicates.

TABLE 3

ANALYTICAL DATA FOR SETS B1 AND B2

Volume of solution = 25 ML

Solution Number		$(Pb)_T$ M x 10^4	$(HDz)_T$ M x 10^4	(HOx) Added M x 10^2
PRB1-	1	0.8836	1.223	1.118
	2 [3]	1.165	1.242	1.003
	3	1.446	1.260	1.483
	4	1.707	1.239	1.212
	5 [2]	0.2594	0.2594	1.371
	6 [3]	0.9246	0.5188	1.315
	7	1.286	0.7882	0.9917
	8	1.647	1.038	1.163
	9 [3]	2.008	1.297	1.480
PRB2-	1 [2]	0.02594	0.02594	0.1095
	2 [3]	0.05188	0.05188	0.1095
	3	0.07882	0.07882	0.1095
	4	0.1038	0.1038	0.1095
	5 [3]	0.1297	0.1297	0.1095

(1) See Table 1 for the concentrations of the starting material. The oxine was added as accurately-weighed solid.

(2) The equilibrium concentrations found for ($PbOx_2$) in SETS A1 and A2 have been subtracted from $(Pb)_T$ in Table 1 to give new value of $(Pb)_T$ for PRB1-5, PRB2-1 to PRB-5.

(3) Prepared in replicates of 5.

TABLE 4

EXPERIMENTAL ABSORBANCES SETS B1 AND B2

Pathlength = 1 cm

Solution Number	Wavelength, mμ							
	575	550	517	500	475	445	425	400
PRB1- 1	0.246	1.515	3.26	3.18	2.18	1.226	0.713	0.507
2*	0.182	1.226	2.99	3.07	2.16	1.227	0.782	0.626
3	0.154	1.160	2.92	3.02	2.18	1.235	0.870	0.745
4	0.186	1.281	3.10	3.14	2.28	1.352	0.985	0.861
5	0.020	0.208	0.585	0.621	0.487	0.318	0.294	0.290
6*	0.063	0.441	1.078	1.096	0.808	0.508	0.434	0.407
7	0.127	0.806	1.945	1.986	1.444	0.864	0.676	0.609
8	0.148	1.184	3.02	3.15	2.31	1.405	1.064	0.976
9*	0.155	1.156	2.99	3.09	2.24	1.321	1.071	0.970
PRB2- 1	0.0056	0.0284	0.0682	0.0692	0.0508	0.0302	0.0254	0.0234
2*	0.0113	0.0576	0.1373	0.1389	0.1014	0.0582	0.0431	0.0373
3	0.0164	0.0862	0.2064	0.2094	0.1524	0.0870	0.0621	0.0530
4	0.0204	0.1120	0.2708	0.2754	0.2014	0.1160	0.0816	0.0690
5*	0.0273	0.1426	0.3412	0.3470	0.2528	0.1432	0.0986	0.0816

* Average of 5 replicates.

TABLE 5

ANALYTICAL DATA FOR SET C

Concentration of stock solution of $Pb(HDz)_2$ = 6.215×10^{-5} M
Concentration of stock solution of HOx = 2.486×10^{-3} M
Volume of solution = 50 ML

Solution Number	$Pb(HDz)_2$ Taken M x 10^5	HOx Taken M x 10^5	Solution Number	$Pb(HDz)_2$ Taken M x 10^5	HOx Taken M x 10^5
PRC- 1	3.729	19.89	PRC- 8	0.3729	1.989
2	3.729	39.98	9	0.3729	3.978
3	3.729	99.44	10	0.3729	9.944
4	1.864	0.9944	11	0.1864	0.9944
5	1.864	19.89	12	0.1864	1.989
6	1.864	39.98	13	0.1864	3.978
7	1.864	99.44			

TABLE 6

ABSORBANCES FOR SET C

Pathlength = 1 cm

Solution Number	Wavelength, mμ							
	575	550	517	500	475	445	425	400
PRC- 1	0.246	1.270	2.289	2.072	1.314	0.665	0.393	0.261
2	0.230	1.192	2.248	2.030	1.280	0.639	0.390	0.244
3*	0.177	1.125	2.202	2.005	1.263	0.624	0.404	0.255
4	0.141	0.672	1.166	1.061	0.681	0.356	0.204	0.140
5	0.133	0.651	1.144	1.055	0.668	0.343	0.208	0.139
6*	0.119	0.614	1.124	1.038	0.672	0.345	0.220	0.143
7	0.0943	0.566	1.103	1.002	0.628	0.313	0.203	0.129
8	0.0308	0.1415	0.2388	0.2158	0.1375r	0.0727	0.0390	0.0279
9*	0.0298	0.1391	0.2365	0.2151	0.1369	0.0717	0.0392	0.0278
10	0.0280	0.1334	0.2330	0.2109	0.1343	0.0692	0.0393	0.0270
11	0.0156	0.0714	0.1200	0.1082	0.0690	0.0366	0.0193	0.0141
12	0.0153	0.0708	0.1195	0.1080	0.0689	0.0364	0.0196	0.0141
13*	0.0146	0.0688	0.1183	0.1068	0.0356	0.0356	0.0195	0.0138

* Average of 5 replicates.

TABLE 7

ANALYTICAL DATA FOR SET D

Molarity of stock $PbOx_2$ solution = 4.342×10^{-5} M
Molarity of stock H_2Dz solution = 2.572×10^{-4} M
Volume of solution = 25 ML

Solution Number	($PbOx_2$) Taken M	(H_2Dz) Taken M x 10^4
PRD - 1*	8.688×10^{-6}	3.077
2	8.688×10^{-6}	4.116
3	8.688×10^{-6}	5.145
4	1.738×10^{-5}	2.058
5	1.738×10^{-5}	4.116
6	1.738×10^{-5}	5.145

* Each solution prepared in replicates of 3.

TABLE 8

EXPERIMENTAL ABSORBANCES FOR SET D

Pathlength = 1 cm

Solution Number	Wavelength mμ								
	618	575	550	517	500	475	445	425	400
PRD- 1*	10.07	6.33	3.76	2.11	2.26	4.55	5.52	4.69	2.72
2	13.67	8.57	5.00	2.67	2.90	6.07	7.44	6.35	3.68
3	17.24	10.80	6.23	3.24	3.53	7.58	9.34	7.98	4.62
4	5.89	3.80	2.66	2.02	2.03	3.12	3.49	2.90	1.71
5	13.03	8.24	5.11	3.13	3.29	6.13	7.29	6.16	3.60
6	k6.59	10.47	6.37	3.76	3.98	7.67	9.20	7.80	4.54

* Each absorbance of each solution is average of 3 replicates.

TABLE 9

ANALYTICAL DATA FOR SETS E1 AND E2

Molarity of stock $PbOx_2$ solution = 8.017×10^{-5} M
Molarity of stock H_2Dz solution = 4.110×10^{-2} M[1]
Molarity of stock HOx solution = 5.00×10^{-2} M
Volume of solution = 50 ML

	SET E1			SET E2		
Solution Number	$PbOx_2$ Taken M x 10^5	H_2Dz Taken M x 10^5	Solution Number	$PbOx_2$ Taken M x 10^5	H_2Dz Taken M x 10^5	Free HOx Taken M x 10^3
PRE1- 1	8.017	16.42	PRE2- 1	8.017	16.42	8.007
2[2]	4.814	9.850	2[2]	4.814	9.850	5.000
3	2.407	4.925	3	2.407	4.925	2.500
4	0.9625	2.056	4	0.9625	2.056	1.000
5[2]	0.8017	1.642	5[2]	0.8017	1.642	0.800
6	0.4814	0.9850	6	0.4814	0.985	0.500

(1) Diluted to 4.925×10^{-4} M for use with PRE1-2 to PRE1-6 and PRE2-2 to PRE2-6.

(2) Prepared in replicates of five.

(3) HOx added as accurately-weighed solid.

TABLE 10

ABSORBANCES FOR SETS E1 AND E2

Pathlength = 1 cm

Solution Number	Wavelength, mμ								
	618	575	550	517	500	475	445	425	400
PRE1- 1	0.1059	0.632	2.70	4.90	4.46	2.89	1.593	0.883	0.601
2*	0.0628	0.408	1.714	3.08	2.80	1.814	0.993	0.545	0.377
3	0.0347	0.2113	0.862	1.532	1.390	0.901	0.493	0.2686	0.7886
4	0.0252	0.0921	0.344	0.602	0.545	0.356	0.1979	0.1090	0.0769
5*	0.0211	0.0793	0.297	0.520	0.470	0.307	0.1705	0.0938	0.0662
6	0.0148	0.0476	0.1728	0.300	0.2715	0.1781	0.0995	0.0551	0.0389
PRE2- 1	0.2090	0.534	2.35	4.48	4.15	2.75	1.578	0.936	0.588
2*	0.1744	0.354	1.431	2.69	2.50	1.669	0.971	0.581	0.364
3	0.1003	0.1887	0.731	1.366	1.267	0.851	0.497	0.298	0.1867
4	0.1078	0.1206	0.3220	0.563	0.522	0.3704	0.2350	0.1493	0.0926
5*	0.0315	0.0623	0.2387	0.447	0.415	0.2794	0.1622	0.0960	0.0608
6	0.0290	0.0454	0.1495	0.2721	0.2526	0.1731	0.1029	0.0616	0.0393

* Average of 5 replicates.

TABLE 11

ANALYTICAL DATA FOR SETS F1 AND F2

Molarity of stock $PbOx_2$ solution in benzene = 5.021×10^{-5} M
Molarity of stock H_2Dz solution in benzene = 1.004×10^{-4} M
Molarity of stock HOx solution in benzene = 9.876×10^{-3} M
Molarity of initial free HOx in each solution of SET F2 = 10^{-3} M
Volume of solution = 50 ML
Total concentration of reactants = 10^{-5} M

Solution Number		$PbOx_2$ Taken M x 10^6	H_2Dz Taken M x 10^6	Initial Mole Fraction of H_2Dz
PJF1, PJF2-	1	10.0	0	0
	2	9.5	0.5	0.05
	3	9.0	1.0	0.10
	4*	8.5	1.5	0.15
	5	8.0	2.0	0.20
	6	7.5	2.5	0.25
	7	7.0	3.0	0.30
	8	6.5	3.5	0.35
	9	6.0	4.0	0.40
	10	5.5	4.5	0.45
	11*	5.0	5.0	0.50
	12	4.5	5.5	0.55
	13	4.0	6.0	0.60
	14	3.5	6.5	0.65
	15	3.0	7.0	0.70
	16	2.5	7.5	0.75
	17	2.0	8.0	0.80
	18*	1.5	8.5	0.85
	19	1.0	9.0	0.90
	20	0.5	9.5	0.95
	21	0	10.0	1.00

* Prepared in replicates of 5.

TABLE 12

ABSORBANCES FOR SETS F1 AND F2

Pathlength = 5 cm

Solution Number	Wavelength mμ 618	517	445	Solution Number	Wavelength mμ 618	517	445
PJF1- 1	0	0	0.087	PJF2- 1	0	0	0.089
2	0.001	0.081	0.104	2	0.001	0.080	0.104
3	0.0015	0.155	0.126	3	0.002	0.150	0.126
4*	0.002	0.238	0.138	4*	0.003	0.234	0.140
5	0.003	0.292	0.140	5	0.004	0.292	0.160
6	0.004	0.399	0.172	6	0.006	0.390	0.176
7	0.006	0.492	0.190	7	0.007	0.486	0.193
8	0.008	0.565	0.201	8	0.009	0.555	0.201
9	0.011	0.608	0.235	9	0.013	0.600	0.225
10	0.015	0.722	0.240	10	0.025	0.700	0.250
11*	0.021	0.782	0.260	11*	0.042	0.775	0.264
12	0.035	0.881	0.279	12	0.054	0.860	0.286
13	0.056	0.941	0.302	13	0.083	0.918	0.313
14	0.089	0.970	0.326	14	0.123	0.926	0.340
15	0.201	0.960	0.386	15	0.226	0.911	0.392
16	0.442	0.885	0.462	16	0.450	0.850	0.465
17	0.760	0.750	0.582	17	0.710	0.730	0.555
18*	0.968	0.624	0.642	18*	0.964	0.625	0.650
19	1.222	0.521	0.738	19	1.229	0.504	0.744
20	1.480	0.422	0.828	20	1.476	0.390	0.825
21	1.735	0.270	0.920	21	1.735	0.270	0.924

* Average of five replicates.

TABLE 13

MOLAR ABSORPTIVITY OF PbOxHDz IN BENZENE AT 25°C

Basic data: SET A1, Tables 1 and 2

λ $m\mu$	a x 10^{-4}	s^2 x 10^{-6}	s x 10^{-4} d.f. = 8	λ $m\mu$	a x 10^{-4}	s^2 x 10^{-6}	s x 10^{-4} d.f. = 8
600	0.04	0.05	0.02	500	2.73	13.34	0.37
590	0.10	0.06	0.02	490	2.49	23.00	0.48
580	0.18	0.23	0.05	480	2.13	5.81	0.24
570	0.31	2.63	0.16	470	1.76	2.31	0.15
560	0.65	1.80	0.14	460	1.37	6.85	0.26
550	1.16	7.15	0.27	450	1.04	5.09	0.23
540	1.78	10.08	0.30	445	0.90	1.20	0.11
530	2.32	3.44	0.18	440	0.78	1.52	0.13
520	2.66	15.21	0.39	430	0.60	0.69	0.08
517	2.72	14.00	0.37	420	0.45	0.53	0.02
510	2.80	19.64	0.44	410	0.36	0.17	0.04
505	2.78	21.32	0.46	400	0.34	0.10	0.03

a is the average of nine samples.

TABLE 14

MOLAR ABSORPTIVITY OF $Pb(HDz)_2.HOx$ IN BENZENE AT 25°C

Basic data: SET C, Tables 5 and 6

λ mμ	a x 10^{-4}	s^2 x 10^{-6}	s x 10^{-4} d.f. = 12	λ mμ	a.x 10^{-4}	s^2 x 10^{-6}	s x 10^{-4} d.f. = 12
600	0.05	0.05	0.02	500	5.36	5.76	0.24
590	0.21	0.08	0.03	490	4.63	5.68	0.24
580	0.38	0.04	0.02	480	3.82	2.78	0.17
570	0.75	0.21	0.05	470	3.09	1.77	0.13
560	1.61	0.36	0.06	460	2.42	3.29	0.18
550	3.00	1.73	0.13	450	1.90	1.19	0.11
540	4.46	1.38	0.11	445	1.66	2.93	0.17
530	5.38	5.80	0.24	440	1.45	0.78	0.09
525	5.65	1.54	0.12	430	1.20	0.60	0.08
520	5.80	3.62	0.19	420	0.98	0.20	0.04
517	5.81	7.27	0.27	410	0.81	0.05	0.02
510	5.81	10.20	0.32	400	0.68	0.05	0.02
505	5.76	6.80	0.26				

a is the average of 13 samples.

TABLE 15

MOLAR ABSORPTIVITY OF PbOxHDz.HOx IN BENZENE AT 25°C

Basic data: SETS B1 and B2, Tables 3 and 4

λ mμ	a x 10^{-4}	s^2 x 10^{-6}	s x 10^{-4} d.f. = 13	λ mμ	a x 10^{-4}	s^2 x 10^{-6}	s x 10^{-4} d.f. = 13
600	0		-	495	2.18	12.25	0.35
590	0		-	490	2.15	7.40	0.27
580	0.02	0.01	0.01	480	1.84	8.05	0.28
570	0.09	0.14	0.04	470	1.50	3.66	0.19
560	0.30	0.63	0.08	460	1.24	3.71	0.17
550	0.59	2.00	0.14	450	1.03	1.88	0.14
540	1.08	2.35	0.15	445	0.94	0.97	0.10
530	1.59	4.53	0.21	440	0.87	11998	0.14
520	1.83	12.00	0.36	430	0.75	1.86	0.14
517	1.95	9.70	0.31	420	0.67	1.08	0.11
510	2.07	8.61	0.29	410	0.64	0.55	0.07
500	2.17	15.03	0.39	400	0.65	0.16	0.04

a is the average of 14 samples.

The experimental data at 517 mμ for solution #PRA1-2 were:

$(Pb)_T = 1.65 \times 10^{-4}$ M; $(HDz)_T = 1.242 \times 10^{-4}$ M

$A_{517} = 3.50$ $a_{3,517} = 6.47 \times 10^4$

Substitution of the data into equations (d)-13 to (d)-15 gave

$$D[PbOx_2] = 1.088 \times 10^{-4}a_3 - 3.002 \qquad \text{(d)-16}$$

$$D[Pb(HDz)_2] = 1.242 \times 10^{-4}a_3 - 3.5 \qquad \text{(d)-17}$$

$$D[PbOxHDz] = -1.036 \qquad \text{(d)-18}$$

Then

$$K_3 = \frac{(-1.036)^2}{(1.088 \times 10^{-4}a_3 - 3.002)(1.242 \times 10^{-4}a_3 - 3.5)}$$

$$\frac{1}{K_3} = 1.265 \times 10^{-8}a_3^2 - 7.056 \times 10^{-4}a_3 + 9.480$$

The average value of $a_{3,517}$ was found to be 2.722×10^4. Substituting this value into (d)-16, (d)-17 and (d)-18 where $D = 2 \times 2.722 \times 10^4 - 6.47 \times 10^4 = -1.026 \times 10^4$

$[PbOx_2] = 3.984 \times 10^{-6}$ M

$[Pb(HDz)_2] = 1.168 \times 10^{-5}$ M

$[PbOxHDz] = 1.008 \times 10^{-4}$ M

$$K_3 = \frac{(1.008 \times 10^{-4})^2}{(3.984 \times 10^{-6})(1.168 \times 10^{-5})} = 218$$

REFERENCES

1. F. W. Jensen and A. L. Parrack, Ind. Eng. Chem., Anal. Ed., 18, 595 (1946).

2. K. Anderson, E. S. Bettis and D. Revinson, Anal. Chem., 22, 743 (1950).

3. G. W. Armstrong, H. H. Gill and R. F. Rolf. In "Treatise on Analytical Chemistry", Part II, Vol. 7. Edited by I. M. Kolthoff & P. J. Elving, Interscience Publishers, New York (1961), pp 363-424.

4. W. J. Blaedel et. al., Anal. Chem., 24, 1240 (1952).

5. E. Pungor, J. Electroanalyt. Chem., 3, 289 (1962).

6. N. Van Meurs, J. Electroanalyt. Chem., 2, 17 (1961).

7. G. S. Bein, Anal. Chem., 26, 909 (1954).

8. R. C. Bowers et. al., Anal. Chem., 33, 190 (1961).

9. Nurjahan Begum, Ph.D. Thesis, Department of Chemistry, McGill University, 1966.

10. J. L. Hall, Anal. Chem., 24, 1236 (1952).

11. C. N. Reilley and W. H. McCurdy, Anal. Chem., 25, 86 (1953).

12. P. H. Sherrick et. al., "Manual of Chemical Oscillometry", E. H. Sargent and Company (1954).

13. E. T. Hitchcock and P. J. Elving, Anal. Chim. Acta., 27, 501 (1962).

14. H. A. Willis and R. G. J. Miller, Spectrochim. Acta., 14, 119 (1959).

15. I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis", 2nd Ed., Vol. II, Interscience Publishers, Inc., New York (1947), pp 251-253.

16. S. Gordon and C. Campbell, Anal. Chem., 27, 1102 (1955).

17. I. M. Kolthoff and J. J. Lingane, J. Am. Chem. Soc., 57, 2126 (1935).

18. H. J. Borchardt and F. Daniels, J. Phys. Chem., 61, 917 (1957).

19. J. Kamecki and J. Trau, Bull. acad. polon. Sci. Classe III, 3, No. 2, 111 (1955).

20. A. J. Martin, Anal. Chem., 30, 233 (1958).

21. C. Léon, Compt. rend., 233, 170 (1951).

22. R. N. Parida et. al., J. Indian Chem. Soc., 29, 377 (1952).

23. M. W. Hanson, J. Chem. Educ., 38, 412 (1961).

24. H. Kubli et. al., Helv. Chim. Acta., 32, 723 (1949).

25. L. J. Anderson, Anal. Chem., 20, 618 (1948).

26. H. A. Laitinen, W. P. Jennings and T. D. Parks, Anal. Chem., 18, 355 (1946).

27. E. Pungor and L. Balázs, Ann. Univ. Sci. Budapest Rolando Eötvös nominate, Sect. Chim., 2, 305 (1960).

28. D. T. Lefferty, Microchem. J., 2, 257 (1958).

29. J. G. Hanna and J. Jura, Anal. Chem., 31, 1820 (1959).

30. P. M. Deschamps, Bull. soc. Chim. France, 126 (1956).

31. P. M. Deschamps, Compt. rend., 238, 100 (1954).

32. V. J. Shiner and M. L. Smith, Anal. Chem., 28, 1043 (1956).

33. W. Clark, J. Chem. Soc., 768 (1926).

34. C. B. Monk, Trans. Far. Soc., 47, 285 (1951).

35. E. C. Righellato and C. W. Davies, Trans. Far. Soc., 26, 592 (1930).

36. R. L. Bateman and D. T. Ewing, J. Am. Chem. Soc., 70, 2137 (1948).

37. H. Flood, Z. anorg. u. allgem. Chem., 229, 76 (1936).

38. H. Flood and B. Brunn, Z. anorg. u. allgem. Chem., 229, 85 (1936).

39. H. Flood and E. Sletten, Z. anal. Chem., 115, 30 (1938).

40. A. Thiel, Z. anorg. u. allgem. Chem., 24, 1 (1900).

41. H. A. Doerner and W. M. Hoskins, J. Am. Chem. Soc., 47, 662 (1925).

42. I. M. Kolthoff and F. T. Eggertson, J. Am. Chem. Soc., 61, 1036 (1936).

43. D. L. Manning and O. Menis, Talanta, 6, 30 (1960).

44. J. L. Hall et. al., Anal. Chem., 26, 1539 (1954).

45. H. I. Schiff and A. R. Gordon, J. Chem. Phys., 19, 752 (1951).

46. R. E. Jervis, D. R. Muir, J. P. Butler and A. R. Gordon, J. Am. Chem. Soc. 75, 2855 (1953).

47. P. C. Blokker, Rec. Trav. Chim., 54, 975 (1935).

48. J. E. Frazer and H. Hartley, Proc. Roy. Soc. (London) A109, 351 (1925).

49. A. Unmack, D. M. Murray-Rust and H. Hartley, Proc. Roy. Soc. (London), A127, 228 (1930).

50. E. Abbruzeze, Private communication.

51. A. Seidell, "Solubilities of Inorganic and Metal-Organic Compounds", 4th Ed., Vols. I and II, revised by W. F. Linke, D. Van Nostrand Co. Inc., New York, (1958 & 1965).

52. Y. Marcus, Chem. Rev., 63, 139 (1963).

53. B. D. Brummett and R. M. Hollweg, Anal. Chem., 28, 448 (1956).

54. E. E. Underwood and A. L. Underwood, Talanta, 3, 349 (1960).

55. J. B. Headridge, "Photometric Titrations", Pergamon Press, New York (1961).

56. G. Schwarzenbach, "Complexometric Titrations", Interscience Publishers, Inc., New York (1957).

57. W. G. Boyle, Jr., and R. J. Robinson, Anal. Chem., 30, 958 (1958).

58. T. L. Marple, G. Matsuyama and L. W. Burdett, Anal. Chem., 30, 937 (1958).

59. I. T. Takahashi and R. J. Robinson, Anal. Chem., 32, 1350 (1960).

60. R. K. Behm and R. J. Robinson, Anal. Chem., 35, 1010 (1963).

61. P. Le Goff and B. Trémillon, Bull. Soc. Chim., 350 (1964).

62. P. Job, Ann. chim., 9, 133 (1928).

63. W. C. Vosburgh and G. R. Cooper, J. Am. Chem. Soc., 63, 437 (1941).

64. A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds", Prentice-Hall, Inc., New York (1952).

65. F. C. J. Rossotti and H. Rossotti, "Determination of Stability Constants", McGraw Hill Book Co., Inc., New York (1961).

66. J. Bjerrum, Chem. Rev., 46, 381 (1950).

67. J. J. Lingane, "Electroanalytical Chemistry", 2nd Ed., Chapter XIII, Interscience Publishers Inc., New York (1958).

68. E. G. Almy, W. C. Griffin and C. S. Wilcox, Ind. Eng. Chem., Anal. Ed., 12, 392 (1940).

69. P. W. Perryman, Analyst, 70, 45 (1945).

70. D. A. Biddle, Ind. Eng. Chem., Anal. Ed., 8, 99 (1936).

71. "Dangerous Properties of Industrial Materials", 2nd Ed., edited by N. I. Sax, Reinhold Publishing Corp., New York (1963).

72. E. Fischer, Ann., 190, 118 (1878).

73. J. H. Billman and E. S. Oeland, J. Am. Chem. Soc., 65, 1300 (1943).

74. H. Fischer, Angew, Chem., 50, 919 (1937).

75. O. B. Mathre and E. B. Sandell, Talanta, 11, 295 (1964).

76. H. Barnes, Analyst, 72, 469 (1947).

77. "Treatise on Analytical Chemistry", Part II, Vol. 12, edited by I. M. Kolthoff and P. J. Elving, Interscience Publishers, New York (1965).

78. Z. H. Skraup, Ber. dtsch. chem. Ges., 15, 893 (1882).

79. K. Bedall and O. Fischer, Ber. dtsch. chem. Ges., 14, 442 (1881).

80. J. J. Fox, J. Chem. Soc., 1124 (1910).

81. H. Irving, J. A. D. Ewart and J. T. Wilson, J. Chem. Soc., 2672 (1949).

82. R. G. Charles and A. Lenger, J. Phys. Chem., 63, 603 (1959).

83. H. R. Fleck, F. J. Greemane and A. M. Ward, Analyst, 59, 325 (1934).

84. M. Delepine, Compt. rend., 146, 981 (1908).

85. H. Bode, Z. anal. Chem., 142, 414 (1954).

86. "Scott's Standard Methods of Chemical Analysis", 6th Ed., Vol. I, edited by N. H. Furman, D. Van Nostrand Co., Inc., New York (1962).

87. J. V. Dubsky, Mikrochemie, 28, 145 (1940).

88. R. G. W. Hollingshead, "Oxine and its Derivatives", Vols. I and II, Butterworth Scientific Publications, London (1954).

89. R. G. Charles, A. Perrotto and M. A. Dolan, J. Inorg. Nucl. Chem., 25, 45 (1963).

90. W. W. Wendlandt and G. R. Horton, Anal. Chem., 34, 1098 (1962).

91. H. Irving and R. S. Ramakrishna, Analyst, 85, 40 (1960).

92. H. Irving, S. J. H. Cooke, S. C. Woodger and R. J. P. Williams, J. Chem. Soc., 1847 (1949).

93. R. W. Geiger and E. B. Sandell, Anal. Chim. Acta, 8, 197 (1953).

94. "Trace Analysis", edited by J. H. Yoe and H. J. Koch, Jr., Chapter on "Ion Exchange" by K. A. Kraus, John Wiley and Sons, Inc., New York (1957).

95. O. A. Weber and V. B. Vouk, Analyst, 85, 40 (1960).

96. G. K. Schweitzer and F. F. Dyer, Anal. Chim. Acta., 22, 172 (1960).

97. B. Trémillon, Bull. Soc. Chim., 1156, 1160 (1954).

98. H. Bode, Z. anal. Chem., 144, 165 (1955).

99. H. Bode, Z. anal. Chem., 143, 182 (1954).

100. S. S. Cooper and M. L. Sullivan, Anal. Chem., 23, 613 (1951).

101. H. A. Liebhafsky and E. H. Winslow, J. Am. Chem. Soc., 59, 1966 (1937).

102. H. Irving, E. J. Risdon and G. Andrew, J. Chem. Soc., 537 (1949).

103. "Biometrika Tables for Statisticians", Vol. 1, edited by E. S. Pearson and H. O. Hartley, Cambridge Univ. Press, New York (1962).

104. J. P. Dismukes, L. H. Jones and J. C. Bailar Jr., J. Phys. Chem., 65, 792 (1961).

105. K. Nakamoto and A. E. Martell, J. Chem. Phys., 32, 588 (1960).

106. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley and Sons, Inc., New York (1963).

107. K. G. Stone, J. Am. Chem. Soc., 76, 4997 (1954).

108. R. G. Charles, H. Freiser, L. E. Hilliard, R. Friedel and W. D. Johnston, Spectrochim. Acta., 8, 1 (1956).

109. J. P. Phillips and J. F. Deye, Anal. Chim. Acta., 17, 231 (1957).

110. R. J. Magee and L. Gordon, Talanta, 10, 851, 961, 967 (1963).

111. J. E. Tackett and D. T. Sawyer, Inorg. Chem., 3, 692 (1964).

112. N. Strafford, Analyst, 78, 733 (1953).

113. I. M. Kolthoff and J. J. Lingane, "Polarography", 2nd Ed., Interscience Publ. Inc., New York (1952).

114. R. I. Martens and R. E. Githens, Anal. Chem., 24, 991 (1952).

115. G. W. C. Milner, Analyst, 76, 488 (1951).

116. G. C. B. Cave and D. N. Hume, Anal. Chem., 24, 588 (1952).

117. K. J. McNaught, Analyst, 67,97(1942).

118. A. Rellet, Compt. rend., 183, 212 (1926).

119. V. V. Nalimov, "The Application of Mathematical Statistics to Chemical Analysis", Pergamon Press, London(1963).

120. F. B. Hildebrand, "Methods of Applied Mathematics", Prentice Hall, New York (1952).

121. "Statistical Methods in Research and Production", edited by O. L. Davies, Oliver and Boyd, Lond. (1957).

122. G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", J. Wiley and Sons, New York(1957).

123. H. Irving and J. J. Cox, Proc. Chem. Soc., 324, (1959).

124. P. S. Pelkis, Doklady. Akad. Nauk. SSSR, 88, 999 (1953).

125. A. K. Chibisov and Y. A. Pentin, Zhur. Obshchei Khim. 31, 11 (1961).

126. S. J. Angyal and C. C. Angyal, J. Chem. Soc., 1461 (1952).

127. D. S. Tarbell et. al., J. Am. Chem. Soc., 83, 3096 (1961).

128. L. J. Bellamy and R. C. Passerini, "Organic Sulphur Compounds" (ed. by N. Kharasch), Vol. I, pp 53-58, Pergamon Press, New York (1961).

129. H. Irving and C. F. Bell, Nature, 169, 756 (1952).

130. H. Irving and C. F. Bell, J. Chem. Soc., 4253 (1954).

131. K. S. Math, Q. Fernando, and H. Freiser, Anal. Chem. 36, 1762 (1964).

132. G. I. Iwantscheff, Angew. Chem., 69, 472 (1957).

133. H. Irving, J. B. Gill and W. R. Cross, J. Chem. Soc. 2087 (1960).

134. M. M. Harding, J. Chem. Soc., 4136 (1958).

135. R. F. Bryan and P. M. Knopf, Proc. Chem. Soc., 203 (1961).

136. A. Foffani, C. Pecile and S. Ghersetti, Tetrahedron Letters, No. 11, 16 (1959).

137. H. Irving et. al., J. Chem. Soc., 1847 (1949).

138. H. Fischer, Mikrochemie, 30, 38 (1942).

139. S. Ahrland, J. Chatt and N. R. Davies, Quart. Rev., 12, 265 (1958).

140. S. F. Mason, J. Chem. Soc., 4874 (1957).

141. J.H. Richards and W. Walker, Trans. Far. Soc., 57, 399 (1961).

142. F. J. C. Rossotti and H. S. Rossotti, J. Chem. Soc., 1304 (1958).

143. G. M. Badger and A. G. Moritz, J. Chem. Soc., 3437 (1958).

144. L. L. Merritt, R. T. Cady and B. W. Mundy, Acta Cryst., 7, 473 (1954).

145. L. L. Merritt, Anal. Chem., 25, 718 (1953).

146. J. C. I. Liu and J. C. Bailar, Jr., J. Am. Chem. Soc., 73, 5432 (1951).

147. J. C. Fanning and H. B. Jonassen, J. Inorg. Nucl. Chem., 25, 29 (1963).

148. R. Kruh and C. W. Dwiggins, J. Am. Chem. Soc., 77, 806 (1955).

149. F. Kanamaru, K. Ogawa and I. Nitta, Bull. Chem. Soc. Japan, 36, 422 (1963).

150. S. F. Mason, Quart. Rev., 15, 287 (1961).

151. L. McMurry, J. Chem. Phys., 9, 231, 241 (1941).

152. J.W. Sidman, Chem. Revs., 58, 689 (1958).

153. G. Oster, L. Citarel and M. Goodman, J. Am. Chem. Soc., 84, 704 (1962).

154. O.Pëppvych and L. B. Rogers, J. Am. Chem. Soc., 81, 4469 (1959).

155. W. E. Ohnesonge and L. B. Rogers, Spectrochim. Acta, 15, 27 (1959).

156. H. Irving, Proc. Symp. Coord. Chem., Tihany, Hung., 219 (1964).

157. T.Sekine and D.Dyrssen, J.Inorg.Nucl.Chem., 26, 1727 (1964).

158. " " 26, 2013 (1964).

159. " " 29, 1457 (1967).

160. " " 29, 1475 (1967).

161. " " 29, 1481 (1967).

162. " " 29, 1489 (1967).

163. T. Sekine and D. Dyrssen, Anal. Chim. Acta, 37, 217 (1967).

164. R.G. Charles, J. Inorg. Nucl. Chem., 26, 2195 (1964).

165. K. Burger, Talanta, 8, 769 (1961).

166. H. Irving and D. N. Edgington, J. Inorg. Nucl. Chem., 27, 1359 (1965).

167. H. Irving and N. S. Al-Niaimi, J. Inorg. Nucl. Chem., 27, 1671 (1965).

168. W. R. Walker and N. C. Liu J. Inorg. Nucl. Chem., 27, 2255 (1965).

169. N. C. Li, S. M. Wang and W. R. Walker, J. Inorg. Nucl. Chem., 27, 2263 (1965).

170. H. Irving and N. S. Al-Niaimi, J. Inorg. Nucl. Chem., 27, 2231 (1965).

171. D. Dyrssen and D. Petkovic, Acta Chem Scand., 19, 653 (1965).

172. H. Irving and D. N. Edgington, Chem. & Ind., 77 (1961).

173. L. Sacconi, G. Lombardo and P. Paoletti, J. Chem. Soc., 848 (1958).

174. D. Dyrssen and M. Hennicks, Acta Chem. Scand., 15, 47 (1960).

175. D. P Gratton and E. C. Watton, J. Inorg. Nucl. Chem., 21, 49 (1961).

176. W. R. May and M. M. Jones, J. Inorg. Nucl. Chem., 25, 507 (1963).

177. R. D. Gillard and G. Wilkinson, J. Chem. Soc., 5399 (1963).

178. J. Bjerrum and P. Anderson, K. danske Vidensk. Selsk., Math-fys. Medd., 22, No. 7, (1945).

179. D. Hall and F. H. Moore, Proc. Chem Soc., 256 (1960).

180. G. J. Palenik, Acta Cryst., 17, 696 (1964).

181. F. Chou, Q. Fernando and H. Freiser, Anal. Chem., 37,361 (1965).

182. D. Dyrssen, Trans. R. Inst. Technol. Stockholm, 188 (1962).

183. H. Irving, F. J. C. Rossotti and R. J. P. Williams, J. Chem. Soc., 1906 (1955).

184. H. Irving and F. J. C. Rossotti, J. Chem. Soc., 1938 (1955).

185. R. E. Connick and W.H. Reas, J. Am. Chem. Soc., 73, 1171 (1951).

186. F. J. C. Rossotti, Rec. Trav. Chim., 75, 743 (1956).

187. L. Ferguson, J. Chem. Phys., 28, 651, 29, 162, 1129 (1958).

188. M. Nardelli, L. Cavalca and A. Braibanti, Gazzetta, 87, 917 (1957).

189. M. Nardelli, A. Braibanti and G. Fava, Gazzetta, 87, 1209 (1957).

190. E. B. Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publ., Inc., New York (1959).

191. J. F. Duncan and F. G. Thomas, J. Chem. Soc., 2814 (1960).

192. L. E. Orgel, "An Introduction to Transition Metal Chemistry-Ligand Field Theory", Methuen and Co. Ltd., London (1960).

193. Y. Tsuchitani, Y. Tomita and K. Ueno, Talanta, 9, 1023 (1962).

194. H. C. Deterding and R. C. Harding, Ind. Eng. Chem., Anal. Ed., 18, 127 (1946).

195. R. A. Krue, "Ionic Equilibria", Pergamon Press, London (1966).