INFLUENCE OF THE COMPOSITION
OF
BASIC LEAD ACETATE
ON
THE CANADIAN LEAD NUMBER
OF MAPLE PRODUCTS

THE INFLUENCE OF THE COMPOSITION
OF
BASIC LEAD ACETATE
ON THE
CANADIAN LEAD NUMBER
OF
MAPLE PRODUCTS.

A THESIS
Presented as Partial Requirement
for
The Degree
of
Master of Science
at
McGILL UNIVERSITY, MONTREAL
by
Claude Ritson Mitchell

May 12th, 1928.

CONTENTS.

INTRODUCTION.

The inconsistencies which have been observed and reported by Snell (1), among others, when the determination of the Canadian Lead Number of maple products is carried out by different investigators, have long been connected with the basicity of the lead acetate reagent used in the determination. However, there is wide divergence not only between the results of different collaborators, but also in different series of experiments by the same investigator. In addition, comparable results have been obtained by different investigators using different basic lead acetate solutions. Experiments (reported by Snell) carried out by Valin with the object of ascertaining whether the variations between duplicates might not be due to variations in the washing of the precipitates led to the conclusion that the differences were not due to washing but to the actual amount of precipitate produced by the reagent.

Lancaster (2) later reported that when the reagent, which varies in hydrogen ion concentration between limits indicated by pH 7.3 and pH 7.7, is the more strongly alkaline, the lead number is inclined to be higher, although the result obtained in one instance was anomalous from this standpoint. He concluded that the washing of the precipitate was the step requiring standardization. Ross (3a) and Fowler (3b) demonstrated that the precipitate is soluble firstly in sucrose; secondly in excess of the basic lead acetate reagent; and thirdly in hot water. Fowler therefore proposes the use of wash water at room temperature and recommends the addition of successive portions of wash water before the preceding portion has run off, in order to prevent cracking of the precipitate and consequent incomplete washing. Using this procedure more concordant results were obtained.

It therefore seems probable that the variations already noted may have been due, in part at least, to errors in washing, especially since the volume of the wash water was not specified. Consequently the effect of the basic lead acetate reagent would appear to require a new interpretation, and the present investigation attempts to determine this influence. With such knowledge it should be possible to develop a basic lead acetate reagent which would consistently give the highest number and therefore enhance the Canadian Lead Number as an analytical value in the determination of adulteration of maple products.

THE BASIC ACETATESOF LEAD.

The investigation was first directed toward the basic acetate itself. The following compounds are reported:

(1) $Pb(C_2H_3O_2)_2.5PbO$. (4).

(2) $Pb(C_2H_3O_2)_2.2PbO$, (5,6,7), existing as needles, insoluble in absolute alcohol but soluble in 5.55 parts of water at 100°C. Payen prepares it by mixing a solution of the normal salt with ammonia. Löwe treats the normal salt with excess of lead oxide. The latter recommends one equivalent of lead acetate to at least two of lead oxide, and specifies at least three equivalents if commercial litharge is used.

(3) $Pb(C_2H_3O_2)_2.PbO$, (8,9), is formed by dissolving the calculated quantity of lead oxide in concentrated lead acetate solution and evaporating at gentle heat; the solution of the litharge is aided by heating the lead acetate to boiling in a silver dish. It may also be prepared by incomplete decomposition of lead acetate solution with ammonia,or potassium or sodium hydroxide, or by dissolving $Pb(C_2H_3O_2)_2$. 2PbO in lead acetate solution. The needles obtained are easily soluble in water and in 90 per cent alcohol.

(4) $3Pb(C_2H_3O_2)_2.2PbO$,(10), is described as"the ordinary basic salt".

(5) $2Pb(C_2H_3O_2)_2.PbO.H_2O$, (11,12) is formed by the action of heat on the normal acetate. When lead acetate is heated in a glass vessel it boils with evolution of acetone and carbonic acid, and then suddenly solidifies to a porous white mass conforming to the above formula. This mass is easily soluble in water, with separation of lead carbonate. In this connection Löwe states that in the decomposition of lead acetate by fusion between 270° and 280°, a residue of either $Pb(C_2H_3O_2)_2.PbO$ or $Pb(C_2H_3O_2)_2.2PbO$ or a mixture of both remains. Krönig (13) has more lately made a study of the thermal decomposition of some pure metal acetates and finds the yield of acetone in the case of lead acetate to be 87 per cent of the theoretical. The mechanism of the decomposition is written:

$$8Pb(C_2H_3O_2)_2 = 7CH_3.CO.CH_3 + 8Pb + 11\ CO_2 + 3H_2O.$$

Lead and copper acetates give the metal, instead of the oxide as in the case of the other metals investigated.

(6) $Pb(C_2H_3O_2)_2 + HO.Pb(C_2H_3O_2)$ is described by Plöchl (14), who prepares it by repeatedly pouring absolute alcohol over lead acetate and crystallizing the residue from hot absolute alcohol, thereby obtaining the "beautiful mother-of-pearl basic lead salt in hexagonal platelets". It dissolves readily in water, difficulty in cold alcohol but more easily in hot alcohol. On recrystallizing from water it decomposes into $Pb(C_2H_3O_2)_2$ and "a more basic salt".

Löwe, (loc.cit.), writing in 1886, states that the compound represented by $Pb(C_2H_3O_2)_2.4PbO$ does not exist. All substances held to be such were to be regarded only as mixtures of lead oxide with the dibasic acetate, $Pb(C_2H_3O_2)_2.2PbO$.

The more recent work of Jackson (15) discredits greatly the work of the foregoing investigators, whose efforts to isolate and purify the basic compounds were carried out under assumptions which are now known to be radically erroneous. As an instance of this Löwe's work may be cited. This investigator boiled lead oxide and lead acetate for an arbitrary length of time and upon obtaining a solution and a residue he assumed that each represented a compound. (In order to identify these compounds he used them to precipitate the insoluble basic nitrate of lead, which was then recrystallized before analysis. Its analysis was assumed to indicate the proportion of basic to neutral lead in the original compound). Similarly, in other instances, the substances obtained must have been heterogeneous; there is nothing other than the analyses to justify the view that the products are chemical individuals. Indeed Jackson showed that it is almost, if not quite, impossible to isolate at least one of the basic compounds. In addition, the danger of obtaining a mixture is so great that the conclusions based on the earlier procedures must be considered invalid. Jackson concludes that the acetates capable of existence are:

(1) $Pb(C_2H_3O_2)_2.3H_2O$, the normal acetate, brilliant monoclinic crystals. It can exist in equilibrium with acid and neutral solutions and with basic solutions containing as much as 15.80 per cent of lead oxide. Its solubility in water is 35.50 per cent.

(2)$3Pb(C_2H_3O_2)_2.PbO.3H_2O$, which crystallizes in plates. It is exceedingly soluble in water and forms solutions of density 1.93 to 2.28. The substance is unstable in solutions of itself. For its existence in equilibrium with a solution there must be an excess of dissolved basic lead. The solutions contain at the extremes of the saturation curve 15.89 per cent PbO,48.95 per cent $Pb(C_2H_3O_2)_2$ and 24.74 per cent PbO, 49.21 per cent $Pb(C_2H_3O_2)_2$.

(3) $Pb(C_2H_3O_2)_2$. 2PbO. $4H_2O$, consisting of needles which may be so small as to seem amorphous. It is capable of existence in contact with solutions of itself but under such conditions has a solubility of but 13.30 per cent. Its saturation curve possesses a very great length. The extremes of solubility are 7.40 per cent PbO, 4.80 per cent $Pb(C_2H_3O_2)_2$ and 24.74 per cent PbO, 49.21 per cent Pb $(C_2H_3O_2)_2$.

The synthesis of the acetates was accomplished by the interaction of lead acetate and lead hydroxide.

Properties and Uses.

The basic acetates of lead owe considerable importance in applied chemistry to the fact that for a large class of crude substances they are the most effective and most convenient clarifying agents known. Unlike lead salts in general and basic salts in particular, basic lead acetate dissolves in water, as already noted, giving a solution which is alkaline to litmus but does not redden phenolphthalein. This solution is employed as a precipitant and clarifier in urine and organic analyses, in the detection of benzoic and formic acids, glucose, cottonseed oil, and carbon monoxide in blood, and also for differentiating dioxybenzenes. It finds its most extensive use, however, in the analysis of crude saccharine products. In commerce it is used to prepare "white lead", and also the arsenate of lead.

Commercial Preparation of Basic Lead Acetate.

The commercial preparation of basic lead acetate is accomplished by the following methods:-

(1) White and Patterson (16) saturate a lead acetate solution (obtained by treating granulated lead with acetic acid and air alternately) with lead oxide. (From this solution white lead is precipitated by addition of a soluble carbonate, such as soda ash, some sodium bicarbonate being added to prevent discolouration of the precipitate). A highly basic acetate solution is said to be obtained by first saturating the lead acetate solution with lead oxide in the cold and then heating the solution with more lead oxide.

(2) Ges (17) blows air through a solution of normal acetate, the surface of which is below the level of a heap of lead so that the liquid is carried upwards and sprinkles

the lead in its descent.

(3) Eyton and Henderson (18) make basic acetate by periodically drenching lead with acetic acid.

(4) Lloyd et al. (19) treat litharge with acetic acid with or without sodium acetate, or with an acetate such as sodium acetate and dilute sulphuric acid, the strength of the acetic acid being 4½ - 60 per cent and the proportions 16 - 22 absolute acetic acid per 100 parts litharge; the product contains 10 - 73 per cent of water at a temperature not exceeding 60°.

(5) Plaueln (20) makes basic lead acetate by oxidizing lead fibres in acetic acid or lead acetate solution by injection of air and vertical circulation of the liquor in a special apparatus. Raw lead containing antimony can be used instead of refined lead and the fibres do not cake together.

None of the products of these five methods are represented in this investigation.

(6) The method of manufacture of Horne's "Dry Lead", an "anhydrous lead subacetate" developed by Dr. W.D. Horne for use in sugar analysis, has not been published. This compound, which is made exclusively by the General Chemical Company, New York, is ascribed the formula $Pb(C_2H_3O_2).PbO$. It is a heavy white amorphous powder having an acetic odour. In this investigation two samples of Horne's salt were used - an old sample, obtained in 1916, and a new sample produred in 1927.

(7) Four basic acetates obtained from the J.T. Baker Chemical Company, Phillipsburg, N.J., in October 1920 were available for the present work, and these are described below. They were made up synthetically "by using theoretical amounts of the ingredients to produce the different compounds", "are all 'dry', but the one designated 'dry, for sugar analysis' is especially prepared for this work and is better suited than the others for the purpose". They are as follows:

(a) Baker 00 - Basic, for sugar analysis. This substance is very similar in appearance to Horne's Dry Lead, though somewhat finer in texture; it possesses an acetic smell.

(b) Baker 01 - Primary, $Pb(C_2H_3O_2)_2.PbO$. This preparation is somewhat granular, and there is a suggestion of pink in its colour. The odour is also acetic.

(c) Baker 02 - Secondary, $Pb(C_2H_3O_2)_2.Pb(OH)_2.H_2O$, was whiter and finer than Baker 01; the smell was similarly acetic.

(d) Baker 03 - Tertiary, $Pb(C_2H_3O_2)_2.\ 2Pb(OH)_2$, was a somewhat coarse powder, pinkish, and decidedly acetic in odour.

The analyses supplied with these preparations are given in Table I. Figures given are per cent.

TABLE I.

Analyses of J.T. Baker Basic Lead Acetates.

Material.	Cu	Fe	CaO	Na	Cl	HNO_3
Baker 00	Nil.	0.010	0.010	Trace	0.008	-
Baker 01	Nil.	0.010	0.001	Trace	0.001	-
Baker 02	Nil.	0.003	0.005	Trace	0.003	Nil.
Baker 03	Nil.	0.020	0.001	Trace	0.001	-

Laboratory Synthesis of Basic Lead Acetate.

The laboratory synthesis of the basic acetate is generally accomplished by digesting litharge with normal lead acetate solution. Reference will be made to these solutions later. Dr. J.F. Snell, in unpublished work carried out at Macdonald College in the winter of 1918, found that when litharge is added to lead acetate crystals which have been melted on the water bath, and the mass stirred, an appreciable rise in temperature occurs and after a short time the mixture stiffens to a hard mass, which is basic in nature and can be pulverized and kept for future use. In this way Snell prepared compounds of varying ratios of neutral to basic lead. The litharge used was an Eimer and Amend sample, originally reddish, which had been heated to 620° for about 1½ hours. The colour became yellow.

(a) J.F.S. 1. - To 115 g. lead acetate crystals melted on the water bath were added 45 g. of litharge and the mixture stirred. The temperature rose to 115° C. After solidification the mass was cooled and ground. Theoretical ratio of neutral to basic lead, 3:2. The colour was a dull white, tinged with cream.

(b) J.F.S. 2. - To 76 g. of the melted crystals, at 80°C., were added 22 g. of litharge; the resulting temperature was 90°C. Heating and stirring were continued until the mass solidified. This product was dried at 100°C. for eighty minutes, whereupon the weight was found to be 88 g.; it therefore still retained some moisture since the dry substance in the ingredients used approximates 87 g. It was ground to pass a $\frac{1}{2}$ mm. sieve. Theoretical ratio 2:1. This sample was not found, but the solution made from it was available for experiment.

(c) J.F.S. 3. - To 71 g. normal crystals at 80° were added 27.85 g. lead oxide, stirring until dry. The product, similar in colour and ratio to J.F.S. 1., was also dried at 100° and ground.

(d) J.F.S. 4 was made in the same manner as J.F.S. 3 but the unheated (red) litharge was used instead of the yellow modification, and 28 g. were used. The preparation was carried out side by side with J.F.S. 3, and it is recorded that the reaction mixture did not go to dryness nearly as soon as the latter. The colour is a rouge pink and the odour acetic. The tare was 90.5 g.; the anhydrous lead acetate and litharge used total 85.6 grams.

In preliminary work carried out by the writer in 1924 the following samples were prepared:

(e) C.R.M. O. - To 18.96g. melted crystals were added 22.32 g. of litharge. The litharge used was the same sample prepared by Snell nearly six years previous. It had become pinkish. Its temperature at the time of addition to the melted crystals was room temperature; the resulting rise is unrecorded. Solidification was almost immediate. The sample was of a cream colour and has a theoretical ratio of 1:2.

(f) C.R.M. 1. - The litharge used was the same six-year old heated sample and 22.32 g. were mixed with 37.93 g. of melted crystals of the normal salt. The highest temperature attained was 94°. The mass solidified about one minute after admixture. The theoretical ratio is 1:1, and the colour was a light cream.

(g) C.R.M. 2. - Litharge (again the J.F.S. litharge) was stirred in with the melted salt, 113.76 g. of the latter to 44.64 g. of the former. Solidification occurred within four minutes. Ratio, 3:2; colour, flesh.

(h) C.R.M. 3. - A freshly heated sample of the same litharge was prepared the week previous and used in this and the two succeeding preparations. To 75.85 g. of lead acetate were added 22.32 g. of litharge. The highest temperature was 93°, and solidification took place in about nine minutes. Ratio, 2:1; colour, pale flesh.

(j) C.R.M. 4. - To 113.76 g. acetate crystals were added 22.32 g. litharge. The maximum temperature was 90°, and the mass remained plastic for a considerable time. After an hour it gradually hardened. This product has a theoretical ratio of 3:1, is of a dull white colour, and smells of acetic acid.

(k) C.R.M. 5. - To 151.69 g. lead acetate were added 22.32 g. litharge. The maximum temperature was 88° and solidification never occurred on the water bath, even after two hours. At the end of this period there was still some molten material on the surface. It was transferred to the drying oven (100 - 105°C.) and after half an hour taken out. It then cooled to a hard mass. This compound was white, and had an acetic odour. Its theoretical ratio is 4:1. It was also very hard, and in reducing it to powder a power grinder was employed.

After sieving some light red-brown particles were observed in the residue. These particles were insoluble in water, but no further tests were made on them. It seems reasonable to assume that they represent uncombined litharge.

In these preparations it may be noted that there is a graded difference in the degree of reaction as shown by the rise of temperature and also by the length of time necessary for solidification. In the case of C.R.M. 5 solidification seemed to be the result not so much of reaction as of cooling after the material was allowed to stand at room temperature. The higher the ratio of neutral to basic lead the more nearly white is the product, and the harder and lighter it is. On the water bath, however, these high-ratio (3:1 and 4:1) compounds remained more or less mobile whilst the others stiffened shortly after admixture.

Litharge and Lead Acetate Used in Laboratory Synthesis.

The object of heating the litharge was to obtain the pale yellow form - the less stable and therefore probably the more reactive form. The colour of litharge (a highly crystalline compound, though the commercial product is usually a fine powder) may be yellowish white, greyish yellow, greenish yellow, sulphur yellow, reddish yellow, red or reddish brown. Mitscherlich (21) showed that the colour of the red form is not due to the presence of red lead, though red lead is sometimes found in litharge. Commercial litharge is usually fairly pure and is seldom adulterated. It may contain a little iron, copper, silver, antimony, silica and metallic lead; sometimes a little sulphate (of calcium) and carbonate are present. Gold, platinum and chlorine have also been reported, though in small quantities. LeBlanc (22) attributes the difference in colour to a variation in physical structure and not in chemical composition since either form may be obtained by regulating the temperature and the rate of cooling. The red variety is formed most abundantly when the cooling is slow. The red form passes into the yellow on heating and the yellow to the red by long continued action of light at ordinary temperatures. Ruer (23) considers that two enantiotropic forms of lead monoxide are involved, the red form being more stable at ordinary temperatures and at all temperatures up to the transition point, which has not been precisely determined but lies between 587° and 620°C. At ordinary temperatures the yellow form is not stable and the reverse change can be induced by prolonged trituration, by heating with concentrated lye, or by dissolving the oxide in molten alkali. The sample of the oxide which had been heated in 1918 was found to have become quite red in 1928; it was uniformly yellow when freshly made. Reheating it to 620o transformed it back into the yellow modification. Appleby and Reid (24) investigated the conditions of existence of crystals of the red, yellow, grey and green forms and found that the colour depends on the concentration of alkali (KOH) used in the preparation(action of a concentrated solution of potassium hydroxide, at a temperature near the B.P., on lead hydroxide) of the crystals. The differences in the physical properties of the two forms were also determined and the conclusion reached that the yellow and red forms exhibit a true case of dimorphism. The yellow form is the more soluble.

The Eimer and Amend sample used in most of the preparations recorded in this work showed a loss in weight of from 0.7 to 1.0 per cent when heated in a nickel dish at 620°C. for from two to three hours. It was taken out of the muffle, cooled quickly and gently powdered to pass a 1 mm. sieve. The aqueous extract gave a reaction of pH 7.6, using recently boiled carbon dioxide-free distilled water having 4.58 as its pH value. To establish the purity of the sample the following procedure was carried out;

(a) 100 g. were dissolved in 450 c.c. nitric acid (1:4), stirring well. The undissolved residue was washed, dried and weighed. To the filtrate was added excess (80 c.c.) of 1:1 sulphuric acid, the mixture allowed to stand overnight, then filtered through a Buchner funnel and washed with sulphuric acid (1:10). The precipitate was rejected. Evaporated filtrate to 5 c.c. and rinsed it into a small beaker with 50 c.c. water; boiled, cooled and filtered. Nearly neutralized the filtrate with ammonia, made slightly acid with hydrochloric acid, cooled, saturated with hydrogen sulphide and allowed to stand three hours. Filtered. Boiled precipitate with 10 per cent potassium hydroxide, and filtered.

(b) The filtrate, containing arsenic and antimony, was evaporated to 10 c.c. and poured into 25 c.c. of concentrated HCl, saturated with H_2S, filtered, washed twice with 5 parts concentrated HCl to 2 parts of H_2S water, then with cold water until free from chlorides. The arsenic sulphide was then dissolved in a little 10 per cent KOH and the solution poured into 70 c.c. concentrated H_2SO_4 in a 300 c.c. flask and heated until colourless. Diluted, boiled to remove traces of SO_2, and nearly neutralized with ammonia. Cooled, added excess of $NaHCO_3$ and titrated against tenth-normal

Iodine, 1 c.c. of which is equivalent to 0.00374 g. As.

(c) The filtrate from (b) was nearly neutralized with ammonia, acidified with HCl, saturated with H_2S; filtered. The precipitate was then dissolved in 2 - 3 c.c. of Bromine water and hydrochloric acid (5 drops), and the bromine just destroyed with sodium sulphite. Boiled for 15 minutes, then titrated against N/10 Potassium Bromate, Methyl orange being used as indicator.

(d) The H_2S precipitate from (a) was treated with hot dilute HNO_3 on the filter paper to dissolve the Bi and Ca, the solution made alkaline with ammonia to precipitate the Bismuth, and filtered. The precipitate was dissolved in dilute H_2SO_4, a little sodium sulphate added, placed in a Nessler tube, a little potassium iodide added and the colour compared with a standard Bismuth sulphate solution, 1 c.c. of which is equivalent to 0.0001 g. Bismuth.

(e) The filtrate from (d), containing copper, was compared with a standard copper solution, using 5 c.c. ammonia. A larger quantity of ammonia affects the results by altering the tints and giving lower readings. The standard was a copper nitrate solution, 1 c.c. of which = 0.001 g. copper.

(f) The filtrate from (c) was boiled to expel H_2S, and ammonia added until just alkaline. Boiled, the precipitate of Iron and Aluminum filtered off, the zinc in the filtrate precipitated with H_2S, the correct concentration of hydrogen ion (pH = 2.1) being established and held by ~~the~~ following procedure recommended by Fales (25). After filtration, and washing, the filter paper and ZnS were placed in a flask, pulped with a little water, 1 c.c. of HCl added and titrated against N/10 iodine, using starch.

(g) One gram of sample was dissolved in 2 c.c. of HCl and 1 c.c. of HNO_3, then diluted, and boiled. Cooled, added 1 c.c. of H_2SO_4 (1:1), boiled down to fumes, diluted. The lead sulphate was filtered off and 5 c.c. of 10 per cent KCNS added and the resulting colour compared in a Nessler tube with a standard iron (in HCl) solution. The observations were made after five minutes (any increase in time tending to increase the colour) and at a temperature of 18° (an increase in temperature causing decrease in colour). Whilst free acid was present in the solution excess had been avoided.

(h) Twenty-five grams of sample were dissolved in dilute HNO_3, diluted to 200 c.c. and standard $AgNO_3$ solution added; filtered, and the excess of $AgNO_3$ determined by titrating back with Ammonium Thiocyanate (1 c.c. = 0.001 g. Chlorine), using 5 c.c. of ten per cent Ferric Alum as indicator.

The results are given in Table 2.. A blank analysis of all reagents used was carried through.

TABLE 2. Analyses of Litharges.

Sample.	As	Sb	Cu	Bi	Zn	Fe	Cl	Insol. in HNO_3
Eimer & Amend. (E. & A.) New York.	.0015	.006	.003	.0015	.0005	.012	.0010	.0354
Sherwin Williams. (S.W.) Montreal.	Trace.	.0019	.0014	.00015	.0022	.0045	.0015	Nil.

The results show the samples to be fairly pure, especially the Sherwin-Williams sample. Unfortunately this sample was not obtained until the work was well advanced. It was made from pig lead free from tin and manganese, having only traces of nickel and cobalt, and .0006 per cent of silver.

The examination for copper and chlorine was significant inasmuch as Wark (26) has shown that the cuprimalate complex is very stable, whilst the predipitation of lead chromate in acetic acid solution (the method adopted in this work) has been shown by Dede and Beckner (27) to be not quantitative in the presence of much chloride.

Both samples were still further tested as follows:-

(j) Substances insoluble in acetic acid. - To 2 g. of oxide mixed with 5 c.c. of water were added 10 c.c. of diluted (5N) acetic acid. No evolution of gas occurred. Boiled for several minutes, filtered when cold, the residue was washed, dried at 100°C. and weighed. The weight did not exceed .0007 in the E.& A. sample, and was nil in the S.W. sample.

(k) Nitrates. - One gram of oxide was mixed with 5 c.c. of water and solution brought about with the aid of 5 c.c. of diluted acetic acid. Then 0.2 c.c. of 1:1000 indigo solution were added, and 10 c.c. of concentrated H_2SO_4. The blue colour remained indicating less than .016 per cent as N_2O_5.

(l) One gram of the oxide in 10 c.c. of diluted acetic acid were diluted with 50 c.c. of water, and the solution saturated with H_2S gas. Filtered, and the filtrate evaporated, ignited and weighed. The weight was nil in both cases, indicating the absence of earths, gypsum and alkalies.

(m) The tetramethyl diaminodiphenylmethane test of Trillat (28) for lead peroxide was applied, and the results obtained were negative. The test was carried out by incinerating 0.1 g. of oxide with H_2SO_4, adding twenty drops of a saturated solution of sodium hypochlorite, expelling the chlorine by heating, and adding a few drops of the tetramethyl reagent (made by dissolving five grams of the salt in 100 c.c. of water and 10 c.c. of acetic acid). If lead peroxide is present a blue colouration is obtained. The test is very delicate.

The normal lead acetate crystals used were also rigorously examined and both samples (one an Eimer and Amend, the other a Merck, C.P.) tested as follows:-

(a) Earths and Alkalies.- The lead in 10 g. of salt in 200 c.c. of water was precipitated with H_2S gas, after preliminary removal with 10 c.c. of HDl, and the filtrate evaporated and ignited. The weights were 0.003 g. and 0.001 g. respectively.

(b) Copper, Iron and Aluminum. - Two grams of salt in 10 c.c. of water were mixed with 3 c.c. H_2SO_4, stood, filtered, and the filtrate treated both with potassium ferrocyanide solution and excess of ammonia. Neither brown nor blue colour nor precipitate was formed in the Merck sample, but the E.&A. sample gave indications of traces of iron.

(c) Nitrates. - One gram in 10 c.c. of water retained the blue colour obtained by the addition of 0.5 c.c. of indigo solution when 10 c.c. of concentrated H_2SO_4 were added.

(d) Chlorides. - One gram dissolved in 20 c.c. of freshly boiled water and acidified with HNO_3 showed no opalescence on addition of $AgNO_3$ solution.

(e) Insoluble Matter. - The solution of 5 g. of salt in 50 c.c. of freshly boiled water was, in both cases, perfectly clear.

(f) Basic Acetate. - The examination for basic salt was made according to Kolthoff (29) who states that the presence of basic salt is difficult to detect as it changes the reaction (pH, 6.0) of the normal salt only slightly. Ten c.c. of a 1:20 solution were treated with 10 c.c. of 10 per cent $Na_2S_2O_3$, 15 c.c. of 0.5N $Ba(NO_3)_2$ solution and five drops of phenolphthalein. The solution obtained, in which a white precipitate gradually flocculated, partially sticking to the walls of the flask, did not react alkaline. The addition, however, of 0.25 c.c. of 0.1N NaOH (instead of 0.20 c.c. specified by Kolthoff) imparted a permanent pink colour.

The reaction of a 10 per cent solution was found to be pH 5.80 and 5.90 for the E.&A. and Merck samples respectively. Both samples melted at 77°C.

Preparation of Basic Acetates.

For the present work it seemed desirable to have compounds of even wider range of ratios and recourse was again sought in the Snell method to obtain preparations varying in ratio from 1:5 to 5:1. The results are summarized in Table 3. The operations were carried out in large evaporating dishes, and the litharge to be used in any individual case was warmed on the water bath, so that the ingredients were approximately at the same temperature (80°C.) when the admixture was made. The rise in temperature therefore more nearly represented the rise due to interaction. In order to minimise loss of acetic radicle from the lead acetate the litharge was added shortly after the crystals had all melted. The resulting products were left on the bath for about five minutes after solidification, then stood at room temperature, and ground to pass a 40 mesh sieve, any residue being rejected. The same graded difference in hardness, colour and density previously noted were again observed. The odour also became more markedly acetic as the ratio became greater.

Table 3.

Dry Basic Acetate Preparations made in 1928.

Marks	Theor.Ratio Neut:Basic Pb.	Grs. used of		Remarks on	
		$Pb(C_2H_3O_2)_2.3H_2O$	PbO	Preparation Phenomena	Compound Itself.
CRM.15	1 : 5	75.86	223.20	Temp.rise 83-96°. Immediate solidification Dried in oven at 105° for ½ hr.	Yellowish buff.
CRM.14	1 : 4	37.93	89.28	Rise from 72°-101°C.,immediately solid.	Light Yellowish buff.
CRM.13	1 : 3	37.93	66.96	Rise from 75°-97°; immediate solidification	Light Yellowish buff.
CRM.12	1 : 2	189.62	223.20	Rise from 83-102°C., setting immediate. On water bath ½ hr. then at 105° for ½ hr.	Buff.
CRM.11	1 : 1	151.72	89.28	Temp.rose from 85° to 100° in three minutes. Completely hardened in 20 minutes.	Dirty White
CRM.43	4 : 3	151.72	66.96	Temp. from 83° -99° in two minutes.	Dull White
CRM.32	3 : 2	170.64	66.96	Temp. from 78° to 99° in two minutes.	Light Cream.

Table 3 (Cont'd)

Marks	Theor. Ratio Neut : Basic Pb.	Grs. used of		Remarks on	
		$Pb(C_2H_3O_2)\cdot 3H_2O$	PbO	Preparation Phenomena	Compound Itself
CRM.21	2 : 1	151.72	44.64	Rise from 77°-98° in 10 mins. with production of a paste of cream like consistency. Color gradually changed from yellowish to white. On water bath 4 hrs. then in oven at 105° for ¾ hr., when taken out had an acetic odor	Fair White.
CRM.31	3 : 1	170.64	33.48	Temp. Rise from 77°-91°. Remained in a plastic state throughout its 50 mins. on the water bath. Hardened on cooling to room temperature.	White
CRM.41	4 : 1	151.69	22.32	Temp. from 79°-91°. Hardening process set in 3 mins. after addition. Taken off bath after a further 4 minutes.	White
CRM.51	5 : 1	94.83	11.16	Temp. from 82°-88°. No solidification occurring after 10 mins, the mass was taken off and stirred to promote admixture whilst cooling. At about room temperature it solidified.	White

Solids (or Residues) Separating from Solutions.

In the preparation of solutions from the "wet" mixes outlined in Tables 4 , 5 (pp.30 and 32) the following residues left after filtration of the solutions were well washed with water, and dried at 100^{o} in vacuo. In the washing of these residues there was a decrease in bulk and the filtrates were all cloudy, with the exception of RCMS. No estimation of the loss in weight due to washing was made. After drying the solids were ground to powder in an agate mortar. The appended remarks are appropriate:

Solid.	Remarks.
RCMP	Pale yellow. Tendency to form lumps from a smooth paste during washing. Wash water used, 400 c.c. Weight of dry substance about 12 grams.
RCMQ	Pale yellow. Wash water, 300 c.c.; nearly all dissolved. Dry substance, 2 grams.
RCMR	Flesh pink. Wash water, 250 c.c. Dry substance 2 grams.
RCMS	Flesh pink. Wash water 380 c.c. Fifty grams.
RCMT	Grey. Wash water 150 c.c. Thirty-five grams.
RCMV	Yellowish; wash water 600 c.c.; from CRMX3.

Synthesis of Basic Acetates by "Wet" Methods.

The preparation of further basic acetates was next accomplished in the following ways:-

CRM. X1. - To 205 c.c. of water at room temperature added 453 grams of yellow litharge, then 57 c.c. of water at

52°C. and the mass thoroughly stirred; to the mixture 200 c.c. of 35 per cent acetic acid were added, and stirring continued. The mixture frothed, the temperature rose from 28°C. to 49°C. and in three minutes the mass thickened to a white slop, but did not harden. It was left in the uncovered beaker for a week then transferred to a porous plate and allowed to remain exposed at room temperature for a further period of ten days. It dried slightly greyish.

CRM.X2.- The above was repeated, using 158 c.c of acid, the initial and final temperatures being 25° and 46°C. The time required for "setting" was only one minute and a half and the mass was quite firm, though soft to the touch. After six days in the uncovered beaker it was transferred to a porous plate and allowed to dry for ten days at room temperature. The unheated, reddish, litharge was used in this preparation.

CRM.X3.- Yellow (heated) litharge was used and the preparation carried out as in the case of CRM.X2; the temperatures were 25° and 49°C. There was no frothing, and "setting" occurred in about half-a-minute. Dried at room temperature in beaker and on porous plate as in the previous two cases.

All three preparations dried to exceedingly hard masses. Yellowish-pink particles could be discerned throughout the mass as it dried, and the exposed surfaces of CRM.X2 were very noticeably pink. They all fizzed slightly on addition of dilute nitric acid.

An attempt was then made to accomplish the synthesis by Jackson's method of interaction of normal acetate and lead hydroxide suspension. The lead hydroxide precipitate was found to contain carbonate due,to absorption of carbon dioxide from the air. On this account the method was not pursued.

Preparation of Solutions.

The different preparations were now dissolved in ordinary distilled water to give an approximately 1.25 sp. gr. solution. The following remarks may be made:

Horne's Salts. - The old did not seem to dissolve as well as the new, requiring 4 - 5 hours boiling instead of 1½ hours, when the A.O.A.C. quantities were used. Equal weights (70 g.) of each were boiled side by side in similar evaporating dishes with equal (600 c.c.) amounts of water for the same length of time. The burners were adjusted to give approximately the same amount of heat. Boiled 40 minutes. The residue from the new weighed 0.70 g., from the old 1.34 g., after being allowed to stand overnight. The residue had a pearly appearance, mixed with Buff in the "old"; both fizzed on the addition of dilute HNO_3. The solutions were quite clear.

Baker's Salts. - The primary salt left red granules in a buff residue on dissolving; the secondary a buff-grey; the tertiary a flesh coloured, and Sample 00 a cream coloured residue. The solutions showed a slight turbidity, except the tertiary. This latter was clear, but possessed a reddish brown colour.

CRM. Salts. - The solutions were all clear or only slightly opalescent. The percentage residue decreased in the order tabulated, becoming negligible at CRM.11. Remarks on these solutions are set forth below. CRM. XI, X2, and X3 could not be made to give solutions of sp. gr. 1.25. When the weak solutions (see Table 7) were evaporated white solid separated out without significant change in density of solution.

Mark.	Residue.
CRM. X1	Whitish.
" X2	Pinkish.
" X3	Pinkish yellowish.
" 15	"
" 14	Cream.
" 13	Flesh.
" 12	Pale flesh.
" 11	Salt nearly all dissolved. Yellowish hue on filter.
" 43	"
" 32	"
" 21	"
" 31	"
" 41	"
" 51	"
" 0	"
" 1	"
" 3	"
" 4	"
" 5	"

Mark.	Residue. (cont.)
CRM. 2	(Insufficient sample.)

The residue from solution of CRM. X3 was saved and labelled RCMV.

With the knowledge of absorption of carbon dioxide from the air by the moist preparations (CRM. X1, X2, X3), the preparations set forth below in Table 4 were extracted with water an hour or so after their manufacture and filtered immediately.

Table 4.

Solutions made from "wet" Mixes of Oxide and Acetate.

Marks	Ingredients			Remarks
	PbO (Yellow E & A)	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$	H_2O	
RCMP	150	50	500	Boiled 20 mins whereupon became of a creamy consistency and flesh colored. Shortly after this it took on the appearance of curdled milk. There was a sheen to the liquid. On filtering there seemed to be slight disintegration of the filter paper around the edges. (See Kellner(30), and Frühling(31).) The residue on filter paper was saved.
RCMP2	75	25	250	Boiled 10 mins. This preparation differs from RCMP only in the length of time boiled. The same fluffiness was beginning to occur when boiling was stopped. A slight residue of unreacted PbO was still present.
RCMQ	50	50	500	Boiled 26 mins. Curdled milk appearance. Light cream color. Sheen. Similar action on filter paper as RCMP. Residue saved.
RCMQ2	25	25	250	Similar to RCMQ, but boiled 13 mins. No separation of solid. Sheen. The negligible residue on the filter paper was yellowish, interspersed with glistening white particles.

The following preparations in Table V were made with acetic acid instead of lead acetate. The "Barton oxide" used in RCMT was a grey-green powder, "an oxide of lead containing free lead". The water used was at 50° or so, the acid and litharge being at room temperature. The order of addition was water to litharge, then acid. In connection with this type of reaction Kolschütter and Rosti (32) report that a dilute solution of acetic acid dissolves the yellow oxide faster than the red one.

Table 5.

Preparation of Solutions from wet Mixes of oxide and acid.

Mark	PbO	Acetic Acid	H_2O	Remarks.
RCMR	37	26 c.c. of 28% (Vol) acid	35	Mixed at Room Temp., rise to 51°C. with solidification. Added 25 c.c. water, heated just to boiling, filtered. Sheen. Residue saved.
RCMS	111	31 c.c. 70%	152	Temp. rise from 41° to 57°. Solidified in one minute. Solution in water accompanied by much frothing during boiling. Sheen. Residue on filtering faint pink, saved.
SW	"	"	"	Prepared by dissolving week-old RCMS suspension kept in tightly stoppered bottle. Highest gravity 1.175, 20°.
RCMT	111 g. "Barton oxide"	31 c.c. 70%	152	Temp. rise 52° to 67°. Solidification in one minute, the color change observed being bluish through slate to a final light grey. Extracted with 100 c.c. H_2O. Residue saved.
WCT	226 (red PbO)	79 c.c. 35%	131	Initial temperature,probably room temperature, unrecorded, final temp. 42°. No solidification. Pinkish-yellowish-buff residue on filtering solution.
WCU	226 (red PbO)	79 c.c. 35%	131	Rise from 44° to 60°, but reaction not appreciably better than in WCT. As in WCT, no solidification, and considerable residue of material did not go into solution.
WCV	226 yellow SW	79 c.c. 35%	131	Rise from 47°to 60.5°. Solidified in one minute. Cream color. Added 100 c.c. of water, heated for 10 mins., filtered and heated at 100° for 4 hours.
ALMR	322	240 g. Glacial	Nil	Temp. rise from 18° to 94°C., liquid thickens. Added 281 c.c. of H_2O, left overnight. Beautiful needle-like crystals in solution next morning. Added 281 c.c. more of H_2O, stood 24 hours. The clear liquid poured off, then filtered. (See Knight (33). Bechamp(34) finds that water free acetic acid unites directly with PbO).

A further solution was then prepared by boiling lead acetate solution with litharge. This treatment is of special interest in that it is one of the methods devised by Dumas to demonstrate the individuality of red lead. Prolonged digestion of red lead with lead acetate solution produces no appreciable change in the weight of the former. The reaction of litharge with lead acetate solution has been studied by Rochleder (35), Kubel (36), Woodman (37), Schindler (8), Wittstein (9), and Browne (38); the latter reports that the resulting basic acetate solution may vary "in the ratio of combined to basic PbO of from 5:2 to 1:1". The variation depends not only on the proportion of ingredients but also on the time and temperature of digestion.

Solution B^2. - Litharge (yellow) 75 g.,lead acetate, 290 g.,water 600 c.c.; boiled half an hour. There was a slight yellow residue. The proportions used above are in the ratio recommended by the A.O.A.C. (39). Theoretical ratio, neutral to basic lead, 1.95:1.

Macdonald College Solutions.

The following solutions already prepared at Macdonald College, were also available for experiment. The methods and materials used in their preparation are given below.

Descriptions of Preparation of Macdonald College Solutions.

AA. Made from Horne's Basic Acetate; boiled 4 minutes.

BA. " " " " " " 40 "

CA. " " " " " " 80 "

DA. Made from Merck's (yellow) PbO and J.T. Baker lead acetate - 65 g., 225 g., 500 cc. water. Boiled 51 minutes.

EA. From Merck's PbO, and lead acetate obtained from the Department of Bacteriology, Macdonald College; weights respectively 36 g., 119 g., and 270 c.c. water; 40 minutes.

FA1. From E.& A. PbO (red) and J.T. Baker lead acetate; 65 g., 215 g., 500 c.c. water, 45 minutes. Heavy red sediment. On standing two days, crystals proven to be $Pb(C_2H_3O_2). 3H_2O$ separated out. Afterwards filtered.

FA2. Made by diluting Stock Solution F, Jan., 1928.

GA. From E.& A. PbO and "Bact." lead acetate. Proportions as in FA. Boiled 55 minutes. Heavy red sediment.

HA. As in GA, but a return condenser used; 30 minutes.

IA. From JFS.1.

JA. From JFS.2.

(These solutions, AA-JA, were all prepared by Dr. J.F. Snell in December 1917.)

MA. From PbO and lead acetate. No details.

NA. From Horne's acetate.

VZB. Ditto.

(MA, NA, VZB were made in September 1918).

VZW. From litharge and lead acetate and some old solution. No details.

MMA. From litharge and lead acetate.

MMB. From Horne's salt.

(MMA and MMB were made by Miss Dorothy Moule in July 1918.)

NCM_2. From litharge and lead acetate in August 1919.

A solution of normal lead acetate as used for clarification was also employed for some lead number determinations.

All solutions if not already clear were filtered. They were kept in tightly stoppered or corked bottles of such capacity as would just hold all the solution. With time nevertheless, a white sediment collected at the surface and at the bottom of each sample, with the single exception of solution ALMR, which remained perfectly clear. The sediments in RCMP and $RCMP_2$ were the most pronounced, that in RCMQ was buff coloured, and in SW fine crystals were perceptible. Solution was drawn off from the centre of the liquid, without shaking the bottle, when desired for use.

ANALYTICAL PROCEDURE.

In the evaluation of basic lead acetate the analytical processes are required to yield the amounts of neutral and basic lead present in the sample. These data are generally obtained by measuring the quantity of standard acid neutralized by the basic lead and the quantity of reagent required for the complete precipitation of lead. Total lead may be estimated gravimetrically as sulphate or chromate, the latter being preferable owing to its lower solubility. Snell (1) used the former, and calculating basic lead from the alkalinity of the solution, derived the neutral lead by difference and therefrom the ratio of neutral to basic lead. Jackson (15) utilized two methods of estimation of total lead, namely, precipitation by one-third normal sodium oxalate and back titration with alkali and permanganate. The oxalate method was the main reliance because of its greater convenience. Lead oxalate is much less soluble than lead sulphate, but the two methods were found to be equally trustworthy. Normal oxalic acid is also used for the precipitation. In addition precipitation with half-normal potassium iodate, first with, and then without addition of acetic acid, decomposition of the filtrate with potassium iodide and dilute sulphuric acid, and titration of the liberated iodine with standard thiosulphate, as outlined by Bergh (40) is available. The method of precipitation with chromate instead of iodate is, however, considered the best. Half a gram of salt is mixed with 5 c.c. of dilute acetic acid and 150 c.c. of tenth-normal potassium chromate, the mixture shaken and diluted to 250 c.c., after which it is filtered. Fifty c.c. aliquots of filtrate are treated with 2 g. of potassium iodide and 10 c.c. of dilute sulphuric acid and the liberated iodine titrated against N/10 Thio aft er a few minutes. A second determination without acetic acid is then made. The equations for the two reactions are:

(a) Total lead,

$$2(CH_3COO)_2\ Pb.\ Pb(OH)_2 + 3K_2CrO_4 + 2CH_3COOH = 3Pb\ CrO_4 + 6CH_3COOK + H_2O.$$

(b) For lead present as neutral acetate,

$$2(CH_3COO)_2\ Pb.\ Pb(OH)_2 + 2\ K_2CrO_4 = 2PbCrO_4.\ Pb(OH)_2 + 4CH_3\ COOK.$$

The equation for the reaction on adding Kl and H_2SO_4 to the(excess) chromate is:

$$2K_2CrO_4 + 6\ Kl + 8H_2SO_4 = 3I_2 + 5K_2SO_4 + Cr_2(SO_4)_3 + 8H_2O.$$

Investigation of Bergh's Chromate Method.

Preliminary experiments were made with the method in view of the criticisms of Chevale and Colle (41) that iodimetric methods of estimation of the higher oxides of lead are unreliable because of side reactions, especially

$$Pb(C_2H_3O_2)_2 + I_2 = CH_3.\ COO\ CH_3 + CO_2 + PbI_2\ .$$

It was found that

(1) The presence of the slight quantities of potassium acetate or slight excess of acetic acid did not increase the solubility of lead chromate. The addition of 10 c.c. of

2N acetic acid to 150 c.c. of N/10 K_2CrO_4 caused no change in the amount of thiosulphate required for titration in the absence of acid.

(2) The reaction of the basic lead with acetic acid, as the estimation is ordinarily carried out is complete. Samples which were allowed to stand overnight gave the same results as those when the excess of chromate was filtered off immediately.

(3) DeLong, working at Macdonald College in 1925, determined the total lead in sample CRM.2 by different methods and found:

(a) By Bergh's Method: 0.7046 g. per g. of salt.
(b) By weighing as $PbSO_4$: 0.7014 g. per g. of salt.
(c) By Bain's Sulphate Method (42): 0.7159 per g. of salt.
(d) By weighing $PbCrO_4$ precipitate: 0.7145 g. per g. of salt.

A variation of the same order was found for the Baker 00 sample.

The basic lead in the same sample was found by the same investigator to be 0.2498 g. per g. of substance, using the chromate method; the sulphate method gave 0.2921 gram. The following comparison now becomes available:

Method.	Basic Lead.	Neutral Lead.
Bergh Chromate.	0.2498	0.4548
Sulphate.	0.2921	0.4093

DeLong therefore attributed the consistently higher ratios he obtained by Bergh's method to the high results for total, and therefore for neutral lead. This contention was enhanced by further work carried out by DeLong on a synthetic mixture of litharge and normal acetate. Three grams of lead oxide (unspecified) and seven grams of normal acetate were ground together in an agate mortar and one gram portions used for analysis. This misture contains 0.2785 g. of lead as PbO, and 0.3825 g. of lead as $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, or a total lead content of 0.6610 gram per gram of mixture. The total lead gound by Bergh's method was 0.6896, and the neutral lead 0.4057. These figures are 0.0286 and 0.0232 g. in excess of the calculated quantities. Since it was impossible to check the solutions used by DeLong the writer made some new experiments, using a freshly made solution of lead nitrate containing one gram of lead per litre. Using 100 c.c., the following amounts of lead were found:

(a) Bergh's Method ; 0.1030 gram.
(b) Sulphate Method: 0.0970 "
(c) Weighing as $PbCrO_4$: 0.1002 gram.

The basic lead in a solution of Horne's salt of specific gravity 1.25 was also determined, and the following values found. The basic lead in the Bergh Method was obtained by difference betwean total and neutral lead.

(a) Bergh's Method......0.0793 g. per c.c.
(b) Alkalinity Method...0.0782 g. " "

These values are well within experimental error, so that the results obtained by DeLong must be regarded as due to some unrecognized error, and the Bergh method therefore reliable.

(4) The addition of chromate reagent, whilst preferably made to a solution of the lead salt, may be made to the

solid direct, provided the mixture is well shaken.

(5) The method, though sensitive to 0.00035 g. of lead per c.c., will not detect one-tenth of this amount in the same volume.

(6) The effect of the volume of the precipitate was the subject of a detailed investigation. In computing the volume of the precipitate the data of Schulten (43) for the density (6.123) of normal lead chromate are available but no work has been reported for the basic chromate. In the belief that the precipitates were of appreciable volume, both the precipitated basic and normal chromate mixtures from 0.5 g. of salt, and from 2 c.c. of two solutions of specific gravity 1.05 and 1.25 were filtered back into their respective volumetric flasks in which precipitation had occurred, using suction and a Whatman No. 3 paper which had been wetted and sucked dry immediately previous to filtration. The amounts of liquid necessary to restore the volume to 250 c.c. varied in duplicate determinations, and were consistently inconsistent, ranging from 0.65 c.c. to 1.9 c.c. and even 3.2 c.cs. The precipitates were therefore dried and transferred as quantitatively as possible to a volumetric flask, the neck of which was graduated in c.cs. from a zero mark, but there was no measurable increase in volume when individual precipitates were added. The weights of the normal chromate precipitates were then determined by filtering through tared Gooch crucibles and drying, and the volumes deduced gave an average of 0.11 c.c.. It was then attempted to confirm this by carrying out the precipitation with quantities of reagents measured to prod-

uce 250 c.c., and measuring the excess over the mark in the flask. The result was an average of 0.22 c.cs., which was taken to signify that the precipitate absorbed its own volume of water.

The determination of the density of the basic chromate was then attempted. The precipitate was washed by decantation and transferred to a calibrated picnometer. The picnometer was nearly filled with water, which was then brought to boiling in a vacuum to remove air. After adjustment and weighing, the contents of the picnometer were transferred to a Gooch crucible, and the weight of the dry precipitate determined. The density deduced was 6.953 at 20°C. Close checks could not be obtained however even when the boiling was done over a naked Bunsen burner for ten minutes; the discrepancies were possibly due to the difficulty of transferring the precipitate to the Gooch. The precipitate sticks to the side of the picnometer and that located at the base of the neck cannot be gotten at with a rubber policeman.

Yet another method was therefore attempted to determine, not the actual volume of the precipitate, but whether there was any appreciable error due to this volume. The lead in one gram samples was precipitated and estimated as usual, making up to 250 c.c. in the flask with the precipitate. A second determination was carried out, the precipitate being filtered off and well washed with distilled water at room temperature into the flask, up to the mark. The amount of Thiosulphate required for back titration was the same in both cases, proving that there is no appreciable error due to the volume of the precipitates. Both normal and basic chromate precipitates were used in this test, from 0.5 g. salt and from 2 c.c. of solutions of 1.05 and 1.25 specific gravity.

Bergh's method was therefore adopted.

Preparation of Reagents.

(a) Dilute sulphuric acid. - Approximately twice normal acid was made by diluting 59 c.c. of concentrated acid to 1 litre.

(b) Dilute acetic acid.- Also approximately 2 N, by diluting 115 c.c. of glacial acid to one litre.

(c) Potassium chromate. - The required weight (1/30 Mol. Wt.) of the Merck's salt of highest purity, previously dried at 100-105°, was dissolved in one litre of water.

(d) Tenth-normal thiosulphate. - Sodium thiosulphate C.P. from J.T. Baker was used. The analysis supplied was as follows:-

Al_2O_3	0.001%
CaO	0.001%
Fe.................	0.002%
NaOH................	Nil.
SO_3	Present.

The crystals were also tested for sulphides by dissolving one gram in 10 c.c. of water and adding zinc sulphate solution. There was no change in appearance, indicating less than 0.013 per cent of sulphur.

The difficulty of making a standard solution of sodium thiosulphate by weighing the salt directly is generally stated to be due to the possibility of water or air being held within the crystals, even where the salt is in a state of great purity. This difficulty may be avoided by treating the ground crystals with pure alcohol and then with ether and finally drying at room temperature. This manipulation is tedious and there is always some slight risk that the crystals may not have been dried in air long enough to give an ultimate prdduct containing the correct amount of water of crystallization. The preparation of an accurate iodine solution for standardization is also a tedious procedure, so that the solution prepared for the present work was standardized against potassium dichromate. The Merck C.P. salt was heated in a platinum dish to 400°, care being taken to exclude all dust and organic matter. (44). The fused salt, after cooling, was crushed to a powder in an agate mortar and 4.903 grams dissolved in 100 c.c. of water and made up to one litre.

Freshly boiled, cooled water, free from carbon dioxide, was used to prepare the thiosulphate solution. Twenty c.c. of dichromate solution were mixed in a Phillips beaker with 200 c.c. of water, 10 c.c. of 10% potassium iodide and 5 c.c. of concentrated HCl. The mixture was allowed to stand three minutes, then diluted with 150 c.c. of water and the thiosulphate solution run in. The addition of starch solution was deferred as long as possible and the titration continued until the liquid passed from a dark blue green, through blue, to light green. The end point is very sharp. Since potassium iodide generally contains traces of iodates a blank was run, using 10 c.c. of Kl solution and 5 c.c. HCl and diluting as before, and 0.1 c.c. found necessary. The thiosulphate solution was adjusted so that after allowing for the blank, exactly 20 c.c. of solution were required for the titration. The solution was preserved in a well-stoppered coloured bottle and standardized every ten days against the original dichromate. The burette used in these titrations was also cleaned on these occasions with a solution of sulphuric acid and bichromate. The solution was also checked against Bausch and Lomb twice recrystallized potassium iodate (free from iodide), dried over sulphuric acid.

(e) Starch solution. - 1 g. of rice starch was boiled with 200 c.c. distilled water to which 1 g. of pure sodium carbonate was added. The solution was then cooled, and concentrated hydrochloric acid added to distinct acidity, two c.cs. being required. Some zinc powder was then added, and the solution allowed to stand 24 hours when the solution was neutral (to litmus). It was then filtered. One c.c. was used in each titration.

The chromate and thiosulphate solutions as made up checked perfectly against each other.

ANALYSES.

The automatic pipette which was used to deliver the chromate solution was calibrated and found to deliver 150.013 c.c. at room temperature, approximately 20°. Except where stated otherwise duplicate determinations checked to within 0.05 c.c.. Care was taken in reading the burette (which was fitted with a shellbach back and an automatic arrangement for filling to zero), since a slight variation of volume causes an appreciable difference in the ratio. Attention was paid to drainage of the burette.

The colour of the precipitate of basic and normal lead chromate varied somewhat in their respective classes. The influence of precipitation conditions on the colour of lead chromate, and the reddening of the freshly precipitated salt havebeen studied by Free (45) and Jblczynski (46) respectively.

The following specific instance illustrates the method of computation of the ratio of neutral to basic lead.

<u>Data</u>.

Amount of Thio required:	(a) With acetic acid solution	19.4 c.c.
	(b) With aqueous solution	23.45 c.c.

<u>Calculation</u>.

N/10 Chromate necessary to precipitate total lead in 50 c.c. aliquot = 30 - 19.40 = 10.60 c.c.

For precipitation of neutral lead, 30 - 23.45 = 6.55 c.c.

$\therefore$ Chromate equivalent to basic lead = 4.05 c.c.

$\therefore$ Ratio Neutral to Basic lead = $\frac{6.55}{4.05}$ = 1.617.

Each c.c. of N/10 Chromate used in precipitation is equivalent to 0.0069 g. of lead. Lead can therefore be very easily determined both in actual weight and in per cent.

The results are given in Table 6 for the solids and in Table 7 for solutions. No determinations were made on the CRM. X1, X2 and X3 solids as they were known to contain carbonate. Snell's figures, with which comparison is made in some instances, are the results of analyses made in 1918, using the sulphate method for total lead and the alkalinity method for basic lead. The figures for "Solution, Horne's, Old" are for a one year old solution of Horne's old salt. This solution was protected from the carbon dioxide of the air by means of soda lime, the system of circulation from bottle to burette (in this one instance) being a closed one. In spite of this precaution a white sediment had collected in the bottle and the year old soda lime tube was therefore immediately replaced with a larger new one, which was renewed at one month intervals; the deposit has not increased perceptibly since this measure was adopted. Ten c.c. of acetic acid were used instead of five for the total lead estimates in Solution CRM. 51, and Compounds CRM.21, 32, and RCMV, in order to effect clear solution.

The amount of total, and also of basic lead, per 2 c.c. of solution, is given in Table 7, and also the volume of each solution containing approximately 0.45 g. of lead. This figure (0.45) was derived by taking the average of the amounts of lead per 2 c.c. of solutions in general as reported by Snell (1).

Moisture.

Determinations of moisture on the solid substances were carried out by drying overnight in vacuo at 80°, weighing, and reheating at 105° for two hours. The second heating caused no appreciable loss in weight. The results are presented in Table 6.

Acetic Acid.

Determinations of acetic acid in the basic acetates were attempted, using the method recently evolved by Vesterberg and Palmer (47). The directions were carefully followed and fair agreement was obtained between duplicates. When the results were computed, however, the figures obtained were in many instances grotesque, though permissible in as many cases. Inasmuch as similarly fantastic percentages were obtained when pure lead and sodium acetates were used the results are not presented.

Alkalinity of Solutions.

Ten c.c. of solution were pipetted into a small Phillips beaker, and exactly 50 c.c. of N/2 sulphuric acid added; mixed, and allowed to stand three hours; filtered into a 250 c.c. volumetric flask, washing the precipitate thoroughly with water; made up to the mark and 50 c.c. aliquots titrated with N/10 sodium hydroxide, using phenolphthalein.

Half the difference between 50 and the number of c.c. of N/10 sodium hydroxide used represents the number of c.c. of N/10 acid neutralized by 1 c.c. of lead subacetate solution. The results are given in Table 7.

Solutions CRM. 1,3,4 and 5 came through the filter paper (E. & D. 613) cloudy, and had to be refiltered; in the second filtration CRM.3 came through slowly. CRM.0, like all the other solutions, filtered perfectly clear. In the titration CRM.0 gave no trouble, but CRM.1,3,4 and 5, as well as Baker 02, gave a mauvish hue to the pink end point. Baker 00 and 03 solutions behaved normally. In the case of Baker 01 it was noticed that the colour faded after the finished titration had been set aside but a third titration substantiated the first two. With Baker 02 close checks were obtained, the mauve tint not interfering seriously. In the case of the CRM. 1,3,4 and 5 solutions a scintillating cloudiness fell early in the titration, becoming a definite white precipitate as the addition of alkali progressed. The mauve colour prevented accurate observation of the end point, and a definite amount of alkali in excess was therefore added, the intention being to titrate back the excess of alkali, since the change from pink to colourless did not cover nearly as wide a range as the reverse change complicated by mauve. The precipitate remained, settling readily. These back titrations, however, also gave inconsistent results.

The original solution was, of course, acid and it seemed impossible that excess of sulphuric acid had not been used. But when sulphuric acid was added to the supposedly lead-free filtrate, a heavy white precipitate was formed; potassium iodide gave a yellow precipitate. The determinations on these solutions were therefore repeated, using 100 cc. of acid, and filtering through Whatman No. 40 paper. The titrations were then normal, a good end point being obtained. This procedure was also carried out on Baker 01.

RCMP, $RCMP_2$, RCMT, WCT and WCV gave the sharpest end points, a deep pink resulting from the addition of the last drop of alkali.

A few remarks concerning the precipitate obtained during titration may be made. It could not have been lead sulphate held in solution in the acid filtrate, since the addition of alcohol caused no cloudiness, and it therefore seemed likely that it was due to the precipitation of lead from some complex ion which is stable in the presence of sulphuric acid, but unstable - probably reacting - in neutral or alkaline solution. The addition of large excess of alkali dissolved the precipitate. A fresh precipitation was made, left overnight, and the substance filtered into a tared Gooch, well washed, and dried at 100°C. The substance as obtained consisted of greenish-grey spangles of mettallic lustre interspersed with hardly noticeable amorphous pinkish (but no yellowish) particles. The weight obtained was 0.2992 gram, and lead (Bergh method) found to be 81.25 per cent. (Lead in $PbO.PbSO_4$ is 78.7 per cent.) No further work was done on the precipitate.

Hydrogen Ion Concentration.

The results obtained electrometrically for hydrogen ion concentration are of a variable and irreproducible nature with the KCl agar bridge. When attempts are made to utilize ammonium nitrate in place of potassium chloride, in order to prevent the formation of lead chloride at the junction, difficulty is experienced regarding the consistency of the agar. The determinations were made colorimetrically. The preliminary use of B.D.H. Universal Indicator gave no colours that would indicate an approximate reaction. In the acid range Bromcresol Green gave a purple incomparable with standards and Methyl Red was therefore substituted. Beyond the range of Methyl Red, Bromphenol Blue was found suitable. Phenol Red was found satisfactory in its higher range but below pH 7.4 the colour tints did not match the standards as well as might have been expected. Bromthymol Blue, however, produced a purplish colour, accompanied by flocculation of material. The figures (7.30, 7.35, 7.30) which are reported for CRM.51, MA and NA obtained with Phenol Red, should therefore be regarded as indicative rather than representing the actual value of the reaction. Cresol Red was used to check the values (up to 8.3) obtained with Phenol Red, and was then itself applied to the determination of values up to pH 8.8; beyond this Thymol Blue (alk.) could not be used as it gave a brown colour, and the seven values above pH 8.80 which are reported were obtained with Phenol Phthalein. Dilution of the reagent ten times, which is the dilution occurring in Canadian Lead Number determinations, caused no change of reaction.

Table 6.

Results of Analyses on Solid Substances.

No	Mark	Thio Reqd.		Ratio		Moisture	Remarks
		Acid	Aq.	Actual	Theoretical		
1	Horne's Old	19.50	23.45	1.65	1 : 1	0.95	Snell found
2	Horne's New	19.40	23.45	1.62	1 : 1	0.65	1.634-1.598
3	Baker 00	19.60	23.00	2.05	?	0.90	$2Pb(C_2H_3O_2)_2.PbO$(?)
4	" 01	21.10	24.83	0.99	1 : 1	0.72	$Pb(C_2H_3O_2)_2.PbO$(?)
5	" 02	20.95	24.95	1.01	1 : 1	1.11	"
6	" 03	19.30	25.85	0.63	1 : 2	1.09	$2Pb(C_2H_3O_2)_2.$ $.3PbO$(?)
7	JFS.1	20.40	24.20	1.52	3 : 2	0.92	Snell found 1.43.
8	" 3	20.40	24.40	1.40	3 : 2	0.99	Snell found 1.35
9	" 4	20.50	24.10	1.63	3 : 2	0.70	Snell found 1.43
10	CRM.0	19.40	26.80	0.43	1 : 2	-	Analysis 1924
11	" 1	20.20	24.80	1.13	1 : 1	-	
12	" 2	20.20	23.80	1.76	3 : 2	-	
13	" 3	20.20	23.30	2.16	2 : 1	-	Analysis 1924
"	" "	21.40	23.37	3.37	2 : 1	0.90	" 1928
14	" 4	20.50	22.70	3.31	3 : 1	-	Analysis 1924.
"	" "	20.05	22.10	3.31	3 : 1	2.01	" 1928.
15	" 5	20.90	22.30	5.50	4 : 1	-	Analysis 1924.
"	" "	20.00	22.34	3.27	4 : 1	3.00	" 1928.
16	" 15	18.30	25.90	0.54?	1 : 5	0.31	Yellow residue in Aq. Solution.
17	" 14	18.00	25.20	0.67?	1 : 4	0.66	Less residue in Aq. Solution.

Table 6,(Cont'd).

No	Mark	Thio Reqd.		Ratio		Moisture	Remarks
		Acid	Aq.	Actual	Theoretical		
18	CRM.13	20.30	24.70	1.20?	1 : 3	1.01	Even less residue in aq. solution.
19	" 12	18.70	24.60	0.92?	1 : 2	0.83	Negligible residue
20	" 11	19.15	24.30	1.11	1 : 1	6.40	
21	" 43	19.70	23.50	1.71	4 : 3	1.50	
22	" 32	19.30	23.45	1.58	3 : 2	1.24	
23	" 21	19.90	22.80	2.48	2 : 1	0.86	
24	" 31	22.20	22.65	3.00	3 : 1	1.48	$3Pb(C_2H_3O_2)_2.PbO$(?)
25	" 41	20.55	22.20	4.73	4 : 1	4.72	
26	" 51	20.40	21.70	6.39	5 : 1	5.24	
29	RCMV	17.85	25.90	0.51?	-	0.60	Considerable yellow residue.
30	RCMP	16.90	27.55	0.23?	-	0.21	Considerable yellow residue.
32	RCMQ	18.50	25.40	0.67?	-	0.53	Some yellow residue.
34	RCMR	18.60	24.78	0.84?	-	0.82	Very slight pinkish residue.
35	RCMS	18.35	24.60	0,86?	-	0.74	Slight residue, pinkish.
37	RCMT	19.10	24.90	0.79?	-	0.98	Grey-yellow residue.

Table 7.

Results of Analyses on Solutions.

No	Mark	Sp.Gr.	Thio Reqd.		Ratio	0.45 g.Pb in c.c.	Lead in 2c.c		Alkalin	pH
			Acid	Aq.			Total	Basic		
1	Horne's old	1.250,21°	16.00	20.60	2.04	1.90	.4830	.1588	7.00	7.65
2	Horne's New	1.254,21°	16.75	21.50	1.789	2.0	.4571	.1639	8.95	7.80
3	Baker 00	1.256,21°	17.60	22.90	1.339	2.0	.4278	.1829	7.35	7.70
4	" 01	1.255, 21.5°	15.90	22.30	1.203	1.85	.4864	.2208	11.80	8.05
5	" 02	1.245,19°	16.10	22.80	1.074	1.76	.5106	.2622	10.80	8.30
6	" 03	1.248,20°	15.70	23.10	0.932	1.82	.4933	.2553	12.20	8.30
10	CRM. 0	1.157,10°	21.20	25.40	1.095	2.96	.3036	.1449	8.30	8.20
11	" 1	1.488,18°	1.72	14.00	1.302	0.93	.9687	.4167	19.05	8.10
12	" 2	Insufficient Sample				-	-	-	-	-
13	" 3	1.485,24°	2.95	10.50	2.582	0.96	.9331	.2604	12.60	7.80
14	" 4	1.464,20°	4.80	10.50	3.420	0.99	.9038	.2304	9.80	7.40
15	" 5	1.445,24°	5.55	10.05	4.433	1.07	.8435	.1552	8.10	7.60
16	CRM.15	1.201,24°	23.30	26.82	0.903	3.89	.2311	.1214	6.60	9.00
17	" 14	1.115,24°	23.30	27.05	0.786	3.89	.2311	.1293	7.20	8.95
18	" 13	1.116,24°	23.30	25.80	1.680	3.89	.2311	.0862	7.30	8.95
19	" 12	1.1616, 24°	20.60	25.55	0.898	2.77	.3243	.1708	9.20	8.70
20	" 11	1.252,20°	15.90	22.20	1.238	1.85	.4865	.2174	5.60	8.25
21	" 43	1.257,21°	16.25	21.20	1.777	2.0	.4743	.1707	8.90	7.90
22	" 32	1.250,21°	16.75	21.85	1.598	2.0	.4571	.1759	8.40	7.90

Table 7, (Cont'd).

No	Mark	Sp.Gr.	Thio Reqd.		Ratio	0.45 g.Pb in c.c.	Lead in 2c.c		Alkalin	pH
			Acid	Aq.			Total	Basic		
23	CRM.21	1.259,20°	16.00	19.90	2.589	1.86	.4830	.1346	7.20	7.65
24	" 31	1.254,23°	16.15	19.50	3.134	2.0	.4778	.1156	5.40	7.40
25	" 41	1.253,22°	17.20	19.20	5.400	2.0	.4416	.0690	4.60	7.50
26	" 51	1.257,20°	16.35	18.25	6.184	2.0	.4709	.0655	4.10	7.30
27	CRM.x1	1.188,15°	19.40	24.80	0.962	2.46	.3657	.1863	9.80	8.70
28	" x2	1.105,13°	24.10	27.10	0.966	4.42	.2036	.1036	6.85	9.05
29	" x3	1.153,14°	21.40	25.10	1.324	3.03	.2967	.1277	7.90	9.00
30	RCMP	1.136,21°	22.65	26.38	0.970	3.55	.2535	.1286	8.40	9.00
31	RCMP.2	1.143,21°	22.10	26.15	0.950	3.30	.2726	.1398	8.00	9.00
32	RCMQ	1.182, 22.5°	19.70	25.25	0.855	2.0	.4243	.2604	10.00	8.70
33	RCMQ.2	1.151,21°	21.25	25.60	1.011	3.00	.3018	.1500	8.45	8.65
34	RCMR	1.232,24°	17.35	23.81	0.958	2.0	.4364	.2229	11.35	8.40
35	RCMS	1.208,25°	18.00	24.90	0.739	2.17	.4140	.2381	10.40	8.50
36	SW	1.175,20°	19.45	25.32	0.797	2.47	.3639	.2024	8.05	8.75
37	RCMT	1.214,22°	18.40	23.90	1.109	2.25	.4002	.1898	10.55	8.35
38	WCT	1.250,22°	16.85	22.90	1.173	2.0	.4536	.2087	11.40	8.35
39	WCU	1.241,22°	17.10	23.10	1.150	2.0	.4450	.2070	10.85	8.25
40	WCV	1.170,21°	20.65	25.60	0.888	2.79	.3225	.1707	9.10	8.75
41	ALMR	1.255,22°	17.20	17.30 (?)	127.0 (?)	2.0	.4450	.0035 (?)	Acid	4.40
42	B.2	1.255, 20.5°	15.80	20.00	2.380	1.84	.4899	.1449	7.60	7.70
43	AA	1.248,20°	17.30	21.70	1.886	2.0	.4381	.1518	7.95	7.75

Table 7, (Cont'd).

No	Mark	Sp.Gr.	Thio Reqd.		Ratio	0.45 g.Pb in c.c.	Lead in 2c.c		Alkalin	pH
			Acid	Aq.			Total	Basic		
44	BA	1.258,18°	16.15	19.90	2.693	2.0	.4778	.1294	7.30	7.65
45	CA	1.244,21°	16.55	21.00	2.022	2.0	.4640	.1535	7.70	7.55
46	DA	1.252,21°	17.00	19.30	4.652	2.0	.4485	.0794	5.5	7.55
47	EA	1.249,21°	16.85	20.53	2.573	2.0	.4536	.1269	6.85	7.55
48	FA.1	1.255,21°	16.78	19.60	3.687	2.0	.4561	.0973	5.5	7.45
49	FA.2	1.257,20°	16.10	20.65	2.054	2.0	.4795	.1569	7.75	7.65
50	GA	1.258,20°	16.20	20.70	2.066	2.0	.4761	.1553	7.8	7.65
51	HA	1.246,21°	16.90	20.70	2.447	2.0	.4519	.1311	6.7	7.55
52	IA	1.2468, 18°	17.25	21.55	1.965	2.0	.4398	.1483	7.60	7.65
53	JA	1.254,	16.25	20.00	2.666	2.0	.4743	.1293	5.75	7.45
54	MA	1.259,	16.30	19.25	3.644	2.0	.4726	.1017	5.15	7.35
55	NA	1.309,	13.25	16.25	4.583	1.56	.5778	.1034	3.4	7.30
56	VZB	1.045,21°	27.45	28.45	1.550	10.2	.0879	.0344	2.0	7.40
57	VZW	1.240,21°	17.05	21.65	1.815	2.0	.4467	.1586	8.00	7.70
58	MMA	1.252,21°	16.45	20.15	2.662	2.0	.4674	.1276	6.90	7.50
59	MMB	1.243,21°	16.60	21.10	1.977	2.0	.4623	.1553	8.20	7.70
60	NCM.2	1.241,21°	17.25	21.45	2.035	2.0	.4398	.1448	5.80	7.45
61		1.051,22°	Clarification lead acetate (normal), 82 g. per litre,							5.30

CHANGES IN BASIC LEAD ACETATE SOLUTIONS.

The white sediment which collects in all basic lead acetate solutions fizzes on addition of acid. Storage in coloured bottles does not prevent the formation of the precipitate. The turbidity which occurs when pure lead acetate is dissolved in ordinary water does not occur when carbon dioxide-free water is used. The precipitate in the solutions which had been stored at Macdonald College for periods ranging from one to nine years varied in quantity, and in colour from the purest white to cream yellowish, and even light buff (MMA). The stock solutions (Sp. Gr. 1.25) showed sediments also but in less quantity. The filtered (clear) solution became cloudy on passing carbon dioxide gas through it; if acetic acid was added to the solution before the advent of carbon dioxide no precipitation occurred. A short resume of the literature of the action of carbon dioxide on lead acetate solutions and of the reaction between lead carbonate and lead acetate follows. The reactions are of commercial importance in the preparation of "white lead".

(1) Rose (48) obtained lead carbonate by passing carbon dioxide into a solution of lead acetate, and Altman (49) added that with solutions ranging from 0.02N to 2N and at temperatures between ~~xx~~ 0 and 100° the proportion of normal carbonate formed decreases with rise of temperature and increased concentration of acetate. With solutions heated

for some time in a reflux at 100° normal carbonate is precipitated, but if the acetic acid set free by hydrolysis can escape the precipitate obtained with dilute solution is a basic carbonate, $2PbCO_3.Pb(OH)_2$; with concentrated solutions a mixture of this basic salt and normal carbonate is precipitated.

(2) Yamaski (50) passed carbon dioxide through a solution of lead acetate with and without an addition of acetic acid or sodium acetate and determined the concentration of acid (acetic) and lead acetate when equilibrium was attained. The experiments were carried out at 15° and $25^\circ C$. Within these limits of temperature it was found:

(a) The precipitate produced is the normal carbonate of lead.

(b) The amount of precipitate from a given quantity of lead acetate increases with the dilution of the solution; but when the concentration is lower than 0.1N, it is independent of dilution (CH_3COOH; $Pb(C_2H_3O_2)_2$ = 4.3:1).

(c) When acetic acid is added to the lead acetate solution the proportion of the free acid and lead acetate in solution after reaction, will be the same as in the case when no acid is previously added, if the total concentration of the acetic acid radical is lower than 0.1N.

(d) In a dilute solution of lead acetate the lead may be almost completely precipitated by carbonic acid when sodium acetate is added in quantity more than equivalent to the lead salt.

(3) Hochstetter (51) found that when carbon dioxide is passed through basic lead acetate solutions until the liquid is neutral, the precipitate has the composition $2PbCO_3.Pb(OH)_2$.

(4) Salvadori (52) says that ordinary basic carbonate is fully as stable as the normal carbonate (if not more so), and that the latter is readily converted into the former by boiling with water or by heating it under water for several hours.

(5) According to Sacher (53), carbon dioxide in the presence of water gradually transforms white lead into the normal carbonate.

(6) Euston (54) found that when various samples of white lead or lead carbonate were stirred with basic lead acetate solution at room temperature lead hydroxide was invariably drawn from the solution and there was a gain in weight; at the same time the carbon dioxide content fell from between 12.0 and 16.3 per cent to as low as 10.1 and 10.3 in extreme cases. The extent of the action depends on the basicity of the lead acetate solution, time, and on the relative proportion of the solid and solution. The reaction is completed only when an excess of the basic acetate solution is present. With a sample containing both normal and basic lead the equilibrium can be disturbed in either direction by the addition of more basic lead acetate solution or normal lead acetate solution.

Solution Sediments.

The sediments listed below were filtered off from their respective solutions, well washed, dried, ground in an agate mortar and analyzed. The Horne sediment was obtained from a solution (Sp. Gr. 1.25) of unknown history. The "Composite" sample was procured by collecting the precipitates from over forty old basic acetate solutions varying in specific gravity from 1.05 to 2.00. These two sediments were air dried, then placed in in a dessicator over sulphuric acid until there was no further loss in weight. The other samples(BA- NAW) were found already prepared in the laboratory and were dried in vacuo at 100 - 105^{o} for twelve hours previous to analysis. The analyses are presented in Table 8. There was a very slight residue, in the form of scattered gelatinous particles, after solution of the composite sediment in dilute nitric acid; filtration through a tared Gooch crucible gave no weighable residue. Qualitative tests on the original sediment failed to establish the presence of silicate. The solution of the Horne sediment in nitric acid was perfectly clear.

The sediments evidently consist of normal or basic carbonate or a mixture of these.

TABLE 8.

Analyses of Precipitates in Lead Subacetate Solutions.

Sediment.	% Pb Bergh's Method.	% PbO Bain's Method.	% CO_2, using Apptus.		Insol. in Nitric Acid.	Moisture %
			Schroedter.	Knorr.		
BA	80.39	-	-	-	-	Nil.
CA	80.39	-	-	-	-	Nil.
DA	82.10	-	-	-	-	Nil.
GA	82.00	86.41[*†]	-	9.86[*]	1.31[*]	Nil.
IA	81.77	-	-	-	-	Nil.
LA	82.00	-	-	-	-	Nil.
MA	82.80	-	-	-	-	Nil.
NAW[‡]	81.07	-	-	-	-	Nil.
Horne's	77.30	-	7.935	9.615	Nil.	0.04
Composite	75.42	-	11.064	12.048	Nil.	0.28

Required by Theory.

	$PbCO_3$	$2PbCO_3.Pb(OH)_2$.	$5PbCO_3.2Pb(OH)_2PbO$
Pb	77.56	80.15	82.70
CO_2	17.52	11.35	10.78

[†] Equivalent to 100.10% $2PbCO_3.Pb(OH)_2$.
[*] Analyses by W.A. DeLong.
[‡] Solution NA diluted four times.

Artificial Ageing of Solutions.

Previous experiments on the changes in lead subacetate solutions at Macdonald College have been carried out with respect to the lead content of the solution from time to time, the ratio of neutral to basic lead, and the alkalinity. The results are conflicting, both plus and minus changes being indicated in each of these three classes. It was therefore decided to age a basic acetate solution artificially and follow the changes.

Carbon dioxide was bubbled into separate 200 c.c portions of Solution No. 62.0 (Horne's) at room temperature at the rate of 100 bubbles per minute, this being the rate at which a drop of barium hydroxide solution on a glass rodd held at the exit opening of the Erlenmeyer flask became cloudy only slowly. The gas was passed through two wash bottles, one containing water and the other empty, before being led into the subacetate solution. Bubbling was continued for 5, 15 and 30 minutes, and 3 and 9 hours respectively in the first five flasks. In the sixth it was attempted to push the reaction as far as possible under the circumstances. After a total period of 30 hours, no further advantage seemed to accrue from continued bubbling, since the filtered solution remained perfectly clear when carbon dioxide was again passed into it. After 3 hours further bubbling only a very slight turbidity could be noticed and the solution was therefore regarded as "totally aged". The ageing was not complete in the previous case of nine hours. Each solution was filtered immediately after its treatment had been completed and analysis made forthwith of the specific gravity, ratio and alkalinity. The hydrogen ion concentration was not determined until five weeks later. The results are presented in Table 9. The chromate precipitates in the acid precipitation of Nos. 66 and 67 were equally the palest yellow of all the precipitates observed in the course of this investigation; that obtained with the aqueous solution of No. 62 was likewise the deepest orange (red) precipitate.

The specific gravity, total lead content, basic lead content and pH value fall regularly as the solution ages and the ratio rises. In the last two cases the solution is acid. Since in these solutions basic lead would hardly exist the figures connected with basic lead are queried though they represent the actual titration. The same occurrence (see Solution ALMR, Table 7) had previously been noticed. In the titration with the addition of acetic acid, a slightly lower result has consistently been obtained than with the titration with the already acid solution but to which no acetic acid has been added. This small difference (from 0.1 - 0.5 c.c.) changes the theoretical ratio of the solution from infinity to a finite number, and gives a (deceptive?) figure for basic lead content.

Attention must be called to the break in the sequence of events, occurring at Solution No. 63. This solution is lower in basic lead but higher in neutral lead content than it was ten minutes previously. No change is recorded in the pH value. The total lead content has increased from 0.457 to 0.465 gram per 2 c.c. in the ten minute interval from Solution 62 to 63. Evidently some of the precipitated lead has returned to solution, at the same time causing a slight increase in alkalinity.

This apparent increase of lead in solution explains the curious changes of lead concentration and of alkalinity which were found when many of the old solutions at Macdonald College were analyzed at different intervals. The only explanation that hitherto seemed possible was experimental error since the bottles were tightly corked in storage. In the case of the plus changes the solutions would appear to be at the stage of natural ageing represented by Solution 63. This explanation is subject, however, to the assumption that the "original" figure reported was not the true original figure but the figure represented by the stage corresponding to Solution 62, since the lead concentration cannot rise above its initial value. The work of Euston (54) already cited, may again be referred to in this connection, and also the work of Falk (58). It is possible that the compound represented by the formula $3Pb\ CO_3.\ Pb(OH)_2.PbO$ may be formed by the interaction of normal lead carbonate with excess of basic lead acetate in the cold, and going into solution, raise both the lead concentration and the alkalinity.

TABLE 9.

Analyses of Artificially Aged Solutions.

No.	History.	Sp. Gr. at 22°C.	Thio Reqd. Acid.	Thio Reqd. Aq.	Ratio.	Grams Lead in 2 c.c. Neut.	Grams Lead in 2 c.c. Basic.	Alk.	pH.
62 O	Orig. Horne's.	1254 (219	16.75	21.50	1.42	.2932	.1983	8.95	7.80
62	Aged 5 min.	1.2495	16.75	21.92	1.56	.2787	.1783	8.60	7.80
63	" 15 "	1.2467	16.52	21.57	1.67	.2908	.1742	8.80	7.80
64	" 30 "	1.2405	17.30	21.97	1.72	.2770	.1611	8.40	7.80
65	" 3 hrs.	1.2083	18.80	22.05	2.45	.2742	.1122	5.50	7.45
66	" 9 "	1.1492	22.52 (?)	23.00	14.55 (?)	.2415	.0165 (?)	Acid.	4.50
67	Totally Aged.	1.1196	24.50 (?)	14.62	44.83 (?)	.1 856	.0041 (?)	Acid.	3.60

DISCUSSION OF RESULTS.

A consideration of Table 6 shows that the laboratory synthesis by Snell's method generally gives a less basic product than is aimed at - in other words, some of the litharge remains unreached. Eighty per cent of the attempts resulted in the less basic product, though it must be pointed out that some of the products included in this class do not show striking differences from the theoretical. In only two cases (Nos. 8, 10), was a more basic substance obtained, though again the variation from theory was not marked. One product only (No. 24) was ideal; one other (No. 7) was very nearly so. The differences in ratios between substances in the same class (Nos. 10, 19; 12, 22; 14, 24; etc.) prepared in 1924 and 1928 shows to what extent the reaction may vary. Attention has already been drawn to the yellow or reddish-yellow residue when these products are dissolved in water, this residue increasing proportionately as the amount of lead oxide in the product increases. Thus in the Series Nos. 16 - 26 (inclusive) the residue is greatest in No. 16 and decreases steadily until it is negligible in No. 19, whereafter it ceases altogether, all the substance dissolving in the case of each of the remaining products. (The residue in Nos. 30 - 35 (inclusive) is as to be expected, considerable, since these substances separated out somewhat precipitately from solutions which were boiling.) It is not impossible that basic acetate compound of definite composition exists in each of these solids, but there is no evidence for it. In this case one would explain the higher ratios generally obtained by the uncompleted stage of the reaction, which would leave an excess of normal acetate. But in Nos. 16 - 19 (inclusive) where the solution of the substance in water shows definite excess of lead oxide the ratios are also higher than the theoretical. These facts may therefore be taken to indicate that the substances are mixtures. Such a conclusion is substantiated by the poor checks obtained in many instances. Using the same physically homogeneous sample duplicates sometimes gave poor checks, and a third determination would sometimes give a figure approximating the mean, and at other times differing from either figure previously determined. The average of the three titrations would in such a case be taken for both the acid and the aqueous solutions, and the mean ratio so obtained reported. This mean ratio may itself vary, as is shown by Nos. 13 and 15. In Compound No. 14 the same ratio is obtained with different figures for the titrations. As the moisture in the original sample is unknown, it is impossible to draw any definite conclusions with respect thereto. (In this connection it may be stated that DeLong also found similar variations in the weight of lead sulphate precipitates when estimating lead in CRM.0 and 2, and Baker 00. The average deviation from the mean in first two was greater than in the last case). These variations do not occur when solutions of these salts are used. The interpretation lies in inconstancy of composition of the sample. Jackson (15) proves the existence of $3Pb(C_2H_3O_2).PbO$ as a solid phase, and Compound No. 24

may represent this; the present work does not attempt to establish this. In the case of the other "dry" products there is no evidence that they are other than mixtures. It was not expected that the laboratory synthesis would give a definite chemical entity; the purpose was the preparation of solids from which solutions of varying basicity might be readily prepared. Whilst this was accomplished it is noteworthy that no solution had the same ratio as the substance from which it was prepared. In general the solution ratios are higher than those of the corresponding salts, yet another indication that the solid substance is a mixture or undergoes some change in the process of solution. In the solid the unreacted lead oxide is estimated in the total lead whilst in the solution it is not. (This error does not occur when the solid all dissolves). Since the amount of basic lead is derived by subtracting the neutral from the total lead, and the neutral lead is not subject to error, the basic lead figures will be higher in the solids than in the solutions, and the ratio will therefore be higher in the latter. The product with the highest ratio was CRM. 51.

The addition of increasing proportions of lead oxide in the attempt to get a very basic salt did not appear to be very effective. The ratio does not decrease beyond a low figure of about 1:2 (see Table 6, Nos. 16-19), and fluctuates quite irregularly - tending to show that some litharge has always remained unreacted, the reaction proceeding to different stages. The ratios on Nos. 23,25 and 26 also indicate unreacted lead oxide, in increasing proportion as the higher ratios are approached. Since the quantities used were the theoretical proportions, there was not excess of $Pb(C_2H_3O_2)_2$, and the high ratios must therefore again be interpreted to mean that the reactions did not proceed nearly to completion. Stirring of the ingredients at the time of admixture was always vigorously practiced, except when solidification did not take place within a reasonable time. Why all the litharge does not react when the lead acetate, constituting the greater part of the mixture, is the vehicle for the reaction, is not quite evident. The ratios within which reaction proceeds nearly according to theory seem to be 1:2 and 3:1. In practice it is quite evident that outside these limits one or other of the constituents is in excess - the mix is poor, or the "setting" period extended. A curious indication is that whilst the reaction in the case of No.10 was good, the reaction in the case of No. 19, which should have given a similar product, occurred to about only half the extent as on the former. The only difference in the preparation of these two substances was the temperature of the litharge when added to the melted lead acetate crystals. In the first case it was at room temperature; in the second case it was between 70 and 80°.

The theoretical possibilities of the Baker salts are indicated in Table 6.

The RCM - substances are all low in ratio, and appear to differ from the solutions from which they separated, as may be seen from the data set out in Tables 6 and 7. It must be constantly borne in mind, however, that the ratio obtained for any substance which leaves a residue in aqueous solution does not connote the true or even the approximate composition of the said substance. All such ratios are queried in Table 6, and indeed may be disregarded altogether. The lead content gives more reliable information concerning such a substance. This content has been calculated for the RCM - compounds and is set forth below. A comparison with the nearest theoretical compound is made. Jackson's isothermal (see Appendix) cannot be used to interpret the possible composition of these substances since their formation took place at the boiling point.

Data on the RCM- Substances.

Substance	% Pb.	Theoretical.
RCMV	84.31	$Pb(C_2H_3O_2)_2.4PbO$. (Pb = 85.05%)
RCMP	92.32	? Pinkish particles observed when grinding.
RCMQ	83.81	$Pb(C_2H_3O_2)_2.3PbO$. (Pb = 83.30%)
RCMR	85.66	$Pb(C_2H_3O_2)_2.4PbO$.
RCMS	86.81	$Pb(C_2H_3O_2)_2.5PbO$ (Pb = 86.25%)
RCMT	83.88	$Pb(C_2H_3O_2)_2.3PbO$.

Horne's compound is the most interesting of the solids. This compound was manufactured in order to meet the necessity for a basic acetate of constant composition for use in sugar analysis, and has been in demand since the year 1903. Browne (38) had found that basic lead acetates sold by reliable chemical firms varied in their content of basic lead oxide from 3.34 to 32.32 per cent, and that solutions made by digesting litharge with normal acetate might also vary, as has already been noted. Since the solutions used in sugar analysis must have a uniform content of basic lead Horne's preparation soon came into general use. Analyses made from time to time at Macdonald College on different samples of Horne's salt by Snell (results unpublished) and the writer show that, unlike the synthetic preparations obtained in the laboratory, Horne's salt is remarkably constant in composition, with a ratio of neutral to basic lead of about 1.6:1, and a lead content of say 73.86 per cent, calculated on the new salt (see Table 6). Browne (10) reports 73.00 for "a very pure anhydrous lead subacetate". Theory requires 72.84 per cent for $3Pb(C_2H_3O_2)_2.2Pb$, and 73.60 for $4Pb(C_2H_3O_2)_2.3PbO$. Either of these formulae would therefore represent the composition of Horne's salt better than $Pb(C_2H_3O_2)_2.PbO$, the formula which is assigned to it by the manufacturers, which denotes a lead content of 75.55 per cent. In communication with the writer Dr. Horne suggests assuming the composition of the salt from the percent of lead.

The constancy of composition of Horne's salt might reasonably be taken to indicate that we are dealing with a pure compound. However, Horne's salt is in reality a mixture of the following two basic salts:

(1) $Pb(C_2H_3O_2)_2.2PbO$

(2) $3Pb(C_2H_3O_2)_2.PbO$.

Jackson, in personal communication with Dr. J.F. Snell, quotes his own experiments which lead to this conclusion. Water was added directly to Horne's salt and the composition of the solution determined, as in the case of the experiments upon the pure material. In every instance the solution fell on the point C (see diagram in Appendix) which is the solution in equilibrium with the two basic acetates when both are present in the solid phase. Upon adding neutral lead acetate the solution took up a position upon the curve BC as was to be expected. This indicates that Horne's material is, or becomes in solution at 25°' a mixture of the two basic acetates.

The constancy of composition is easily explained when one considers the relative position of the saturation curves and the solid phases. If a solution say of the basicity represented by the point B is evaporated, the solid phase which begins to separate is less basic than the solution in equilibrium with it. This can readily be seen by drawing the straight line GE. The solution therefore becomes still more basic and moves down the curve BC until it reaches the point C. At this point the two basic acetates separate out in exactly constant ratio and the material after the initial stages of the evaporation must have a constant composition. This is probably the reason why basic acetates of other constant ratios are not manufactured. The material will be intermediate between the composition of the two solid phases since they have an identical solubility. This mixture will therefore be $Pb(C_2H_3O_2)_2 . 2PbO$ - $3Pb(C_2H_3O_2)_2 . PbO$, or written together, $4Pb(C_2H_3O_2)_2 . 3PbO$, which, requiring 73.60 per cent of lead is approximated most closely by the figure (73.86) obtained in the Macdonald College laboratories. Jackson's paper for equilibrium at 25° does not preclude the possibility of Horne's salt being a <u>compound</u> of this composition, provided it is formed and dried at some temperature other than 25°C., but it seems improbable. In aqueous solution at 25°C. such a compound, if it did exist, would decompose into a mixture and fit into Jackson's diagram.

Solutions.

The solutions do not call for extended comment. A general feature is that a solution is always slightly less basic than the solid from which it is prepared. In the light of the results obtained during the course of this investigation the reason becomes apparent. During boiling a small amount of basic lead is precipitated - the residue from which the clear supernatant liquid is decanted - and in consequence the ratio rises. Horne's solutions are always decidedly more basic when freshly prepared than similar solutions prepared by boiling lead acetate (430 g.) and litharge(130 g.) according to the A.O.A.C. directions. The quantities used are in molecular ratio of 3:2, the ratio supposed to have existed in Horne's compound, and consequently to yield a solution identical with Horne's. From the previous discussion of the composition of Horne's salt, it appears that the quantities indicated by four molecules of lead acetate (anhydrous) and three of litharge are the quantities that should be used to give the Horne's solution. The prevalent conception regarding the high ratio hitherto obtained has been that the litharge has not all reacted. The same high ratio (vide Solution No. 42, Table 7) is obtained, however, when solution has been complete. It would appear that the purity of the reacting chemicals used, the physical state of the litharge, the degree of agitation as well as the time of heating, and possibly other factors, offer such wide latitude for variation that the use of Horne's salt is preferable. Even with Horne's compound the only way to obtain a solution of an absolute ratio, akin to a standard solution, is to analyze the solution and adjust it. As to why the freshly manufactured substance (Horne's subacetate) should go into solution more readily than an older sample, to which attention has already been drawn (p. 27) the following theoretical considerations are advanced. Both the old and the new compounds are themselves free from carbonate. Since carbonate is formed during boiling it is possible that the substance which appears to be undissolved subacetate consists of subacetate granules protected by carbonate, the formation of which has taken place earlier in the case of the old substance. The sooner the concentration of acetic acid which inhibits formation of carbonate is passed, the sooner will precipitation occur. In addition the particles of the new salt, being finer (the old salt is granular, the new salt powdery) will be more likely to escape protection. The fact that this residue does go into solution to a certain extent after protracted boiling may be due not only to solutinn of hitherto protected acetate but also to solution of carbonate. It may be correlated with the increase in lead content noted in the ageing experiments, for lead carbonate is soluble both in carbonic acid (57a) and in acetates (57b). The precipitation of lead carbonate by the action of carbon dioxide on lead acetate itself decreases with rise in temperature, and the absorption of carbon dioxide by lead monoxide at 100° is not appreciable (Erdmann (55) and Dennstedt and Hassler (56), so that formation of lead carbonate does not occur to any great extent. The formation of basic carbonate by hydrolysis of the normal carbonate, however, does occur above 70°. (In the cold the formation of a carbonate of composition $3PbCO_3.Pb(OH)_2.PbO$ by the action of excess of basic acetate on the normal carbonate is advanced by Falk (58)). This explanation is based on the following observations:-

(1) The old Horne salt smells very strongly of acetic acid, whilst the newly manufactured compound is almost odourless. If the old salt is freer from acetic acid radical, reaction with carbon dioxide will take place with greater ease.

(2) When CO_2-free water (25 c.c.) is added to equal weights (0.5 gr.) of the old and new salts, and allowed to stand, the "old" solution becomes more turbid in the same length of time than the "new".

(3) The old salt remains as a flocculent sediment whilst the new seems to be distributed evenly in the suspension prior to boiling. The old salt suspension is white, having the appearance of thin paint; the new is slightly yellowish in colour.

No experiments have been made regarding the basicity of freshly prepared solutions from the old and new salts. According to the above explanation the solution of the old salt should be higher in ratio than the new.

It must also be recorded that greyish particles remain when both salts are dissolved in water. The amount of these particles, though in both cases insignificant, is always greater in the new than in the old salt. These particles remain, however, on warming with dilute nitric acid; the liquid gives no test for lead.

Boiling Horne's salt for varying periods does not appear to affect the basicity of the solution - ratios of 1.634, 1.626, and 1.598:1 being found for 4,40 and 80 minute periods (Solutions 43, 44, 45) shortly after preparation. Age has raised the ratio in all of them, though to different degree. A similar change in ratio is seen in Solutions 46 - 51, all showing higher ratios than when made. Solution FA2 showed by its ratio that there had been no material change in the ratio of Stock Solution F, but storage of the 1.25 sp. gr. solution had been accompanied by a rise in ratio.

Solution No. 41 was prepared by a method supposed to give a very basic acetate, but glacial acid was inadvertently used instead of 30% acid. The results with the solution are presented nevertheless.

Solution No. 42, prepared by the A.O.A.C. method, was higher in ratio than either of the Horne solutions. Solution VZB is evidently reagent solution for the Winton Lead Number.

The range covered by the basic solutions extends from Ratio 6.2 (No. 26) to Ratio 0.74 (No. 35); and from pH 7.3 to pH 9.05. No pH values above 7.7 for basic lead acetate solutions have previously been recorded.

THE CANADIAN LEAD NUMBER.

The literature on the Canadian Lead Number has been reviewed by Fowler (3b), whose findings, since they embrace the work of all previous investigators, are summarized below:

(1) The volume of lead subacetate solution required to produce maximum precipitation is from 1 to 2 c.c., the actual amount varying with different samples of syrup.

(2) The precipitate is soluble both in excess of lead subacetate and in sucrose.

(3) The weight of the precipitate decreases as the volume of hot wash water is increased.

(4) The weight of the precipitate increases as the time which it is allowed to stand in contact with the solution before filtering is increased.

(5) More consistent, and higher numbers are obtained if cold (room temperature) wash water is used and the precipitate not allowed to crack in the crucible (thereby insuring even washing).

(6) The percentage of lead in the water-soluble portion of the precipitate was less than in the original precipitate - indicating that the precipitate is a mixture. The portion not dissolved when again treated with hot water in the same way is much less soluble than the original precipitate.

(7) The ratio of basic to neutral lead in the precipitate is greater than 1.0.

(8) The percentage of malic acid corresponds very closely with the malic acid equivalent of the total acids, indicating that malic is practically the only acid present.

(9) The undetermined portion of the precipitate amounting to about 15%, is very rich in carbon.

The uncertainty of the composition of the precipitate is one of the chief difficulties in work on the Canadian Lead Number. Whilst it undoubtedly consists largely of the normal malate of lead, various other substances are present, since other organic acids and their salts, as well as sulphates, chlorides, carbonates, colouring and other organic matter are also precipitated by basic lead acetate. In the presence of these salts, also, reducing sugars are precipitated. The use of the normal acetate has not been widely practiced, for although it does not precipitate reducing sugars, it gives very low Lead Numbers. The average results of the basic lead acetate Numbers taken from the work of Bryan (59), 2.70 for the basic and 0.79 for the normal, indicate what may happen when the basicity of the acetate is changed. The acidity of the sample itself has but little effect on the Number. (These indications are of course subject to the delicacy of the method as carried out by Bryan).

The determination of the Canadian Lead Number is generally made by dissolving the quantity of prepared syrup containing 25 g. of dry matter in water, diluting to 100 c.c. and mixing 2 c.c. of lead acetate reagent with 20 c.c. of syrup solution. The precipitate formed is allowed to stand two hours, filtered through a tared Gooch crucible having an asbestos mat at least 3 mm. thick, washed four or five times with boiling water, dried at 100°, and weighed. The weight of the dry precipitate multiplied by 20 is the Canadian Lead Number.

In the present investigation the precipitation was done in 50 and 150 c.c. beakers, which were left uncovered during the time that the precipitate stood. The reagent acetate was added seriatim to a series of these beakers each containing 20 c.c. of the syrup in question. Ordinary distilled water (temperature 20°,+- 2) was used, having a pH value of 4.58; only two determinations of this value were made, at the beginning and the end of the experiments. The amount of wash water used was 150 c.c. in each case, and the washing was done in precisely the same way, the water being added in about eight portions (in the smaller crucibles, twelve). Each portion was added before the preceding one had run through. Adhering froth bubbles were then washed down into the crucible with a wash bottle. In only a few cases did the precipitate part, or crack, and in every case this occurred whilst the precipitate was still under water. It is considered, however, that they were well and evenly washed. The precipitates were filtered in series of nine, this number being conveniently handled. The rate of settling of the precipitate was the same in all cases, except where otherwise stated.

The amount of wash water used was found to wash the precipitate free from lead and from sugar. In only a few cases was there any darkening at the edges of the dried precipitate and these were discarded. An attempt to determine whether precipitation of malic acid was complete by testing the first filtrate with B-naphthol sulphuric acid showed only the blackening caused by the decomposition of sucrose; when diluted there was a suggestion of mauve. Later portions of the filtrate were not tested, since it would have been impossible to distinguish between the reaction given by lead malate dissolved in the wash water and unprecipitated malic acid. No experiments were made on the use of alcohol (50%) as wash water, though the recent work of Auerbach and Weber (60) on the solubility of lead malate suggests such washing. A fresh clean, dry, pipette was used to measure each reagent for transfer to the syrup solution.

It is not proposed to interpret the results obtained within 0.20%, since this difference may be caused by a weight of only 0.010 g., and it was observed that five minutes after the weighed crucible was put aside there was an average increase of weight of 0.008 gram. The actual weighings were all done rapidly, the average time any crucible being on the pan not exceeding one minute and a half. In a series of twenty duplicate determinations, very carefully performed for the express purpose of calculating the personal error it was found that whilst very close results were obtained in the majority of cases, the average variation in the weight of the precipitate was 0.0056 gram.

The colour of the individual precipitate is described in most cases. In the synthetic solution all the precipitates were snow-white, with the single exception of that obtained with the use of Solution 6 (Baker 03). This solution, itself reddish brown, gave a flesh-coloured precipitate.

The history of the three syrups on which determinations were carried out is set out below:

Syrup No. 40. - From Joseph Roy, Ste Hinodone, Que. Made with midseason sap in a Champion evaporator. Solids in sample prepared for analysis, by Refractometer, 65.59%; pH of diluted syrup, as prepared for lead number determination, 5.80; colour, 20^+.

Syrup No. 44. - From Louis Mercier, Ste. Hinodone. Midseason sap, old iron evaporator. Solids in prepared sample 65.14%; pH of diluted syrup 6.00; colour, 7^-.

Syrup No. 46. - From producer (name unrecorded) in Megantic County, Que. Solids in prepared sample 66.19%; pH of diluted syrup 6.50; colour 7.

Preliminary Experiments on the Canadian Lead Number.

The preliminary work was carried out on a sample (BM) of syrup received from Byron Mizener, Foster, Que. Solids in prepared sample 68.50%; pH, diluted sample, 6.20; colour, 7.

Experiment 1. - The first preliminary experiment was planned to show whether there was any change in the composition of the precipitate as a result of standing. Sample BM was precipitated with new Horne's (1.25) solution, the pH of which was 7.20. The precipitate was allowed to stand (a) the regulation 2 hours, (b) 100 hours. At the end of these respective periods the precipitates were filtered off, well washed with cold water, and dried in vacuo in a dessicator over sulphuric acid for (a) 14 days, and (b) for 10 days. They were then ground in an agate mortar and lead determined, using Bergh's Method. The salt all went into solution with 15 c.c. of acetic acid. The percentages of lead so obtained were:

(a) 67.33; (b) 66.58

showing that there had been no fundamental change in composition on standing. The precipitates themselves were both of light brown colour. One litre of syrup solution was used, so that the precipitates were quite representative. Both percentages obtained lie midway between the normal malate (Pb = 61.07%) and basic malate (Pb = 73.80%).

Experiment 2. - The object of the second experiment was to determine whether the composition of the lead acetate had any effect on the composition of the precipitate. The reagents used were (a) Solution No. 6, Ratio, 0.93; (b) Solution No. 35, Ratio, 0.73; and (c), Solution No. 61, normal lead acetate. The precipitates were obtained using 540 c.c. of syrup solution, and they were allowed to stand six hours. The precipitates in (a) and (b) were buff-coloured; (c) was chocolate-coloured. The former remained as a very fine suspension in the liquid, the latter was much more flocculent, and settled readily after five minutes. After the precipitates had been prepared as in Experiment 1 (except that drying was performed in vacuo at 105° for 12 hours) they were analyzed for lead content with the following results:

(a) 68.30; (b) 67.95; (c) 62.10.

There was a very slight residue in the acetic acid solution remaining undissolved, even on boiling, in (a) and (b), which would mean that the figures above do not connote the true lead percentage; the true percentage would be slightly higher. The undissolved residue glistened somewhat, having the appearance of small pellicles of lacmoid. The chromate solutions had to be refiltered before a clear solution could be obtained, in (a) and (b). The solution of (c) in acetic acid suffered the same drawbacks as (a) and (b), but the percentage obtained though again not absolute; tends to show that the normal reagent produces a precipitate tending towards the normal malate, and that more basic solutions give a precipitate containing a higher percentage of lead.

Experiment 3. - The purpose was to ascertain the effect of different periods of standing on the weight of the precipitate. The results are enumerated below. The syrup used was No. 40, the reagent a Horne's solution. The beakers were covered with watch glasses. Single determinations only were performed. That the increases may be due to formation of carbonate and not to further precipitation of lead malate compound is suggested by the following observation. Excess of reagent was added and the lead-maple precipitate dissolved. The mixture was allowed to stand. A cloudiness first appeared, then a precipitate fell, gradually increasing each week. At the end of four weeks, the unfiltered mixture was tested with dilute nitric acid and vigorous effervescence obtained.

The maximum amount of precipitate seems to be obtained in about 25 hours.

Effect of Standing on Weight of Precipitate.

Time, in Hours.	Colour of Ppt.	Weight of Ppt.
20	L. chocolate.	.2870
4.0	L. clay	.3182
6.1	Chocolate.	.2976
16.0	Chocolate.	.3125
25.0	L. clay.	.3290
50.0	Clay	.3025
100.0	Slate.	.3153

Experiment 4.- Experiment 4 was to find out the point of maximum precipitation. The precipitates, from 20 c.c. of syrup and Horne's solution, were allowed to stand six hours. The precipitate seemed to dissolve greatly when 9 c.c. of subacetate solution had been added. The results obtained are presented below.

Point of Maximum Precipitation.

No. c.cs. Added.	Colour of PPt.	Weight of Ppt.
0.5	Buff.	0.1339
1.0	Buff-clay.	0.1854
2.0	M. buff.	0.2016
5.0	L. buff.	0.1267
7.5	M. buff.	0.0660
10.0	D. fawn.	0.0156

Experiment 5. - This experiment was a corollary to Experiment 4, and was carried out to see the effect of adding 2 c.c. of reagent solution containing different amounts of lead. The check experiment was carried out by using that number of c.cs. of reagent that contained 0.45 g. of total lead. The weights of lead per 2 c.c. of the same reagent is shown adjacent. The results are tabulated in Table 10.

Table 10.

Effect of Varying Total Lead Content of Reagent.

Reagent Soln.	Canadian Lead Number.		Gms. of Pb per 2 c.c.	Color of ppt.	
	Check(.45g.Pb)	Using 2 c.c.		Check	Using 2 c.c.
4	3.32	3.18	.4864	LBr.	DiW.
5	3.44	3.49	.5106	B.	GW.
6	2.73	3.80	.4933	VLBr.	GB.
10	3.65	5.15	.3036	LBr	W.
11	3.69	4.18	.9687	LBr.	G..
13	2.84	2.20	.9331	LB.	B.
14	2.97	2.29	.9038	B.	LBr.
15	2.88	2.12	.8435	B.	B.
16	4.05	4.98	.2311	B.	W.
17	4.14	5.83	.2311	DiW.	GW.
18	3.84	4.89	.2311	B.	W.
19	3.87	4.22	.3243	B.	W.
20	4.05	3.32	.4865	B.	B.
23	3.21	3.14	.4830	S.	B.
27	4.01	4.16	.3657	VLBr.	B
28	4.01	4.55	.2036	B.	DiW.
29	4.18	4.71	.2967	SF.	YW.
36	4.05	4.31	.3639	LBr.	GW.
55	2.45	2.46	.5778	B.	B.
56	3,38	2.23	,0879	S.	S.

Note:- For Key to colors, see Table 11

Determinations of Genuine Syrups.

The determinations on the three genuine syrups were all made using the number of c.cs. of reagent containing 0.45 g. of total lead. The actual number used is indicated in Table 7, a slight amount of latitude being allowed. Thus with solutions containing from 0.43 to 0.47 gram of total lead per 2 c.c., 2 c.c. were used.

The standing time was about 22 hours, the extremes being 18 and 25 hours, in order to get the maximum weight of precipitate. In any one series, however, the total time of standing was the same for each determination, the filtrations being carried out seriatim in the same order as the reagent was added. Table 11 gives the results of these determinations.

Determinations on a Synthetic Malate Solution.

In order to determine whether the degree of precipitation of malic acid by the different reagents was the cause of the variation in weight of the precipitate, determinations were carried out on a solution closely approximating the composition of the maple syrup solution it its composition of malates. By this means the complicating effects of precipitation of caramel, reducing sugars and other precipitable substances present in the syrup solution were avoided. This synthetic solution was made up as follows:-

Constituent.	Weight, Grams.
(a) Sodium malate, $Na_2(C_4H_4O_5)4H_2O$	0.6394
(b) Magnesium malate, $Mg(C_4H_4O_5)$	0.7376
(c) Potassium malate $K_2(C_4H_4O_5)$	3.1183
(d) Calcium malate, $Ca(C_4H_4O_5).H_2O$	3.740
(e) Water, to	Two litres.

The sodium malate and calcium malate used were samples prepared at Macdonald College in 1922 and 1923 respectively. Since potassium and magnesium malates crystallize, like sodium malate, only with great difficulty and after long periods of time, malic acid (M.P. 99.08^{o}) was exactly neutralized with potassium hydroxide (using phenolphthalein), and in the second case treated with the theoretical quantity of magnesium carbonate. The concentrations of the solutions were then determined by evaporating 10 c.c. to dryness, and the number of c.cs. representing the required weight taken for the synthetic solution. This solution contains approximately 0.95 per cent of malic acid as salts, (the bases being present in the same ratio as in the genuine syrup,) which is the average figure for the natural product. It had a pH value of 6.80. An inappreciable amount of the calcium malate did not dissolve and was separated from the solution by filtration.

The precipitate obtained in this case was quite white, and gelatinous, settling readily. There was a slight tendency to stick to the beaker after it had stood

24 hours, except in the case of the Solutions 41, 61, 66 and 67. These four solutions all had pH values below 7.0. The best "break" was observed in Solution No. 61. The amount of these precipitates was much less than usual, and in common with those produced by these reagents with the three syrups investigated, did not crack whilst filtering or even after drying. The rate of settling of the precipitate obtained with all the artificially aged solutions was much better than in the other cases.

The amount of lead in the precipitate thrown down in the synthetic solution was determined. Seven hundred c.c. of solution were precipitated with Horne's subacetate and after appropriate preparation (drying was overnight at 100 - 105° in vacuo) the lead was determined, using the Bergh method as before. The determination was made in triplicate and the per cent of lead found to be

(1) 74.90 (2) 73.623 (3) 74.90.

The difficulties of solution of the precipitate in acetic acid which were experienced in Experiment 2 did not occur. The precipitate in this instance approximates very closely the basic malate of lead.

The results of the precipitation of the synthetic solution are presented in Table 11, as Lead Numbers. No experiments were made in this solution to which sucrose had been added.

Table 11.

Canadian Lead Numbers.

Reag, Sol'n.	Syrup 40	Ppt. Color	Syrup 44	Ppt. Color	Syrup 46	Ppt. Color	Synthetic Solution.
1	6.28	DG	3.72	B	2.96	DiW	4.28
2	6.56	Br.	4,46	MB	3.11	-	4.45
3	6.22	G	3.82	S	2,88	-	4.20
4	7.62	MG	4.32	S	3.32	LBr	4.70
5	7.13	G	4.22	B	3.44	B	4.81
6	8.85	G	4.79	S	2.73	VLBr	5.13
10	10.94	S	2.75	MB	3.65	LBr	5.17
11	7.05	F	4.03	Cr.	3.69	LBr	4.70
13	5.72	F	3.78	LB	2.84	LB	4.15
14	4.13	LBr	3.27	MB	2.97	B	3.64
15	4.48	DG	3.10	DB	2.88	B	4.96
16	10.11	G	7.00	LB	4.05	B	6.27
17	12.70	G	3.91	LB	4.14	DiW	6.35
18	10.86	G	5.34	B	3.84	B	6.30
19-	8.79	G	4.88	B	3.87	B	5.42
20	8.18	G	3.68	MB	4.05	B	4.85
21	6.82	F	4.37	VLB	3.30	B	4.51
22	6.63	SI	3.40	MB	3.39	B	4.54
23	6.23	LG	3.96	MB	3.21	S	4.07
24	5.17	Sl	3.76	MB	2.23	B	2.07
25	4.90	G	3.92	MB	2.69	GB	3.77

Table 11 (Cont'd).

Reag, Sol'n.	Syrup 40	Ppt. Color	Syrup 44	Ppt. Color	Syrup 46	Ppt. Color	Synthetic Solution.
26	4.22	G	3.33	LB	2.57	DB	3.59
27	8.99	F-	4.87	MB	4.01	VLBr	5.39
28	10.59	Sl.	5.68	MB	4.01	B	6.16
29	9.98	Sl.	5.71	MB	4.18	SF	6.20
30	10.19	F	6.57	B	4.06	B	6.50
31	10.79	G	5.97	MB	4.44	B	6.99
32	8.17	LF	5.64	B	4.03	LB	5.36
33	9.01	LF	5.66	MB	3.50	B	5.02
34	5.05	Sl.G	4.86	B	3.53	YB	5.10
35	9.78	Sl.	4.91	B	3.62	LB	5.16
36	8.54	LBr	4.98	VLB	4.05	LBr.	5.42
37	8.20	G	4.57	LCr.	3.24	SY	5.04
38	9.15	DG	4.96	B	3.43	B	4.84
39	8.50	Sl.	6.26	B	3.47	GB	3.89
40	9.39	VLBr.	4.87	LB	3.86	B	5.32
41	0.43	VDC	0.09	W	0.16	DBr.	0.10
42	6.17	DG	4.00	B-	2.98	B	4.15
43	6.90	G	3.94	B	3.75	LBr.	4.45
44	6.20	Sl.	4.09	LB	3.13		4.17
45	6.48	LSl.	4.04	B	2.96		
46	4.82	SlBr	3.63	B	2.55		3.86
47	6.42	Sl.	3.98	B	3.04		4.30
48	5.11	DSl.	3.32	LB	3.02		3.89

Table 11 (Cont'd).

Reag. Sol'n.	Syrup 40	Ppt. Color	Syrup 44	Ppt. Color	Syrup 46	Ppt. Color	Synthetic Solution.
49	6.36	Sl.	3.97	MB	3.08		4.26
50	6.17	DSl.	3.98	MB	3.03	DiW.	4.29
51	5.74	Br.	3.92	MB	3.09		4.08
52	6.18	GBr	4.37	MB	2.83		4.37
53	5.92	DSl	4.03	MB	2.89		4.18
54	4.82	Br.	3.86	MB	2.93		4.23
55	3.80	C	3.27	LB	2.45	B	3.57
56	6.10	Br.	4.10	MB	3.38	S	2.96
57	6.39	Sl.	4.24	MB	3.42		4.26
58	5.99	Sl.	4.09	B	3.05		4.10
59	6.59		4.18	Sl.	3.05	MB	4.28
60	5.57		4.11	LSl.	2.99	LBr.	4.15
61	1.15		1.31	LCBr.	0.10	GB	0.94
620	6.77		3.93	LF	3.12	B	4.50
63	6.98		6.58	Sl.	3.37	MB	4.60
64	6.54		4.38	Sl.G	3.46	B	4.46
65	6.26		4.11	SlG	3.27	B	4.03
66	1.91		0.15	DCBr.	0.90	CrB	0.136
67	1.18		0.072	CBr.	0.50	F	0.018

Key to Colours.

B - Buff
Br - Brown
C - Chocolate
Cr - Cream

D - Dark
Di - Dirty
F - Fawn
G - Grey

L - Light
M - Medium
S - Sand
S - Slightly

V - Very
W - White
Y - Yellowish
Sl - Slate

Discussion of Results.

A cursory examination of Table 11 reveals the wide variation which occurs. Regarding only the basic solutions, a Lead Number of 12.70 is obtained in Syrup 40 with Solution No. 17, (pH 8.95) and a Number of 3.80 with Solution 55 (pH 7.30). In Syrup 44, Solution 16 (pH 9.00) gives a number of 7.0, and solution 10, (pH 8.2) a number of 2.75. Solution 10, however, gives one of the higher values (5.17) with the synthetic solution; here Solution 31 (pH 9.00) gives the highest and Solution 24 (pH 7.40) the lowest Lead Number. The lowest Lead Number (2.45) in Syrup 46 is given by the solution (55) with the lowest pH (7.30); solutions (25,26,54) of similar pH (7.50, 7.30, 7.35) giving similar low values (2.69, 2.57, 2.93); the high value for Syrup 46 is likewise given by a reagent (Solution 31) of high pH value (9.00). All the reagents of pH less than 7.0 gave extremely low results.

The results with the "aged" solutions indicate what may happen when old subacetate solutions are used. Figure 1 effectively depicts the interrelation of hydrogen ion concentration and Lead Number. The behaviour of the synthetic solution is curious. It appears that within the range covered by pH 7.2 and pH 7.5, precipitation may increase rapidly without respect to pH. The change of reaction has relatively greater effect within this range than on either side. Were it not for the fact that an increase of pH is accompanied by increase in precipitation, one would be inclined to regard 7.35 as the point at optimum precipitation of the lead malate compound. In all four cases the maximum precipitate is given at this pH of about 9.00. The fact that the change from pH 7.2 to 7.5 may be accompanied by a change in Lead Number of 1.9 to 4.2 is significant, inasmuch as the reaction of the basic lead acetate solutions generally used in the Canadian Lead Number has been within this range.

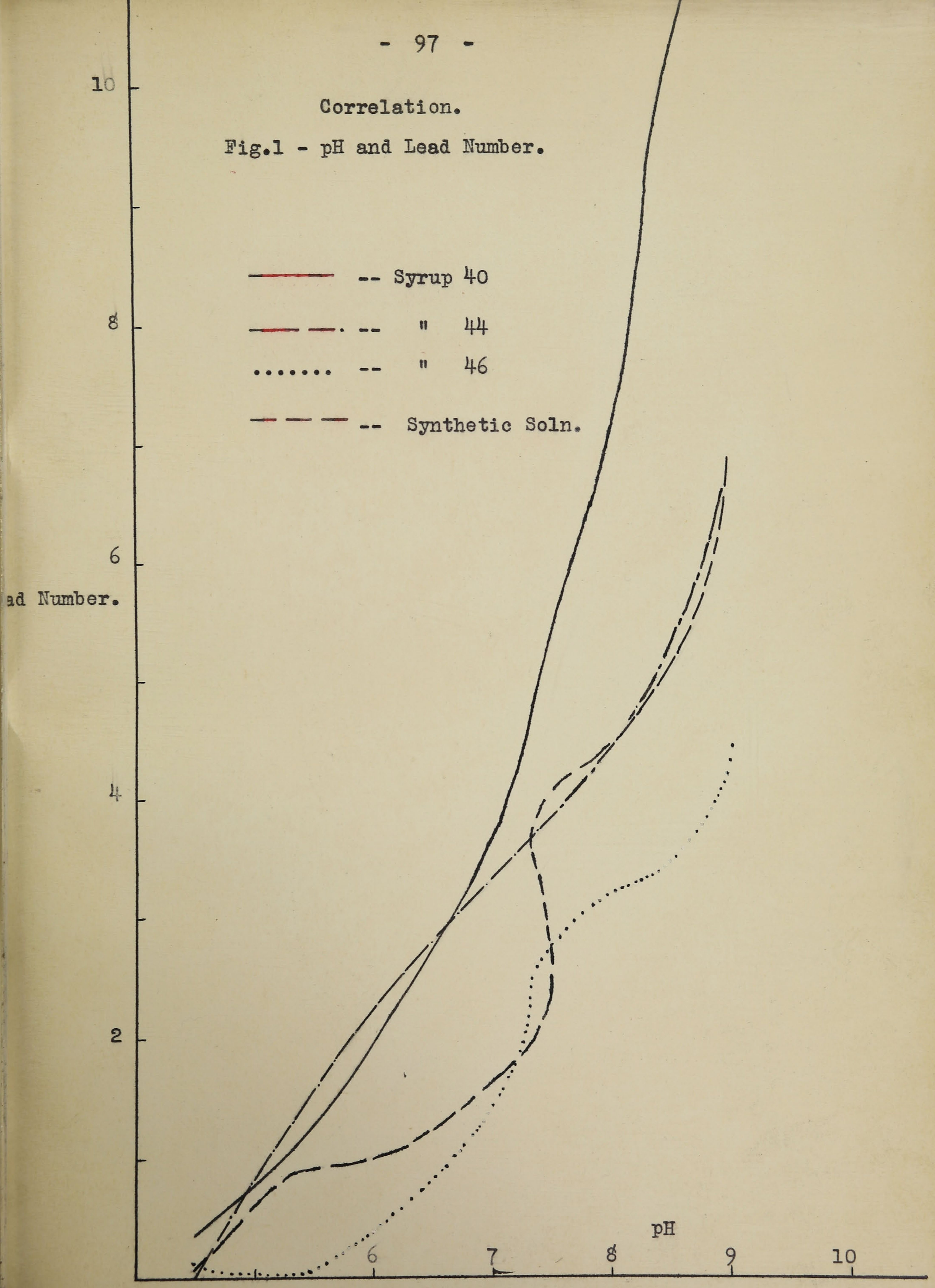
Lest, however, an undue amount of importance be attached to pH, attention must forthwith be drawn to the results of Preliminary Experiment No. 5, from which it appears that 2 c.c. of reagent is not always the amount to be used for best precipitation. The complicating factor arises that this optimum amount will vary not only with the reagent itself, but also with each syrup. The fundamental cause seems to be that for maximum precipitation the amount of basic lead must be at an optimum concentration. With dark-coloured syrups and products of high ash and reducing sugar content the amount of basic lead necessary to effect domplete clarification will naturally be higher than in a product where the values are low, so that using the same solution different amounts must be used with every individual syrup. When different reagent solutions are used the amount will also vary with the basicity of the solution; it will not be necessary to use as much of one solution as of another which is lower in ratio. If the volume of reagent is specified, the addition of such volume of a very basic solution, even though of identical specific gravity, may result in excess of basic acetate required for maximum precipitation, whereupon some of the precipitate will dissolve. This can be avoided only by making tedious preliminary experiments on every individual sample before analysis. Since in control work such a procedure is undesirable, it was considered best in this work to adopt the practice of adding a definite amount of total lead, what appeared to be best for precipitation, i.e.,0.45 gram, and since each separate reagent differed in ratio, to attribute any difference in results to amount to basic lead or in other words, the alklainity. This is not strictly correct, because neutral lead also contributes to the precipitate - the neutral salt giving values in Lead Number work as well as the basic salt. It is not considered, however, that the error introduced can be appreciable enough to invalidate the broad conclusions which may be reached.

In order to assign an effect to the basic lead content the Lead Numbers have been plotted against both the Alkalinity and the Ratio, in Figures 2 and 3. Both these values are measures of the basic lead content. The curves do not show the steady character of the pH curves. Evidently at a point B, corresponding to a basic lead content expressed in terms of alkalinity as 7.4, we have the best conditions for precipitation. A glance at Table 7 will suffice to show that pH and alkalinity are not related so it must be deduced that the point of maximum precipitation is the result of the cumulative effect of at least two factors. Yet another factor the effect of which is unknown is the presence of sucrose. The extreme range obtained in Syrup 40 (3.80 - 12.70) suggests that possibly varying degrees of precipitation of other solids in the syrup may be the cause, since these extreme variations do not occur in the synthetic solution. The extent of the comparison is, however, limited since it is not known precisely how the solids in the syrup (40) in question compare with the average composition as represented by the synthetic solution.

Figure 3 shows that the importance which has hitherto been placed on ratio properly attaches elsewhere. As the ratio rises the general tendency is for the Lead Number to fall. Higher numbers are obtained with low ratio, but whether importance is to be attached to the ratio _per se_. or to the ratio because it influences the amount of basic lead which is used when the customary volume of reagent is measured, cannot be stated from the results of the present investigation. The question as to _why_ there should be an increase in weight deserves further study.

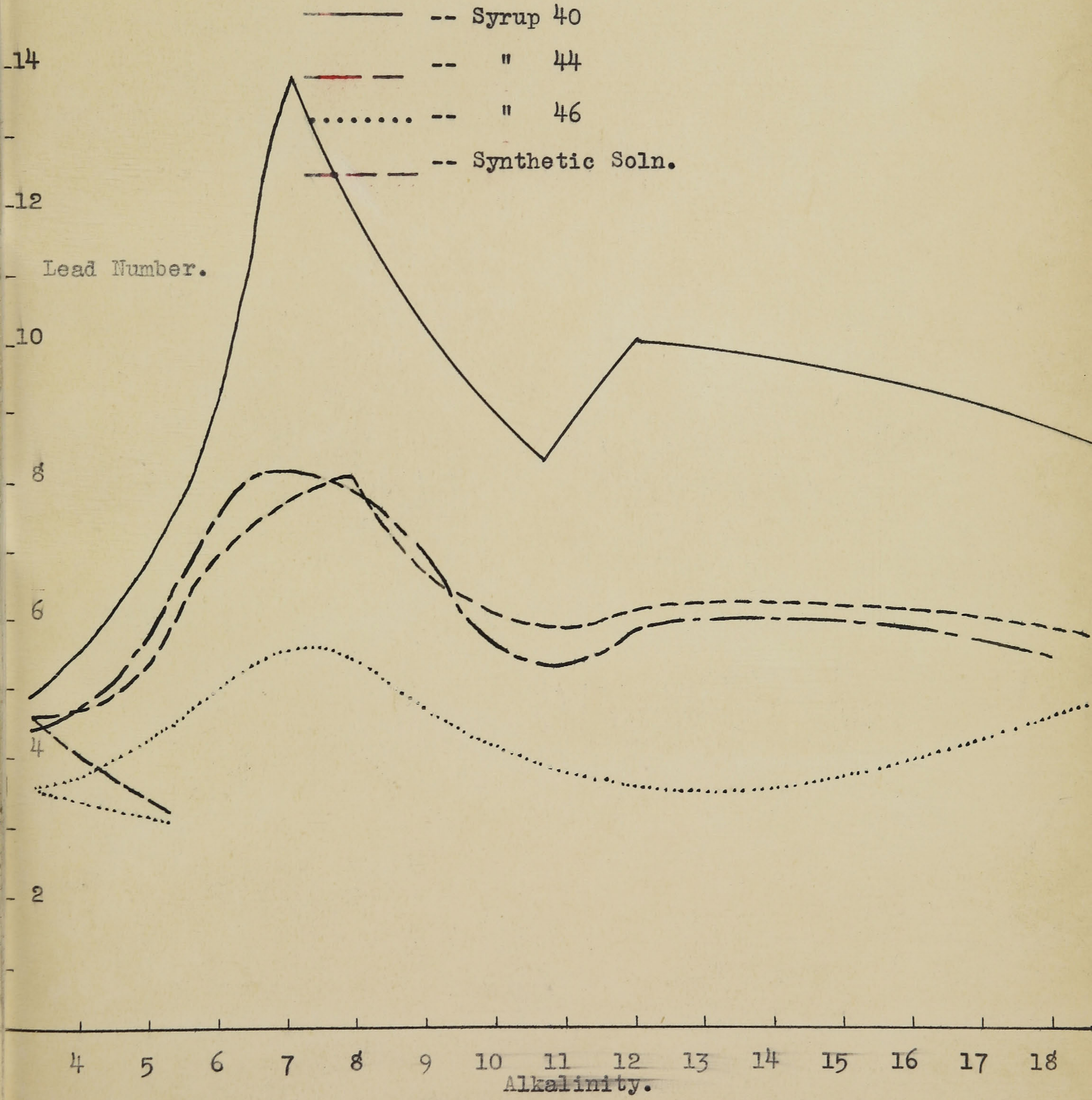
Correlation.

Fig.1 - pH and Lead Number.



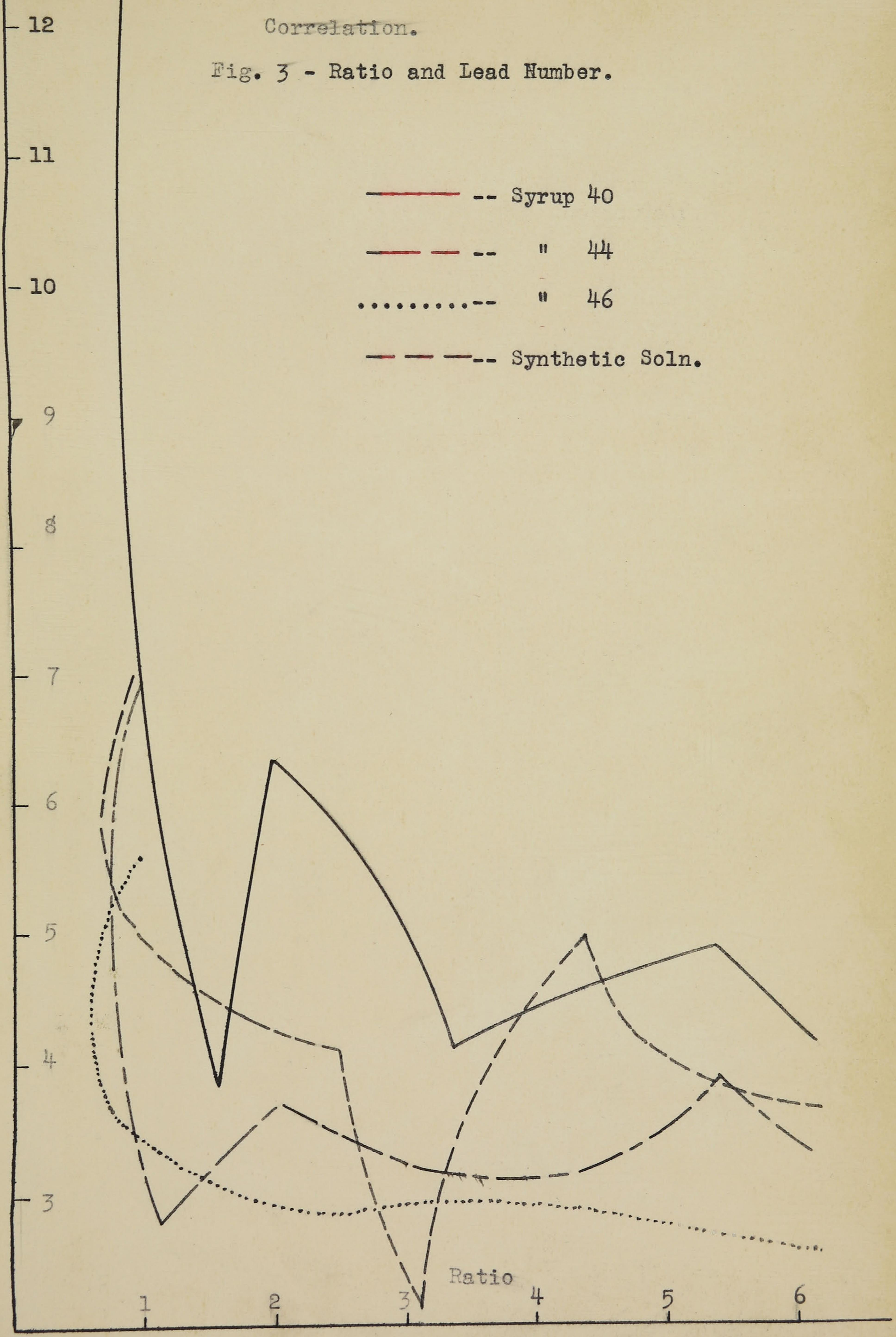
Correlation.

Fig. 2 - Alkalinity and Lead Number,



Correlation.

Fig. 3 - Ratio and Lead Number.



SUMMARY.

1. Basic Lead Acetate preparations have been made by "dry" interaction of lead oxide and lead acetate. Solutions have been prepared varying widely in ratio of neutral to basic lead, and in pH.
2. Determinations of the Canadian Lead Number show that higher Lead Numbers are obtained with reagent solutions of high pH value. The normal acetate solutions low in pH (acid) gave low numbers.
3. Indications have been obtained that maximum precipitation also occurs at an alkalinity of about 7.4.
4. The changes occurring in lead subacetate solutions on standing are explained.

ACKNOWLEDGMENTS.

The writer wishes to acknowledge his indebtedness to Dr. J.F. Snell, Professor of Chemistry, Macdonald College, for valuable assistance and advice extended throughout this investigation. Besides supervising the work Dr. Snell very willingly allowed access to his private notebooks and correspondence, and also to Departmental Records.

It is also a pleasure for the writer to express his keen appreciation and gratitude to Mr. S.P. Newton of the Sherwin-Williams Co. Ltd., Montreal, who supplied samples of basic lead acetate for study, and also to Mr. F. Bull, who carried out the Analysis on Litharge, and furnished samples of "Barton oxide".

References.

(1) Snell, J.F., J.A.O.A.C., 4, 428-443, (1921).

(2) Lancaster, H.M., J.A.O.A.C., 8, 372-4, (1925).

(3a) Ross, S.H., U.S.D.A. Bur. Chem., Circular No.53 (1910).

(3b) Fowler, D.E., "A Study of the Reactions between Solutions of Maple Syrup and Basic Lead Acetate with Particular Reference to the Canadian Lead Number." M.Sc. Thesis, McGill University, 1928, (unpublished).

(4) Wittstein and Kühn, Buchners Rep., 84, 181.

(5) Payen, Ann. Chim. phys., (2), 66, 46, (4), 8, 303.

(6) Löwe, J. prakt. Chem., (1), 98, 385 (1886).

(7) Pelouse, Lieb. Ann., 42, 206 (1842).

(8) Schindler, Archive d. pharmazie, 91, 133.

(9) Wittstein, Annalen, 52, 523.

(10) Browne, C.A., Handbook of sugar analysis, p.207.

(11) Stolle, Handbuch für Zucherfabriks Chemiker, p.527.

(12) Wohler, Lieb. Ann., 29, 63 (1839).

(13) Krönig, Walter, Z. angew. Chem., 37, 667-72 (1924), in C.A. 19, 221, (1925).

(14) Plöchl, Berichte der Deutschen Chemischen Gesellschaft, 13, 1647.

(15) Jackson, R.F., "Equilibrium in the System: Lead Acetate, Lead Oxide, and Water, at 25°C.." J.A.C.S., 36, 2346 (1914).

(16) White, C., and Patterson, J.W., British Patent 9638, April 23, 1912, in C.A., 7, 3425 (1913).

(17) Ges, Dr. Kalkow, British Patent 29048, Dec.16, 1913, in C.A., 9, 1551 (1915).

(18) Eyton, A.T., and Henderson, F.J., U.S. Patent 1206685, in C.A., 11, 192, 2720 (1917).

(19) Lloyd, G.F., Clapp, F.B., and Campbell, F.H., British Patent 203301, July 1923, in C.A., 18, 573 (1924).

(20) Plaueln, R., British Patent 224,199, Oct.30, 1923, in C.A., 19, 1181 (1925).

(21) Mitscherlich, E., Jour. prakt. Chem., (1), 19, 451 (1840).

(22) LeBlanc, F., Jour. Pharm. Chim., (3), 8, 181 (1845).

(23) Ruer, Rudolph, Z. Anorg. Chem., 50, 265 (1906).

(24) Appleby, M.P., and Reid, R.D., J. Chem. Soc., 119. 1689, 1914 (1921).

(25) Fales, Harold A., "Inorganic Quantitative Analysis," p. 248.

(26) Wark, I.W., "The Copper Complexes with Hydroxyacids", Chem. Eng. Mining Rev., 19, 76-7 (1926), in C.A., 21, 544 (1927).

(27) Dede, L., and Becker, T., Zeit. Anorg. Chem., 152, 185, (1926).

(28) Trillat, Auguste, Compt. rend., 136, 1205, (1903).

(29) Kolthoff, M., Pharm. Weekblad, 57, 252-265, (1920) in C.A., 14, 1409 (1920); also in "Indicators", (John Wiley & Sons, Inc.,).

(30) Kellner, J., Chem. Umschau Fette, Gele, Wachse Harze, 34, 330 (1927), in C.A., 22, 743 (1928).

(31) Frühling, "Anleitung", p.457, in Browne "Sugar Analysis" (1912), p.208.

(32) Kolschütter, V., and Rosti, H., Ber., B 285, (1923).

(33) Knight, W.A., Chemist and Druggist, 102, 934 (1925), in C.A., 20, 2389 (1926).

(34) Bechamp, J., quoted in Mellor "Treatise on Inorganic and Theoretical Chemistry", Vol.7, p.657.

(35) Rochleder, F., Sitzber. Akad. Wein, 29, 3, (1858).

(36) Kubel, W., Arch. Pharm., 230, 175 (1892).

(37) Woodman, D., J.A.C.S., 19, 339, (1897).

(38) Browne, C.A., U.S.D.A., Bur. Chem. Bull. 122, p.223 (1908).

(39) "Methods of Analysis", Assoc. Off. Agr. Chem., p.114 (1921).

(40) Bergh, G.F., Apoth. Ztg., 24, 291 (from Svensk Farmaceutisk Tidskrift, pp.101-7 (1909).), in C.A., 3, 2611, (1909).

(41) Chwala, A., and Colle, H., Z. Anal. Chem., 50, 209-249, in C.A., 5, 2609 (1911).

(42) Bain, J.W., and Wynn-Roberts, R.I., Can. Chem. and Mett., 8, 62 (1924).

(43) Schulten, A., Bull. Soc. franc. mineral, 27, 129 (1904).

(44) Vosburgh, W.C., J.A.C.S., 44, 2120 (1922).

(45) Free, Jour. Phys. Chem., 13, 114, (1909).

(46) Jbloczynski, J.S., Chemische Industrie, 31, 731 (1908).

(47) Vesterberg, K.Alb., and Palmer, Eva: Arkiv. Kemi. Mineral. Geol., 9, #43, 6 pp. (1927), in C.A., 22, 43 (1928).

(48) Rose, H., Pogg. Ann., 84, 59 (1851), Jour. prakt. Chem., (1) 54, 24 (1854).

(49) Altmann, A., Z. Anorg. Chem., 52, 219-228 (1907).

(50) Yamaski, J., Mem. Coll. Sc. Eng., 1, 177-183; 275-76, in C.A., 1, 2533 (1907).

(51) Hochstetter, C., Jour. prakt. Chem., (1), 26, 338, (1842).

(52) Salvadori, R., Gazz. Chim. Ital., 34, i, 87 (1904).

(53) Sacher, J.F., Chem. Ztg., 35, 326, (1911).

(54) Euston, E., Jour. Ind. Eng. Chem., 6, 382 (1914).

(55) Erdmann, O.L., Jour. prakt. Chem., (1), 81, 177, (1860); (1), 82, 317, (1861).

(56) Dennstedt, M., and Hassler, F., Zat. anal. Chem., 42, 417, 1903.

(57) (a) Mellor, J.W., loc. cit., p.835; (b) p.836.

(58) Falk, L., Chem. Ztg., 34, 937; in C.A., 5, 213 (1911).

(59) Bryan, A.H., U.S. Dept. of Agr., Bur. Chem. Bull. 134, p.89.

(60) Auerbach, Fr., and Weber, H., Zeit. anorg. Chem., 147,68-80 (1925).

APPENDIX.

EQUILIBRIUM IN THE SYSTEM: LEAD ACETATE, LEAD OXIDE, WATER.

Isothermal Equilibrium at 25° (after Jackson).

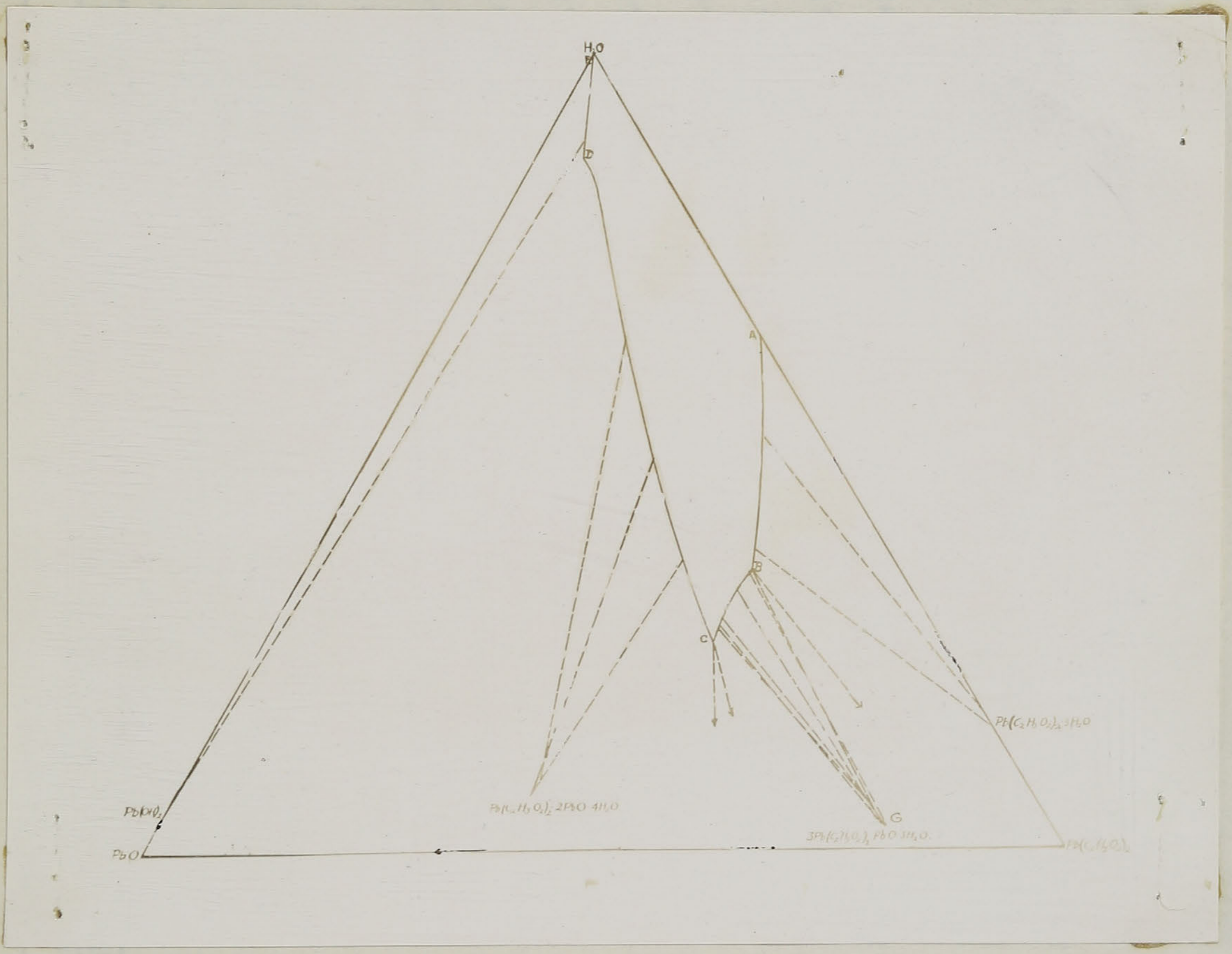


Figure 1. - The curves AB, BC, CD, and DE represent the composition of the solution in equilibrium with the respective solid phases. The area ABCDE encloses the region of unsaturated solutions. Note the great increase of solubility of the neutral acetate in basic solutions, the high solubility and limited range of stability of the monoxyacetate and the very great range of stability of the dioxyacetate. The data are computed with respect to weight per cent.

Changes in Basic Lead Acetate Solutions at Macdonald College.

Mark	Total Lead per c.c.						Ratio (N-B.Lead)		Alkalinity		
	Dec.'17	Jan.'18	Aug.'18	Jan.'19	Ap.'24	Feb.'28	1917-8	1928	Jan.1918	Jan.1920	Feb.1928
AA	.2381	-	-	.2305	-	.2190	1.634	1.886	8.73	8.57	7.95
BA	.2324	-	-	.2295	-	.2389	1.626	2.693	8.55	8.52	7.30
CA	.2308	-	-	.2300	-	.2320	1.598	2.022	8.58	8.675	7.70
DA	.2287	-	-	.2315	-	.2243	1.910	4.652	7.59	7.95	5.50
EA	.2297	-	-	.2305	-	.2268	1.907	2.573	7.63	6.97	6.85
FA	.2343	-	-	.237	-	.2281	1.997	3.687	7.55	6.58	5.50
GA	.2290	-	-	.244	.2232	.2381	1.853	2.066	7.75	6.645	7.80
HA	-	.2315	-	.2335	-	.2259	2.050	2.447	7.33	6.13	6.70
IA	-	.2339	-	.2333	-	.2199	?	1.965	9.31	8.065	7.60
JA	-	.2357	-	.2365	-	.2321	?	2.666	7.72	6.79	5.75
KA	-	.2387	-	.2430	-	-	1.349	-	9.91	9.88	-
LA	-	.2324	.225	.2250	-	-	1.426	-	9.25	7.17	-
MA	-	-	-	.2390	-	.2363	?	3.644	?	7.075	5.15
NA	-	-	-	-	-	.2889	?	4.583	?	8.875	3.40
VZB	-	-	.2341	-	-	-	?	1.550	8.55	8.89	-
VZW	-	-	.2329	-	-	.2234	?	1.815	9.65	8.675	8.00
MMA	?	-	-	-	-	.2327	?	2.662	?	-	6.90
MMB	-	-	.2320	-	-	.2311	?	1.977	9.15	8.65	8.20
NCM.1	-	-	.2370	-	-	-	?	-	8.10	7.525	-
NCM.2	-	-	.2150	-	-	.2199	?	2.035	7.45	6.515	5.80