MICROCHEMICAL DETERMINATION OF MINERALS

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OF MINERALS

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ABBREVIATIONS AND SYMBOLS

N = Index of refraction.

O = Ordinary ray.

E = Extraordinary ray.

No = the index of refraction of the ordinary ray in uniaxial minerals.

Ne = the maximum (in positive) and the minimum (in negative) index of refraction of the extraordinary ray in uniaxial minerals.

X = the vibration direction of the fastest ray.

Y = the vibration direction of the intermediate ray.

Z = the vibration direction of the slowest ray.

Np = the index of the fastest ray in biaxial minerals. The least index of refraction.

Nm = the index of the intermediate ray at right angles to X and Z.

Ng = the index of the slowest ray in biaxial minerals. The greatest index of refraction.

2V = the optical axial angle.

The description of each method of detection is given in the following order:

Reagent:

Product:

General description, including procedure, test solution used, reaction, physical properties, chemical properties, optical properties, and characteristics of the crystalline precipitates separated.

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PREFACE

ABBREVIATIONS AND SYMBOLS

PREFACE

Microchemical analysis is one of the many methods used in the chemical examination of minerals. This method requires a petrographic microscope and also a knowledge of optical mineralogy. Since the microchemical method requires only a small sample, it is preferable to other methods in determinative mineralogy. The purpose of this paper is to present a description of the characteristic reactions and of the optical properties of the resultant crystalline precipitates of certain common elements. The optical constants are worked out in detail, in so far as the technique used permits. It will be noted that a number of these are not in complete agreement with those given in authoritative tables. An attempt has been made to interpret the interference reactions resulting from the test solution of some complex minerals with the reagents, in the hope that they may prove useful to the detection of cations and, therefore, to the determination of the composition of minerals.

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INTRODUCTION

Historical Review

Microchemistry has been developed only in the last fifty years. The earliest work was done in biological and pharmaceutical fields. The pioneer investigations in microchemistry were carried out by Sachs, a German botanist, who worked out methods for the investigation of germination in 1860. In 1867 Wormley published his "Microchemistry of Poisons" (22). Although the application of microchemistry to determinative mineralogy had been suggested by Boricky (4) in 1877, development along this line was slow up to the time of Behrens (1), whose "Manual of Microchemical Analysis" was published in 1894. Since 1923 when Pregl received the Nobel Prize for his work in microchemistry, microchemistry has gradually developed as an important method for the investigations of its allied sciences. Substantial progress in the technique of qualitative micro-analysis has been made by Behrens and Emich (1, 8). In America the first systematic work was introduced by Chamot and Mason, 1930 (6).

It is noteworthy that many descriptions of detection of minerals by microchemical tests have been published in recent geological literature. This shows that the microchemical method has attracted the serious interest of many mineralogists and it has become an important tool in the fields of economic geology and mineralogy. Short has written some works on microchemical tests of ore minerals (16), but it is lacking in some of the interference reactions which are often met in the detection of elements in minerals of heterogeneous composition. Recently, the relation of interference reactions has been emphasized and the identification of crystalline precipitates by their optical properties has come to be considered more important than the mere recognition of coloration and crystal form.

Scope and Advantage of the Present Work

Microchemistry is a term of broad sense. According to the quantity of sample used in analysis, the microchemical work may be operated in various scales, such as spot tests in semi-microanalysis, chemical microscopic analysis in intermediate, and spectrochemical analysis in ultra-micro scales. For purposes of investigation, special instruments are employed, as the micromanipulator for biology, polarizing microscope for mineralogy, and the spectrograph for physics. The most simple and convenient way for micro-qualitative analysis of minerals is by means of the microscope. 'Chemical Microscopy', introduced by Chamot and Mason, includes the micro-methods of identifying crystalline precipitates by their colors, geometrical forms, and optical properties, under the microscope. In preparing these precipitates for the detection of elements, the writer follows the procedures somewhat like those proposed by Chamot and Mason (6).

There are many advantages in the use of the microscope in microchemical determination of minerals. Less material, reagents, and time are required; also the crystalline compounds can be correctly and accurately detected by optical crystallography than by other analytical methods.

Many useful methods of detection of elements have been offered by Chamot-Mason, Short and Staples (17). The last edition of Chamot-Mason is the most complete and exhaustive so far published, but to date not much work in interference reactions has been done. Fortunately, Fraser (10) presented concise information regarding these and the characters of the interference products. His work appears to be quite important in the testing of minerals of heterogeneous composition. In this aspect the present writer will give some new descriptions of other reagents as will be shown in the section of "Interference Reactions and Group Reactions".

There are twenty-two common elements to be discussed in this paper. The methods of detection are selected for the availability of reagents, sensitivity of reactions, and the rapidity of crystalline precipitation. The reactions between many of the reagents and the individual elements are mentioned in chemical literature and will not be discussed in detail in this paper. The last section deals with the possible interference reactions of elements with the eight reagents which are the important ones suggested by the writer for the present work.

The present investigation is intended to emphasize the identification of crystalline precipitates based on the determination of their optical properties. Further studies remain to be done on the isomorphous compounds from various reactions and on the interference reactions of other reagents, which do not appear in this thesis but are found very useful.

PREPARATION OF MATERIAL FOR MICROCHEMICAL DETERMINATION

Physical and Chemical Examination of Minerals

In order to reduce labor and time, a preliminary physical examination of the mineral to be tested is advisable. If a hand specimen or a large-sized fragment of the mineral is to be tested, sufficient information regarding its properties can be obtained from its crystal habit, cleavage, fracture, hardness, luster, streak, specific gravity and associated minerals. If the mineral is of small size or in the form of a polished section, some characteristics should be noted, such as genetic relationship, and behaviour in various reagents by etching tests. If the mineral is opaque, the optical properties in vertical and oblique illumination by reflected light should be observed. All the physical properties of a mineral may serve for its positive identification. These are dealt with fairly exhaustively in the literature of optical and determinative mineralogy.

The chemical properties of a mineral are of fundamental importance, for upon them all other properties are in great measure dependent. Based on chemical composition minerals can be classified into various divisions, such as native elements, sulphides, sulphosalts, sulphates, oxides, silicates, etc. With some exceptions, minerals of each main division exhibit an analogous solubility in certain solvents. The solubility of minerals is given in a complete list in Rogers' "Introduction to the Study of Minerals", and also appears separately under the chapter "Descriptive Mineralogy" in many textbooks. In most cases, the resistance of minerals to acids may furnish excellent information leading to the analytical process. This work may well be carried out in connection with the preparation of the test solution. When a small grain of the mineral to be tested is insoluble in acids, useful information may be obtained from the results of fusion or sublimation by blowpipe test.

Preparation of the Test Solution

In order to produce the precipitates or colorations characteristic of a given element, it is first necessary to dissolve or decompose the mineral. In general, minerals insoluble in water should be treated with acids or fused with fluxes. Dilute nitric acid, or concentrated if required, usually serves as one of the best solventsfor the preparation of test solution. If the mineral is soluble in nitric acid, all cations of the mineral may be converted into a form existing as nitrates or oxides. On evaporation, any isotropic crystal resulting from the nitric test drop indicate the possible presence of As, Ca, Ba, Pb, or Sr (see section on Detection of Arsenic).

If nitric acid fails to dissolve the mineral, aqua regia or sulphuric acid may be applied as a solvent. The material is then converted correspondingly to chlorides or sulphates. For the characteristics of the precipitates of chlorides and sulphates, refer to the section on Interference Reactions and Group Reactions.

If the mineral is soluble neither in water nor in acids, it is necessary to fuse it with fluxes to obtain a solution. Some insoluble sulphates, chromates, tungstates, molybdates, and silicates, should be treated by the method summarized as follows:

In preparing a soluble bead for the test solution of the mineral, the important fluxes to use are borax, sodium carbonate, and sodium peroxide. A clear and transparent bead of Na_2CO_3 or Na_2CO_3 and Na_2O_2 is prepared on a small loop of platinum wire in an oxidizing flame. This bead is dipped into the mineral powder, and heated again. Any coloration of the fused mass resulting from heating should be noted and may give some information concerning the composition of the mineral. Transfer the bead to a micro-beaker and dissolve in water. The solution is well stirred and centrifuged, thus separating into two groups. The filtrate which includes Al, As, Be, Br, Cl, Cr, F, I, K, Mo, Na, P, S, Sb, Se, Si, Sn, V, and W is called Group I. The residue which includes Ag, Au, Ba, Bi, Ca, Cd, Co, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sr, Ti, U, Zn, and Zr is called Group II. The Group II residue is then treated with a few drops of 6N-HCl, and the solution diluted with water, if desired. It should be noted that the following cations may be present in both groups: Al, As, Be, Mn, U, and Zr.

Since the primary examination of physical and chemical properties of the mineral often indicates the possible presence of certain elements, and the successive application of different reagents may confirm this, the identification of elements will not necessarily be carried out in accordance with a fixed analytical scheme. However, the writer recommends the use of the systematic scheme of qualitative analysis without hydrogen sulphide, such as proposed by Cornog (7), Moore (14), Brockman (5), or Whitmore-Schneider (19), for cases of necessity. The latter two have been employed by the writer and have been found quite satisfactory for microanalysis in a mineralogical laboratory.

Manipulative Methods

Owing to the limited scope of this paper, it is not thought necessary to give a detailed description of apparatus and the application of reagents to the test solution. The important apparatus are the polarizing microscope, glass slides, capillary tubes, micro-flame, micro-mortar, and platinum wire. For the precise determination of index of refraction, a complete set of immersion liquids with a range of 1.41 to 2.00 with a regular step of 0.005 should be prepared. Reagents of liquid and solid form are kept in small bottles in wooden blocks. The immersion media and reagents should be checked frequently and renewed if impurities are found.

If a minute amount of the doubtful mineral is to be tested, it may be ground into powder with an agate mortar or scraped down from a polished section into fine grains with dissecting needles or knife points. Transfer the mineral powder to a glass slide or into a test tube, and bring it into solution by means of acids or by fusion with fluxes. If a large fragment of the mineral is employed for the test, it is better to prepare a large amount of test solution in a microtube for successive reactions.

When the test solution is obtained, test for the expected elements by means of suitable reagents. The selection of reagents is based on the nature of the expected mineral and possible presence of interfering cation or anion. The amount and acidity of the test drop, as well as the amount and form (solution or solid) of the reagent, vary with the tests, and will be described under different procedures which the tests must follow. Gentle warming or evaporating to dryness, after or before the application of reagent, should be performed carefully with a micro-flame. Too rapid heating may obstruct the separation of characteristic crystals, and insufficient warming usually produces no reaction products.

If the reagent to be used is in the form of a solution, it is advisable to introduce it by placing a drop of the reagent in the corner of the slide and then cause it to flow into the test drop by inclining the slide or by the aid of a loop of platinum wire. When a fragment of a solid reagent is used for the reaction, it should be added directly to the centre of the test drop to ensure its uniform distribution by convection currents in the test drop. In both cases, the quantity of the reagent introduced should be very small, successive additions of the reagent are applied in the same manner if no reaction is obtained at first.

All the procedures cited above are performed on a work table of convenient size and height. After the addition of the reagent, the slide is transferred to the microscope stage. Observe frequently and note any reactions resulting from the preparation. Objectives of high magnifying power are often used for the resolution of fine-grained products. Great care must be taken to protect the objectives. It is wise to use a cover glass on the object to protect the objective from damage by chemicals. When some characteristic crystals of stable compounds produced on the slide are desired to be used as a permanent preparation, they may be mounted by sealing the edges of the cover glass with Canada balsam.

Microscopical Examination

Microscopical examination is of great importance for the identification of the crystalline precipitates. In the present work the following characteristics were considered necessary for the purposes of description or partial identification:

1. Behaviour in acids, on warming, in suitable amount of reagent, and in excess of reagent.
2. Interference reactions; reactions checked by known solutions.
3. Crystallinity of the reaction product.
4. Crystal habit.
5. Colors by transmitted light, and by reflected light.
6. Optical properties with one nicol and between crossed nicols.
7. Determination of index of refraction.

For characteristics from 3 to 7, the methods are based on the knowledge of optical mineralogy as given in Larsen's description (11), or others. Since a single preparation does not ordinarily give many crystals with different optical orientation, the same reaction products must often be prepared several times for complete determination of refractive-indices.

The description of optical properties given in this paper for some reaction products are incomplete. Reasons for this are: (1) There are very few publications with references to the optical constants of artificial minerals or chemical compounds, because these have not yet been studied thoroughly by chemists or mineralogists. (2) Some crystals separate in extremely thin plates or with abnormal habits, or, due to the surface tension of the drop, float on the drop with their similar crystal faces parallel with each other, so that only one orientation is obtained. (3) For the determination of index of refraction, the immersion media should be applied to the dried-up drop in which the crystals have grown. Unfortunately, some crystals are dissolved or decomposed by certain index oils. (4) Inaccuracy of the value of refractive-indices, reported in this paper, may be caused by the volatility of immersion media and the effects of temperature.

DETECTION OF INDIVIDUAL ELEMENTS

Twenty-two common elements were studied in the present work and the tests chosen include only a limited number of reagents that give sensitive reactions. The following brief descriptions deal with the important reaction products in various chemical environments, and their optical properties. The real identification of any reaction product rests largely upon its optical properties, for the mere observation of coloration and crystal habit usually give unreliable information as to its actual composition.

Detection of Aluminum

1. Ammonium Molybdate Test.

Reagent: Ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$).

Product: Ammonium aluminum molybdate ($3(NH_4)_2O\cdot Al_2O_3\cdot 12MoO_3\cdot XH_2O$) (Figure 1).

Procedure: A drop of the preparation is added to the dried-up drop of the acid test solution. No evaporation is necessary.

Ammonium aluminum molybdate is orthorhombic. Crystals are rhombic, or nearly square 001 plates. Twinning and zoning are commonly seen on 001. Crosses of rhombic crystals are usually produced from moderately concentrated test drop. Gentle heating gives radiating needles and aggregates of slender prisms of unknown composition.

Ammonium aluminum molybdate is biaxial (?) positive. Rhomb-shaped crystals exhibit symmetrical extinction. Optic plane normal to c axis; Ng = 1.740, Np = 1.700 ±. Color white.

2. Crystallization of Alum.

Reagent: Potassium hydrogen sulphate.($KHSO_4$).

Product: Potassium alum (hydrous double sulphate of aluminum and potassium, $KAl(SO_4)_2 \cdot 12H_2O$) (Figure 26).

Procedure: A large drop of the nitric acid test solution is evaporated to dryness on a slide. After cooling, dissolve the residue in one drop of 1:5 HNO_3, and add a small fragment of $HKSO_4$ to it. Gentle warming for a few seconds is required to accelerate the crystallization of the potassium alum.

Another procedure is suggested as follows: When a hot solution of aluminum sulphate is mixed with potassium sulphate, potassium alum separates slowly on cooling. Both procedures give satisfactory results except that alum shows a great tendency to form a supersaturated solution. Often the formation of alum crystals does not take place in spite of the fact that a high concentration of aluminum is present in the test drop. Scratching the surface of the slide with a platinum wire will cause the separation of alum crystals.

This salt is an isomorphous compound called alum. The general formula is $M'M'''(SO_4)_2 \cdot 12H_2O$, where M' represents the monovalent base -- K, Na, NH_4, Rb, Cs, Ag, and M''' represents an atom of trivalent metal -- Al, Fe, Cr, Mn, Co, Rh, In, etc. In the test for Al, the other trivalent metals should be confirmed and, if present, removed.

The hydrous sulphate of potassium and aluminum seems to be dimorphous. The isometric modification forms colorless, thin octahedral or cubic crystals. N = 1.454.

The same compound crystallizes in monoclinic plates and scales, or in fibrous crystals, usually at the periphery of the drop. Colorless. Biaxial negative. Ng = 1.458, Nm = 1.452, Np = 1.430; 2V = 52° ±. Both forms are not always recognizable directly on account of their overlapping development. The monoclinic phase forms at the expense of the isometric phase. The crystalline precipitates of both phases may be attacked and dissolved by immersion oils.

Detection of Antimony

1. Tartaric Acid Test.

Reagent: Tartaric acid ($H_2C_4H_4O_6$) and potassium chloride (KCl).

Product: Potassium antimonyl tartrate ($KSbO{\cdot}C_4H_4O_6{\cdot}H_2O$).

Procedure: This test is valuable for the detection of antimony in the presence of bismuth. The hydrochloric acid test solution containing antimony and bismuth is first precipitated as $(SbO)_2C_2O_4$ and $(BiO)_2C_2O_4$ by oxalic acid. Dissolve the precipitates in tartaric acid, in which the precipitate of $(BiO)_2C_2O_4$ is insoluble. Decant, filter, or separate by centrifuge. To the clear tartaric solution a small quantity of KCl is added. On gentle warming $KSbO \cdot C_4H_4O_6 \cdot H_2O$ is formed and separates in colorless, highly refractive (Nm = 1.636) tetrahedra, square, rectangular, and six-sided tablets of the orthorhombic system.

2. Potassium Iodide Test (see section on Interference Reactions and Group Reactions).

Detection of Arsenic

1. Ammonium Molybdate Test.

Reagent: Ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$).

Product: Ammonium arsenomolybdate ($(NH_4)_3AsO_4 \cdot 12MoO_3 \cdot XH_2O$) (Figure 2).,

Procedure: Various procedures for the test of arsenic with ammonium molybdate as reagent have been proposed by chemists. Short suggests that the best results are obtained by adding a drop of moderately concentrated reagent to the dried-up residue of 1:7 HNO_3 test solution.

Chamot's procedure has the advantage of removing other cations that may interfere with the test: Remove Si, Cd, Ta, and W by repeated evaporation of the material to be tested with HCl. The arsenic test solution is thus obtained by extracting with a few drops of dilute HNO_3 in which the other complex chlorides are insoluble or nearly so. Ammonium arsenomolybdate forms on careful heating of the test drop to which the reagent has been added.

Both methods may give a satisfactory result. The test results seem to depend upon the concentration of the reagent and of test drop, and the time of warming. A suitable concentration for test is 1.5% ammonium molybdate in 1:7 HNO_3.

Ammonium arsenomolybdate is hydrated in composition, with an unknown number of molecules of water. Even the actual formula of the reagent has not been definitely established. Ammonium arsenomolybdate is isotropic. Crystals in tiny spherulites, cubes, and octahedrons. High refractive; $N = 1.765 \pm$. Color brilliant yellow.

2. By Oxidation of Arsenic.

Reagent: Concentrated nitric acid (HNO_3).

Product: Arsenic trioxide (As_2O_3) (Figure 10).

Procedure: In a closed tube a small fragment of arsenic mineral is reduced by sublimation to a brilliant black mirror of metallic arsenic. The mirror is then oxidized to trioxide by heating in an open tube. This procedure is applicable only when the mineral is large in size. When a minute grain of mineral is to be tested, proceed as follows:

Arsenic mineral is powdered and slowly heated with nitric acid. At first, the arsenic trioxide is a glassy precipitate or a clear saturated solution. On exposure to the air, the saturated solution gradually forms octahedral crystals of As_2O_3. If a hot saturated solution of As_2O_3 in KOH is cooled, monoclinic crystals of As_2O_3 separate. This test is sensitive for the detection of arsenic in the simple sulphides.

Isotropic As_2O_3 crystallizes in octahedrons and combinations of octahedrons and dodecahedrons. $N = 1.755$; colorless.

The monoclinic phase of As_2O_3 is unstable. Crystal habit as shown in the micro-drop is not characteristic and usually in grains and monoclinic rods. Penetrating twins were found. Biaxial positive. The optic plane is 010; $Z \wedge c = +6°$; $2V = 58°$. $Ng = 2.01$, $Nm = 1.92$, $Np = 1.87$; colorless.

Under similar condition, the isotropic crystals of $Ca(NO_3)_2$, $Sr(NO_3)_2$, $Ba(NO_3)_2$, and $Pb(NO_3)_2$, hexagonal or trigonal crystals of $LiNO_3$, $NaNO_3$, and $CsNO_3$, and orthorhombic crystals of $RbNO_3$, NH_4NO_3, $TlNO_3$, and $AgNO_3$ may be produced by evaporating the nitric test solutions. $Ca(NO_3)_2$ is stable at very high temperature only; at room temperature the compound separated from the nitric test solution of calcium minerals by gentle heating is $Ca(NO_3)_2 \cdot 4H_2O$ which crystallizes in monoclinic crystals with $Nm = 1.498$. The indices of refraction of the isotropic crystals of other nitrates are known as follows: $Ba(NO_3)_2$ is 1.571, $Sr(NO_3)_2$ 1.587, and $Pb(NO_3)_2$ 1.780. $Ba(NO_3)_2$ is miscible in all proportion with $Pb(NO_3)_2$; but so far as known minerals containing lead and barium are very rare.

3. Magnesia Mixture Test (see Detection of Phosphorous).

4. Potassium Iodide Test (see Section on Interference Reactions and Group Reactions).

Detection of Barium

1. Oxalic Acid Test.

Reagent: Oxalic acid ($H_2(C_2O_4)\cdot 2H_2O$).

Product: Barium oxalates ($BaC_2O_4\cdot 3H_2O$ and $BaC_2O_4\cdot H_2O$) (Figure 13).

Procedure: Two barium oxalates are formed by adding the reagent to a neutral or weakly acidic test solution.

$BaC_2O_4\cdot 3H_2O$ is isometric, well-formed square crystals with N = 1.635. Colorless. Differs from $CaC_2O_4\cdot 3H_2O$ by sharp edges on squares.

$BaC_2O_4\cdot H_2O$ is monoclinic. Crystals monoclinic plates, branches, or single elongated prisms. Biaxial positive. X normal to 010; $Z \wedge c = 7° - 12°$. 2V greater than 60°. Ng = 1.638, Nm = 1.540, Np = 1.458; Ng - Np = 0.18. Colorless.

2. Hydrochloric Acid Test.

Reagent: Hydrochloric acid (HCl).

Product: Barium chloride ($BaCl_2$) and hydrous barium chloride ($BaCl_2 \cdot 2H_2O$)(Figure 12).

Procedure: If a barium mineral is dissolved in 1:1HCl and the solution allowed to evaporate slowly, $BaCl_2$ and $BaCl_2 \cdot 2H_2O$ will be formed.

$BaCl_2$ is often formed from concentrated HCl and test solution. Crystals are minute grains and sharp edged squares or 001 tablets. Isometric. N = 1.538. Colorless.

$BaCl_2 \cdot 2H_2O$ is monoclinic and separates in 001 plates or 010 elongated prisms with corners truncated by narrow faces. Polysynthetic twinning on 001 or 100 is common. Biaxial positive. The optic plane is 010; the angle between Z and c is 8°. 2V = 84°. Ng = 1.660, Nm = 1.641, Np = 1.635. Colorless.

The precipitation of barium as $BaCl_2 \cdot 2H_2O$ provides a valuable test to distinguish from Sr and Ca; the latter two do not give precipitates with HCl under the same condition.

3. Ammonium Bichromate Test.

Reagent: Ammonium bichromate ($(NH_4)_2Cr_2O_7$).

Product: Barium chromate ($BaCrO_4$) and bichromate ($BaCr_2O_7$) (Figure 11).

Procedure: If the Ba concentration is too high, a brilliant yellow, granular precipitate is formed. Orthorhombic and monoclinic crystals are produced by adding a minute quantity of reagent to the dilute test drop.

Barium chromate is orthorhombic and occurs as yellow aggregates of minute grains and rods. A high magnification is required for their identification.

The monoclinic form is more commonly present in the precipitates and its formula is probably $BaCr_2O_7$. Crystals are monoclinic plates and prisms. Biaxial positive; negative elongation. Optic plane is normal to 010 and contains c - axis. Nm = 1.715. Color yellow.

4. Sulphuric Acid Test (see section on Interference Reactions and Group Reactions).

Detection of Bismuth

1. Potassium Sulphate Test.

Reagent: Potassium sulphate (K_2SO_4).

Product: Bismuth and potassium sulphate ($Bi_2(SO_4)_3 \cdot 2K_2SO_4$)(Figure 15).

Procedure: The material is brought into solution by means of HNO_3. Evaporate to dryness. To the residue a sufficient quantity of 1:1 H_2SO_4 is added. Gentle warming is required to convert the bismuth into sulphate. A small quantity of K_2SO_4 is introduced to the test drop on the slide. Colorless, well-formed hexagonal scales of $Bi_2(SO_4)_3 \cdot 2K_2SO_4$, closely resembling PbI_2 in crystal form, are produced on heating. If the preparation becomes cold or has not been sufficiently evaporated, large orthorhombic crystals of K_2SO_4

may separate out. Antimony gives no such reaction.

$Bi_2(SO_4)_3 \cdot 2K_2SO_4$ is hexagonal. Optical constants are indeterminable in the tiny thin hexagons. Refractive indices near to that of K_2SO_4. K_2SO_4 is recognized by its crystal form. Crystals are tabular parallel to 100 or 010 of the orthorhombic system. Polysynthetic twinning common. Biaxial positive. The optic plane is 100; Z = c. 2V = 67°. Ng = 1.502, Nm = 1.499, Np = 1.498. Colorless.

Detection of Calcium

1. Sulphuric Acid Test.

Reagent: Dilute sulphuric acid (H_2SO_4).

Product: Calcium sulphate dihydrated ($CaSO_4 \cdot 2H_2O$) (Figure 19).

Procedure: A drop of 0.1N sulphuric acid is added to a cold, neutral or slightly acidic, concentrated test drop. Gentle warming of the preparation with a few drops of alcohol may hasten the complete precipitation of the salt. The resulting crystals are all long, colorless needles in clusters or radiating masses. They can be recrystallized into large-size crystals by the following procedure: Evaporate the preparation until no more fumes of SO_3 are emitted. Add a drop of water and a little of alcohol, and warm again. With rapid evaporation (which should be avoided), bundles of needles are generally formed. On the other hand, with slow evaporation, the crystals produced are slender prisms, and / or leaflets with rhomboidal outlines and sharp angle of 53°, and twins.

$CaSO_4 \cdot 2H_2O$ is monoclinic; crystals are acicular, prismatic or rhombic, occurring singly or as aggregates more or less parallel to c. Twinning on 100 is common in the arrow-head forms. Soluble in HCl. The optic plane is parallel to 010; the angle between Z and c is about 52°. Biaxial positive. 2V is about 58° at room temperature. Ng = 1.529, Nm = 1.523, Np = 1.520. Colorless.

2. Oxalic Acid Test.

Reagent: Oxalic acid ($H_2(C_2O_4) \cdot 2H_2O$).

Product: Calcium oxalate trihydrate and monohydrate ($CaC_2O_4 \cdot 3H_2O$ and $CaC_2O_4 \cdot H_2O$) (Figure 16).

Procedure: To a weakly acidic test solution, a small quantity of reagent is added. Calcium yields three crystal varieties described as follows:

Isometric $CaC_2O_4 \cdot 3H_2O$ crystallizes in octahedral grains with regular, sharp edges. Highly refractive; N = 1.628. Colorless.

Another crystal phase of $CaC_2O_4 \cdot 3H_2O$ is probably tetragonal. It is characterized by a higher index than that in the isometric phase crystals. In squares with rounded corners, or in small spherulites; rectangular rods rare. No = 1.634. Colorless.

The monohydrated calcium oxalate separates from hot solution. Crystals are in monoclinic plates (010) or in rectangular prisms (100). Biaxial positive. Optic plane normal to 010; angle between Z and c varies from + 10° to + 25° (+ 29° given by Winchell). Ng = 1.650, Nm = 1.555, Np = 1.490. Colorless.

Detection of Chromium

1. Silver Nitrate Test.

Reagent: Silver nitrate ($AgNO_3$).

Product: Silver chromate and bichromate (Ag_2CrO_4 and $Ag_2Cr_2O_7$) (Figure 28).

Procedure: If the test solution is in the form of chromate, it is necessary to convert it to bichromate by acidifying the test solution with HNO_3. Silver chromate and bichromate separate instantly, upon the addition of the reagent. The characteristics of these two salts will be discussed under Silver.

2. Lead Acetate Test.

Reagent: Lead acetate ($Pb(C_2H_3O_2)_2 \cdot 3H_2O$).

Product: Lead chromate ($PbCrO_4$)(Figure 21).

Procedure: Prepare the test solution as described above. To the dilute nitric acid test drop add the reagent. Lead chromate can be separated either from chromate or bichromate solution, because the weak acidity of the reagent is sufficient to convert the chromate, if present, in part to bichromate. The addition of lead acetate to the concentrated test solution causes the separation of a heavy, bright yellow, granular precipitate. These crystal aggregates remain small in size; a high magnification is required to disclose their habit.

The best results are obtained from dilute test solution. In this case the lead chromate separates in monoclinic tablets and prisms. Biaxial positive. The optic plane is 010; the angle between Z and c is -5°; 2V about 57°. Ng = 2.66, Nm = 2.37, Np = 2.31. Differs from barium bichromate in its higher relief and from strontium chromate in its crystal form.

Detection of Cobalt

1. Potassium Mercuric Thiocyanate Test.

Reagent: Potassium mercuric thiocyanate ($K_2Hg(SCN)_4$).

Product: Cobalt mercuric thiocyanate ($CoHg(SCN)_4$) (Figure 17).

Procedure: A moderately concentrated drop of the reagent is introduced to the dilute nitric test solution. This is warmed gently to facilitate the separation of the crystals.

Cobalt mercuric thiocyanate is tetragonal (?). Crystallizes in clusters, radiated masses, or X's of slender prisms and needles. Characterized by its "cobalt blue" color and crystal habit. Weakly dichroic with more absorption when the elongation is normal to the vibration plane of the light. Uniaxial (?) positive. No = 1.785, Ne = 1.795 (±). Since this salt is chemically metastable, the indices may vary from the values given above affected by even a slight change of temperature.

2. Double Nitrite Test.

Reagent: Potassium nitrite (KNO_2).

Product: Potassium cobalt nitrite ($K_3Co(NO_2)_6 \cdot 1\frac{1}{2}\ H_2O$).

Procedure: Small fragments of $NaNO_2$ and KNO_2 are added to the neutral or dilute acetic acid test solution. Any cobaltous cation will be converted to cobaltic cation and unites with NO_2^- to form the complex ion $Co(NO_2)_6^{---}$. Gentle warming is required to hasten the precipitation of $K_3Co(NO_2)_6 \cdot 1\frac{1}{2}\ H_2O$ which crystallizes in tiny, highly refractive, yellow cubes. When concentrated test solution is employed for the test, a finely-divided granular precipitate is formed. Tutton states that the crystals of this salt form four-arm stars from a very dilute test solution, but this form was not seen by the writer. Potassium cobalt nitrite is slightly soluble in hot water and insoluble in alkalies. The corresponding salt of nickel appears as tiny pale yellow isotropic squares and is more soluble.

Theoretically KNO_2 also forms double nitrites with Pb and Ni, but since the cubic crystals of these salts are difficult to obtain, and metastable solutions prevail, the double nitrite reaction is satisfactory only for the detection of Co. This test is not masked by other elements.

Detection of Copper

1. Potassium Mercuric Thiocyanate Test.

Reagent: Potassium mercuric thiocyanate ($K_2Hg(SCN)_4$).

Product: Copper mercuric thiocyanate ($CuHg(SCN)_4 \cdot H_2O$?) (Figure 18).

Procedure: A concentrated drop of the reagent is added to the dilute nitric acid test solution. The reaction product separates instantly.

Whether this salt produced is monohydrated or anhydrous is not known. From a concentrated test solution this salt separates in greenish yellow moss-like aggregates or in branches and clusters of acicular and dagger-shaped crystals. From dilute test solution arrow-head crosses or grains of cube combinations are formed on standing. These are best seen with high power objectives.

This salt is orthorhombic (?). Biaxial negative; negative elongation in crystals of elongated habit; very weakly pleochroic. 2V larger than 50°. Nm varies from 1.575 to more than 1.78. This salt is metastable and is always characterized by its color and moss-like aggregates. The crystallinity of this salt is unchanged in test solutions of different concentration. It seems that its indices vary with the concentration of copper in the test solution.

2. Triple Nitrite Reaction.

Reagent: Potassium nitrite (KNO_2) and lead acetate ($Pb(C_2H_3O_2)_2$).

Product: Potassium-lead-copper nitrite ($2KNO_2 \cdot Pb(NO_2)_2 \cdot Cu(NO_2)_2$) (Figure 27).

Procedure: The nitric or neutral solution of the mineral is evaporated to dryness. The residue should be dissolved in concentrated acetic acid, and KNO_2 and $Pb(C_2H_3O_2)_2$ added. If copper is present, highly refractive, orange red cubes and rectangular plates will form on standing. These crystals are isotropic and slowly become orange brown, then dark brown, and finally so dark as to appear black by transmitted light. For a discussion of the triple nitrite reaction and its application to the detection of other elements, see the section on Interference Reactions and Group Reactions.

Detection of Iron

1. Ammonium Molybdate Test.

Reagent: Ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$).

Product: Ammonium ferri-molybdate (Figure 5).

Procedure: A drop of the water saturated solution of the reagent is added to the neutral solution of iron minerals. A fine-grained yellowish-white material is first precipitated if ferric iron is present. In the case of ferrous iron, a blue-colored solution is slowly formed due to the reduction of the molybdate.

In both cases, the first separated crystals are in the form of colorless to white squares. In a few seconds combination of squares and crosses of short rhombs and long rhombs develop. If the reagent is added to the dried-up test solution, more rhombic crystals separate at the periphery of the test drop.

The definite formula of this salt is not known. Orthorhombic. Biaxial negative; optic plane normal to c. Ng = 1.712, Nm = 1.705, Np = 1.697. Colorless to white. Prismatic cleavage develops in the crystals as the drop passes to dryness. This salt is identical with the corresponding salt of aluminum in crystal habit, but on adding NH_4OH the crystals of ferric iron salt become brown as they dissolve, whereas the aluminum salt remains white on dissolving. It also differs from the aluminum salt in its higher relief.

2. Ammonium Chloride Test.

Reagent: Ammonium chloride (NH_4Cl) and hydrochloric acid (HCl).

Product: Monohydrated ammonium ferric chloride ($FeCl_3 \cdot 2NH_4Cl \cdot H_2O$) and mixed crystals of ammonium chloride and ferric chloride (Figure 4).

Procedure: The nitric solution of the mineral is acidified with sufficient HCl, and a grain of NH_4Cl added. If considerable ferric iron is present, the crystals produced are orange brown $FeCl \cdot 2NH_4Cl \cdot H_2O$ crystallizing in highly refractive, orthorhombic grains and pseudo-octahedrons. With low concentrations of iron, "anomalous mixed crystals" of NH_4Cl and $FeCl_3$ may develop, as isotropic, orange-yellow well-formed squares and octahedrons, on gentle warming. The intensity of the coloration of these mixed crystals increases with the rise in ferric iron concentration. No other cations yield such characteristic crystals.

Detection of Lead

1. Potassium Iodide Test.

Reagent: Potassium iodide (KI).

Product: Lead iodide (PbI_2) (Figure 22).

Procedure: The test is best performed by adding a minute fragment of the reagent to a dilute nitric test solution of the mineral. A slight excess of the reagent should be avoided as it may cause the recrystallization of KI as isometric crystals from saturated solution or that the lead iodide could dissolve to form the acicular and prismatic crystals of $PbI_2 \cdot KI \cdot 2H_2O$. In the presence of chloride or sulphate anions, lead with potassium iodide yields a complex salt of iodide instead of lead iodide.

Lead iodide separates as aggregates of hexagonal scales. Owing to the surface tension, the thin scales and plates of PbI_2 always float on the drop with the basal sections (0001) parallel to the surface of the drop. Uniaxial negative with No greater than 1.78. Faint yellow by transmitted light and bright yellow by reflected light. It is often hard to determine the optic sign of PbI_2 from the thin hexagonal plates. Trivalent arsenic with KI occasionally gives isomorphous crystals, but they are reddish yellow in color and are usually accompanied by an amorphous precipitate, other than the small individual hexagons.

2. Hydrochloric Acid Test.

Reagent: Hydrochloric acid (HCl).

Product: Lead chloride ($PbCl_2$) (Figure 20).

Procedure: To the nitric acid test solution of the mineral to be tested add a suitable quantity of dilute HCl. Lead chloride first separates in feathery and X-form crystals. This salt is quite soluble in hot solution, but recrystallizes upon cooling the solution. The crystals of recrystallized $PbCl_2$ become large in size and develop as elongated plates with sharply truncated ends, as individuals or as X's. $PbCl_2$ is orthorhombic. Optic plane is 010; Z paralles to c. Biaxial positive; 2V = 66°. Ng = 2.260, Nm = 2.217, Np = 2.199. Transmitted light gives a white color in individual crystals and a greenish yellow when in aggregates. It is distinguished from the mercurous and silver chlorides by its solubility in hot solution. Crystal habit, higher index of refraction, and a ready solubility in hot water are all diagnostic.

3. Ammonium Bichromate Test.

Reagent: Ammonium bichromate ($(NH_4)_2Cr_2O_7$).

Product: Lead chromate ($PbCrO_4$) (Figure 21).

Procedure: (a) Cold solutions. The test solution is evaporated to dryness in order to expell the strong acids. The residue is dissolved in dilute acetic acid or nitric acid. To the cooled, weakly acidic test drop add a small fragment of the reagent. A dense, yellow granular or amorphous precipitate of $PbCrO_4$ without recognizable crystal form results. This is characterized by its brilliant luster in transmitted light.

(b) Hot solutions. In warming the preparation lead with the reagent gives monoclinic crystals of $PbCrO_4$. These take the form of plates, slender prisms or elongated leaf-like crystals. It is soluble in NaOH or other alkaline solutions. The optical constants of this salt have been given under Chromium.

(c) In the presence of a trace of alkali. The addition of a minute quantity of alkali is insufficient to dissolve the yellow precipitate of $PbCrO_4$ already formed but usually leads to the formation of a basic salt $PbO \cdot 2PbCrO_4$, that crystallizes in faint reddish yellow, rectangular grains and plates, or slender prisms. This basic chromate is orthorhombic.

Negative elongation; X is parallel to the elongation; 2V very small. Ng = 2.57 - 2.62, Nm = 2.57, Np = 2.42. Pleochroism: X, clear yellow, Y and Z, orange yellow.

4. Nitric Acid Test.

Reagent: Nitric acid (HNO_3).

Product: Lead nitrate ($Pb(NO_3)_2$).

Procedure: The nitric acid solution of the mineral to be tested for lead is evaporated. If lead is present, colorless, highly refractive octahedral crystals of lead nitrate may separate before the test drop becomes dry. Later, a latticework precipitate, in which the branches are arranged normal to one another, may be formed in the residue. Lead nitrate is isotropic with index of refraction of 1.780. Colorless. Soluble in water. It differs from the nitrates of the alkaline earths by its higher relief and is miscible in all proportion with barium nitrate (see Arsenic).

5. Sulphuric Acid Test.

Reagent: Sulphuric acid (H_2SO_4).

Product: Lead sulphate ($PbSO_4$).

Procedure: A drop of the reagent is added to a test drop that has had a little of alcohol introduced. On gentle warming, individual, dendritic or X-formed slender prisms of lead sulphate are formed. The crystallinity of the crystals varies with the amount of the reagent introduced and the concentration of lead in the test drop. The best results are obtained when the dilute test solution reacts with a small quantity of the reagent. If the concentration of lead in the test solution is too high, the precipitate appears to be amorphous and does not develop any recognizable crystals. The amorphous precipitate of lead sulphate differs from that of barium sulphate in its white color and its high index of refraction. If the amorphous precipitate of lead sulphate is boiled with dilute HNO_3 and cooled, rectangular plates and rhombs separate out.

Lead sulphate is orthorhombic. Optic plane is 010; Z is normal to 100. Biaxial positive; 2V = 60° - 75°. Ng = 1.895, Nm = 1.883, Np = 1.878. Color white to yellowish grey.

Detection of Manganese

1. Potassium Chromate Test.

Reagent: Potassium chromate (K_2CrO_4).

Product: Manganese chromate of complex composition (Figure 24).

Procedure: When a tiny grain of potassium chromate is added to the neutral or weakly acidic solution, there separate in a few seconds orange brown rectangular prism, needles and leaflets, in bundles or radiating masses, around the reagent. If excess of the reagent is used, there will form tiny dark reddish brown globules. The prismatic crystals are often arranged in a manner somewhat like that of cobalt mercuric thiocyanate or of silver chromate, but differ from them in color. Crystal exhibits negative elongation; strongly pleochroic, orange yellow parallel to the vibration plane of polarizer and reddish brown normal to that direction. The composition of this complex salt is uncertain. With bichromate manganese does not yield precipitate.

2. Ammonium Molybdate Test.

Reagent: Ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot4H_2O$).

Product: Ammonium manganese molybdate ($(NH_4)_3H(Mn(MoO_4)_6)\cdot3H_2O$) (Figure 6).

Procedure: The dilute HCl solution of the mineral is evaporated to dryness. To the dried-up test drop a concentrated drop of the reagent is added. Monoclinic prisms and plates of ammonium manganese molybdate separate as the drop becomes dry at the edge. Warming which should be avoided may obstruct the separation of the well-formed crystals.

Ammonium manganese molybdate is monoclinic. Prismatic cleavage is developed. Biaxial negative. The optic plane contains c - axis and is normal to 010; X is perpendicular to 010. Strongly pleochroic, Y or Z = colorless, X = yellowish brown to orange yellow. Ng = 1.785, Np = 1.73. The characteristic clusters and bundles of tiny prisms and needles are formed only in dilute test solution.

When concentrated test solution is employed, a heavy granular precipitate or aggregate of crystals is obtained. These also exhibit the same optical properties.

Detection of Mercury

1. Double Thiocyanate Test.

Reagent: Cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) and potassium thiocyanate (KCNS).

Product: Cobalt mercuric thiocyanate ($CoHg(SCN)_4$) (Figure 17).

Procedure: To the hydrochloric or nitric acid test drop add the fragments of solid cobalt nitrate and potassium thiocyanate. Blue spherulites or branches of pleochroic prisms will form depending upon the concentration of test solution applied. In solutions concentrated with respect to mercuric ions dendritic masses or spherulites are formed. When it is low in concentration the crystals are obtained in the form of individual rectangular prisms. The characteristics of this salt have been discussed under Cobalt. Mercurous salts give no such reaction.

A similar procedure for mercury utilizes zinc sulphate instead of cobalt nitrate. The resulting salt is zinc mercuric thiocyanate which will be discussed under Zinc.

2. Potassium Iodide Test.

Reagent: Potassium iodide.(KI).

Product: Mercuric iodide and mercurous iodide (HgI_2 and HgI) (Figure 25).

Procedure: Apply a suitable quantity of the solid potassium iodide to the nitric or hydrochloric acid test solution. If a strongly acidic test drop is employed for the test, no crystal is formed as the reagent is completely dissolved. When excess of the reagent is added to a moderately concentrated or dilute test drop, there may be formed the double iodide $2KI \cdot HgI_2$ instead of mercurous and mercuric iodides, because the latter two are quite soluble in excess of KI. The double iodide $2KI \cdot HgI_2$ separates in colorless, needle-like or slender prismatic crystals. This reaction is of little value for the identification of mercury.

The treatment is best performed by causing the liquid reagent to flow over the test drop, so that the quantity of the reagent applied can be adjusted if required. Mercurous salts form the precipitate of yellowish green HgI which is soluble in excess of reagent. In mercurous solutions no crystals of HgI_2 are formed in any condition. Mercuric salt with the reagent yields the crystals of HgI and HgI_2.

HgI_2 is metastable and has two crystal phases. One phase is orthorhombic, occurring as yellow to reddish yellow rectangular plates. Optic plane is 001 and Bxa coincides with b - axis. Weakly pleochroic; absorption equal in the direction of X and Y, and greatest in the direction of Z.

The stable HgI_2 takes place at the expense of the orthorhombic phase. Crystals are in aggregates or single squares, rectangular plates and tablets of the tetragonal system. Uniaxial negative with No = 2.600, Ne = 2.375. Weakly dichroic with O = blood red, E = orange red.

3. Hydrochloric Acid Test.

Reagent: Dilute hydrochloric acid (HCl).

Product: Mercurous chloride (HgCl) and mercuric chloride ($HgCl_2$).

Procedure: Mercuric salt gives no precipitate with HCl except when a sufficient quantity has been added to the test drop. If mercuric solution is used for the test, proceed as follows: To the nitric test drop containing a little alcohol a drop of the reagent is added, and allowed to evaporate. The crystals of $HgCl_2$ separate in cubic grains and slender prisms at the periphery of the drop. $HgCl_2$ is orthorhombic, and white in color. The optic plane is 001; X is c - axis. Biaxial negative; 2V = 85°. Ng = 1.965, Nm = 1.850, Np = 1.725.

Mercurous salt with HCl immediately yields a heavy, white crystalline precipitate of Hg_2Cl_2, without the addition of alcohol to the preparation. From very dilute test solution, crystals of Hg_2Cl_2, as examined under a high power lens, appear as white, tiny slender prisms, needles, and cubic grains. Hg_2Cl_2 is tetragonal. Soluble in aqua regia.

Uniaxial positive with No = 1.955, Ne = 2.600. But it is often difficult to obtain good crystals of Hg_2Cl_2 and $HgCl_2$.

Wash the white precipitate with warm water, and repeat a few times. Then a drop of dilute NH_4OH is added to the white residue; it turns grey to black owing to the formation of a mixture of metallic Hg and $HgClNH_2$. This reaction is very characteristic for the detection of mercury. With a high magnification the metallic mercury appears as dark grey to black grains, and $HgClNH_2$ as white slender prisms, rectangular plates and grains. $HgClNH_2$ is uniaxial (?) positive with No = 2.19, Ne = 2.21.

Detection of Molybdenum

1. Ammonium Acid Phosphate Test.

Reagent: Ammonium acid phosphate ($NH_4H_2PO_4$). Dipotassium hydrogen phosphate and ammonium chloride may utilize to substitute for ammonium acid phosphate.

Product: Ammonium phosphomolybdate ($(NH_4)_3PO_4 \cdot 10MoO_3 \cdot H_2O$?) (Figure 8).

Procedure: To the dilute nitric test solution a small grain or a drop of saturated water solution of the reagent is added. Gentle warming then hastens the precipitation of the complex salt ammonium phosphomolybdate.

This salt separates first in yellow, tiny squares and octahedrons, which develop into four-pointed stars, as the drop passes to nearly dryness, at the circumference of the drop. They are isometric with an index of refraction greater than 1.785. The four-pointed star form of ammonium phosphomolybdate is nearly similar in crystal habit and color to that of ammonium arsenomolybdate, but the latter does not crystallize in square form. Ammonium phosphomolybdate is insoluble in hot water and in dilute nitric acid.

Tungstate salt forms with the reagent ammonium phosphotungstate having the formula $(NH_4)_3PO_4 \cdot WO_3 \cdot XH_2O$ (?). This salt is identical with ammonium phosphomolybdate in appearance, but differs from the latter in its transluscence and white color.

Detection of Nickel

1. Dimethylglyoxime Test.

Reagent: 2% dimethylglyoxime solution in alcohol plus an equal amount of water ($C_4H_6(NOH)_2$).

Product: Nickel dimethylglyoxime ($Ni(C_4H_7N_2O_2)_2$).

Procedure: Iron, if present in the test drop, must be precipitated to iron hydroxide by adding a drop of 1% NH_4OH. Otherwise the brick-red coloration that results from iron with the reagent may color the solution red. Evaporate the test solution to a small concentrated drop and make it ammonical; a drop of the saturated solution of reagent is then added. No precipitation takes place in HNO_3 or HCl test solution.

Nickel dimethylgloxime is first precipitated in a more or less amorphous condition. On standing, pink, clusters or aggregates of minute needles and radiates of finely divided slender prisms are formed. Color is pink to rose-red. Highly pleochroic; interference color blue to pink. No other element yields a similar reaction. This test was originally proposed by Tschngajeffe for macro-analysis and was said to be capable of detecting one part of nickel in 400,000 parts of water. Moderately large amounts of cobalt do not interfere with the test.

2. Potassium Mercuric Thiocyanate Test.

Reagent: Potassium mercuric thiocyanate ($K_2Hg(SCN)_4$).

Product: Nickel mercuric thiocyanate ($NiHg(SCN)_4$).

Procedure: To a concentrated nitric test solution of nickel mineral add the reagent. Nickel yields a pale yellow to colorless precipitate of spherulites and small hexagonal grains. A high magnification is required for the resolution of the crystals. This salt is hexagonal; uniaxial negative. No such crystal is obtained from a dilute test drop.

3. Triple Nitrite Reaction (see Interference Reactions and Group Reactions).

4. Ammonium Molybdate Test (see Interference Reactions and Group Reactions).

Detection of Phosphorous

1. Ammonium Molybdate Test.

Reagent: Ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$).

Product: Ammonium phosphomolybdate ($(NH_4)_3PO_4\cdot 10MoO_3-\cdot H_2O$?) (Figure 8).

Procedure: When a drop of saturated water solution of the reagent is added to a drop of the acid solution of the mineral, there separate crystals of ammonium phosphomolybdate without heating. Its characteristics have been discussed under Molybdenum. Silicates and arsenates produce isomorphous crystals and may cause confusion. Before the test for phosphorous, it is necessary to confirm the presence or absence of silicates and arsenates.

2. Silver Nitrate Test.

Reagent: Silver nitrate ($AgNO_3$).

Product: Silver acid phosphate (Ag_2HPO_4) or silver phosphate (Ag_3PO_4).

Procedure: To the test drop, which should be dilute and has been made weakly acidic with acetic acid, a drop of the dilute solution of reagent is added. Warm gently. A yellow granular precipitate followed by yellow three-armed or four-armed crystals, dendritic stars, and radiates or crosses of prick-pointed crystals are formed. Soluble in HNO_3. Arsenates forms dark red or reddish brown isomorphous crystals.

The compound resulting from silver nitrate with phosphate solution is probably silver acid phosphate that is very unstable in light or moisture. Hexagonal; uniaxial negative with No = 1.804, Ne = 1.798. On gentle warming of the preparation, yellow cubes of Ag_3PO_4 may occasionally develop at the periphery of the drop.

3. Magnesia Mixture Test.

Reagent: Magnesium acetate ($Mg(C_2H_3O_2)_2$).

Product: Ammonium magnesium phosphate ($MgNH_4PO_4 \cdot 6H_2O$).

Procedure: The mineral to be tested should be converted to orthophosphate by dissolving in HNO_3. Transfer a drop of the solution to the slide and evaporate to a volume of about one drop. Cool, cautiously neutralized with NH_3, adding a drop in excess; then introduce a drop of magnesium acetate to the neutral test drop. Ammonium magnesium phosphate is slow to form. Gentle warming is required to hasten the separation of the reaction product. This salt first appears as a white granular precipitate. On standing, this precipitate develops into dendritic and star-like groups, and finally into well-formed rectangular tablets, prisms, combinations of domes and prisms, and hemimorphic crystals of the orthorhombic system. Biaxial positive; 2V = 37°. The optic plane is 100, Z = b. Ng = 1.504, Nm = 1.496, Np = 1.495. Strong dispersion. Colorless to pale yellow. This reaction does not take place in acid test solution.

Arsenates in strongly ammonical test solution yield a crystalline precipitate of $MgNH_4AsO_4 \cdot 6H_2O$ identical with that of $MgNH_4PO_4 \cdot 6H_2O$ in form and in color. Stannic compounds do not give such reaction.

The precipitate $MgNH_4AsO_4 \cdot 6H_2O$ cannot be distinguished by its form from the analogous phosphate. But a differentiation is possible in that, if the precipitate has been washed with dilute ammonium hydroxide, is treated with silver nitrate, the arsenate becomes brown, the phosphate yellow.

Detection of Silver

1. Ammonium Bichromate Test.

Reagent: Ammonium bichromate $((NH_4)_2Cr_2O_7)$.

Product: Silver bichromate $(Ag_2Cr_2O_7)$ and chromate (Ag_2CrO_4) (Figure 28).

Procedure: The material to be tested is dissolved in concentrated HNO_3 and evaporated to dryness. The residue is treated with 1% HNO_3. To the test drop, a grain of reagent is added. Silver salts are precipitated as silver chromate and silver bichromate, the latter produces only in dilute test solution.

Silver chromate forms blood-red prisms, rectangular plates, rhombs and acicular crystals. Orthorhombic, with polysynthetic twinning. Biaxial positive; Y = c. Nm = 1.755.

2V greater than 55°. Least absorption to Y.

Silver bichromate is triclinic, in scale-like crystals, triangles, or monoclinic plates. Color is lemon yellow to orange yellow; asymmetrical extinction. Silver bichromate is more soluble than chromate.

2. Hydrochloric Acid Test.

Reagent: Hydrochloric acid (HCl).

Product: Silver chloride ($AgCl$) (Figure 29).

Procedure: A small drop of dilute hydrochloric acid is introduced to a dilute test drop. The first separation of the reaction product is often a curdy, white precipitate, in which no distinct crystal form can be observed. In this case the best results can be performed by recrystallization in NH_4OH as follows: Wash the preparation on the slide with water which has been slightly acidified with HNO_3. The residue is dissolved in dilute NH_4OH and allowed to evaporate to expell the excess of NH_3. Silver chloride separates in tiny isotropic crystals by the decomposition of $AgCl \cdot 2NH_3$. It is essential that the NH_3 should be completely expelled from the preparation, since, if remained even as a trace, $AgCl \cdot 2NH_3$ may be thrown down as masses of white, pleochroic crystals by which the crystals of AgCl will be obscured. With slow evaporation, the crystals of silver chloride produced are regular octahedra and cubes. With rapid evaporation they crystallize in combined forms of isometric crystals. Silver chloride is isotropic, greyish white in color. N = 2.07.

Detection of Strontium

1. Oxalic Acid Test (see Interference Reactions and Group Reactions).

2. Sulphuric Acid Test (see Interference Reactions and Group Reactions).

3. Ammonium Bichromate Test (see Interference Reactions and Group Reactions).

Detection of Sulphur

1. Calcium Acetate Test.

Reagent: Calcium acetate ($Ca(C_2H_3O_2)_2$).

Product: Calcium sulphate dihydrated ($CaSO_4 \cdot 2H_2O$) (Figure 19).

Procedure: Most sulphides and sulphosalts are easily decomposed by nitric acid or aqua regia, the sulphur being oxidized to H_2SO_4. Some sulphates that are insoluble in acids should be first treated by fusion with sodium carbonate and then carried down into solution. If the sulphate solution obtained reacts with barium chloride, the resulting barium sulphate occurs as a heavy, white, granular precipitate instead of recognizable crystals. For microchemical reaction, the sulphur ions should be precipitated as calcium sulphate by calcium acetate, proceed as follows:

The test drop on the slide is evaporated. The residue is treated with dilute HCl or brought into a neutral solution. On addition of the reagent, $CaSO_4 \cdot 2H_2O$ separates in characteristic needles, sheaves and radiates. These forms can be recrystallized to arrow-headed twins (with the vertical axis as twinning-axis) and broad foliated plates by warming in water containing a little alcohol. If a strong acid test solution is used for test, anhydrate ($CaSO_4$) predominates instead of microchemical gypsum crystals. This procedure is just the reverse of the sulphur acid reaction with calcium (see Detection of Calcium).

Detection of Tin

1. Ammonium Chloride Test.

Reagent: Ammonium chloride (NH_4Cl).

Product: Ammonium chlorostannate ($(NH_4)_2SnCl_6$)(Figure 3).

Procedure: A drop of the nitric solution of the mineral should be evaporated to dryness. To the dried-up residue a large drop of HCl and a tiny fragment of NH_4Cl are added. If tin is present, there separate at once well-formed, colorless, large octahedra and cubes at the edge of the drop. $(NH_4)_2SnCl_6$ is isotropic with an index of refraction higher than 1.78. Spinel twins (twinning plane 111)are common.

Detection of Tungsten

1. Ammonium Acid Phosphate Test (see Detection of Molybdenum).

Detection of Zinc

1. Potassium Mercuric Thiocyanate Test.

Reagent: Potassium mercuric thiocyanate ($K_2Hg(SCN)_4$).

Product: Zinc mercuric thiocyanate ($ZnHg(SCN)_4$) (Figure 35).

Procedure: The best results are obtained when the reagent is added to a moderately concentrated test drop. Zinc mercuric thiocyanate separates as colorless to white feathery crosses having branching crystals perpendicular to the four main arms. From dilute test drop the crystals produced are single prisms with occasional oblique branches at both sides. Uniaxial or biaxial (?); positive elongation; Nm (?) = 1.582-1.584. It is often difficult to reveal the optical constants from these forms.

2. Oxalic Acid Test.

Reagent: Oxalic acid ($H_2C_2O_4 \cdot 2H_2O$).

Product: Zinc oxalate dihydrated ($ZnC_2O_4 \cdot 2H_2O$)(Figure 34).

Procedure: The reagent is added to the neutral or slightly acid test solution. Zinc oxalate separates slowly as a fine, granular, colorless precipitate; later spherulitic grains appear and finally tiny pseudo-octahedra, united end to end in combinations. The formula of this compound is probably $ZnC_2O_4 \cdot 2H_2O$. The crystals are pseudo-octahedral in habit and optically biaxial negative; X is parallel to the elongation. Ng = 1.618, Nm = 1.609 (estimated), Np = 1.600. No other elements with the reagent gives this characteristic crystal form.

INTERFERENCE REACTIONS AND GROUP REACTIONS

It is obvious that any reagent may not give the normal reaction and crystal habit in test solution containing impurities or other elements which retard or interfere with the formation of the normal reaction product. A test drop containing two or more salts differing in both cations and anions may yield puzzling results, which are often not interpretable at first. Furthermore, similarity in reaction and the formation of crystals with similar habits may result from the reaction of different elements with the same reagent. It is also known that various reactions occur, varying with the concentration and the nature of the test solution. Since some cations are present in minute amounts in minerals of heterogeneous composition, they can not be further separated by the methods of macro-analysis. It is desirable to examine the precipitates from interference reactions and group reactions in known chemical system to provide data for the detection of cations present in unknown samples and thus to shorten the time required for the completion of an analysis. The reagents employed are chosen for their sensitive reactions with a number of elements and for the fact that they are all less expensive and easily obtainable in a general laboratory. It is impossible at this time to give a list of reagents which satisfy all demands; only the alternative use of different reagents and a skill in determining the interference reactions will afford a rapid means of identifying the expected elements. In the following pages, there are a number of reagents and reactions which have been systematically studied. These prove useful in interpreting the reactions and in identifying the reaction products.

Ammonium Bichromate

The ammonium bichromate test is very reliable for the detection of silver and has the advantage of giving no reaction with a number of the metallic elements. In all the examples cited below, unless otherwise noted, it is assumed that a small concentrated drop or a tiny fragment of the reagent is added to the dilute nitric acid test solution on the slide.

Ag Lemon-yellow to orange triclinic blades of silver bichromate, and blood-red feathery or narrow plates of orthorhombic crystals of silver chromate.

Pb Lead often yields a yellow, finely-divided, granular or amorphous precipitate; no distinct crystal forms are observable. Monoclinic crystals of $PbCrO_4$ separate from a weakly acidic, dilute test drop with a very dilute solution of the reagent. Prisms and rectangular grains of $PbO \cdot 2PbCrO_4$ (orthorhombic) separate from neutral or slightly alkali test solution with excess of the reagent.

Sr No precipitate from an acid test solution. In dilute ammonical test solution yellow, fusiform crystals, spherulites and globulites separate. Symmetrical twins are found in globular crystals. Index of refraction about 1.77. Anisotropic.

Ba From moderately concentrated test solution barium is precipitated as $BaCrO_4$ in a yellow formless mass. Yellow monoclinic crystals of $BaCr_2O_7$ and triclinic crystals of $BaCr_2O_7 \cdot 2H_2O$ are obtained from a weak acid test solution with a minute quantity of the reagent.

Bi From acid, concentrated test solution, a greenish brown granular precipitate separates. If too dilute a test solution is used, the reagent colors the test drop greenish brown without precipitate being formed. The precipitate produced from a weakly acidic, moderately concentrated test drop, contains greenish red grains, crosses and individual crystals of stout prisms.

Hg In a concentrated test solution mercurous salts yield a yellowish red, granular precipitate of Hg_2CrO_4, which becomes lemon yellow or yellowish green on warming. With a weak acid, concentrated solution of mercurous compounds, dark red bundles of monoclinic prisms and needles of $Hg_2O \cdot 2Hg_2CrO_4$ may develop. Mercuric salts under similar conditions give no such precipitates.

As Ordinarily arsenic itself gives no precipitate with the reagent. Orange monoclinic plates, leaf-like crystals and fine grains may separate out as the drop becomes dry toward the edge. It must be borne in mind that these crystals are the recrystallization products of a reagent from the saturated solution (ammonium bichromate and chromate are monoclinic). Arsenic, according to Fraser, will slowly form colorless octahedrons with ammonium bichromate. The writer can not confirm this statement. Probably those octahedral crystals are arsenic trioxide carried down from the nitric test solution before addition of the reagent.

Fe In some cases, a white amorphous precipitate is formed, due probably to the hydroxide radical in a water solution of the reagent combined with iron.

Mo Colors the test drop yellow.

Sb, Sn, Zn, Cu, Co, Ni, Mn, Cr, Al, Ca. No precipitate.

Interference Reactions With Silver.

Pb-Ag No interference with silver. Lead rarely gives yellow prisms.

Sr-Ag Immediate precipitation of blood-red silver chromate and bichromate. No strontium test.

Ba-Ag Orthorhombic crystals of silver chromate are well-developed. A fine-grained precipitate of barium bichromate forms later.

Bi-Ag Bismuth yields a yellowish green amorphous precipitate easily distinguishable from the crystals of silver chromate and bichromate. If bismuth is present in high proportions, Ag crystals may be partly masked by the amorphous precipitate. The presence of silver can be confirmed by the hydrochloric acid test in a solution containing silver and bismuth cations.

Hg-Ag The test for silver is partly masked when mercurous mercury is present in excess. In the presence of silver, mercurous salt can be detected by the iodide test.. Silver does not produce blood-red isotropic squares, thence this test affords a means of differentiating silver and mercury when they are present in the same solution.

As-Ag The test for silver is satisfactory. Highly refractive, dark triangle and octahedra of uncertain composition accumulate at the periphery of the preparation.

Cu-Ag Crystals of silver chromate and bichromate colored blue or green.

Ammonium Molybdate

The test drop should be first evaporated to dryness. Dissolve the residue in a small drop of 1:7HNO_3. To the weak acid test drop a minute quantity of saturated water solution of the reagent is added. In some cases, gentle warming is required to accelerate the separation of characteristic crystals.

As Tiny, highly refractive, lemon yellow octahedrons and four-armed stars separate in cold, concentrated test drop. Among the common elements, only lead and mercurous mercury interfere with the arsenic test. In the presence of aluminum, As crystals become indistinguishable.

P Octahedral crystals resemble those formed from the arsenic test solution. Light yellow in color. No precipitation takes place from cold solution. The test for P is easily confused with the As precipitate. Pb, Hg (mercurous), or Ni masks the test for phosphorous.

Al Colorless to white squares and rhombs; foliated cubic cleavage well developed. Orthorhombic; twinning on 001 common. Crystals also obtained from neutral solution. Test masked by Cr, Cu, Fe (ferric), Mn, Pb, Sn, Zn.

Fe Ferric iron gives crystals identical with those of ammonium aluminum molybdate. Test is partially masked by Cr, Hg, Pb, Zn, and more so by Al, Cu, Ni, Sn. Solution of ferrous sulphate with the reagent results in a brown coloration. In the case of ferrous nitrate, a blue-colored solution or formless aggregates is slowly formed due to the reduction of molybdate.

Ni Gives crystals analogous to those obtained from aluminum and ferric iron. They are light yellow to colorless, and more transparent and foliated in appearance than the corresponding salts of aluminum and ferric iron, but the differences are too slight to afford a means of distinguishing them from the other two salts. The index of refraction estimated in squares (001 of orthorhombic) is greater than 1.75. Test for Ni is masked by Mn, Cu, Sn, Pb, Hg, Cr, Zn, and is indistinguishable when Al or ferric iron is present.

Mn Colorless to yellowish orange monoclinic plates and narrow prisms at the periphery of the drop. Biaxial negative; X parallel to the direction of prismatic cleavage or of elongation; positive elongation. Strongly pleochroic, Y = Z = yellowish brown to orange yellow, X = colorless. No other element gives such characteristic crystal with the reagent. Test for Mn is masked by Co, Ni; indistinguishable in the presence of Al, As, P, and distinguishable in the presence of Ba, Ca, Cu, Fe, Hg, Ni, Sr.

Sn Chlorostannic solution gives a dark blue precipitate at first. On warming, there separate the feathery and acicular crystals at the edge of the drop as the amorphous precipitate is partly dissolved.

Pb White, heavy, amorphous precipitate.

Cu White acicular crystals in clusters. Reactions not obstructed by other elements.

Hg Very slender needles, white to colorless, in clusters or radiates.

The following outline comprises the important behaviour of ammonium molybdate with some common elements, and may serve as a guide to identification of them. It is obvious that this reagent is useful for the detection of As, P, Al, Fe (ferric), Ni, and Mn.

1. White, dense granular or amorphous precipitate separates at first.
   - (a) On gentle warming, the white precipitate is partly dissolved; no characteristic crystals are formed except clusters or aggregates of white acicular crystals at or near the edge of the preparation: Cu; Co; Hg; Cd; Ca; Sr; (Ba); (Ni); (Mn).
   - (b) On gentle warming, the white amorphous precipitate is completely dissolved, and white acicular crystals are rarely obtained: Bi; Sb; (Ca); (Ba).
   - (c) On heating, white amorphous precipitate remains insoluble; no acicular crystals separate: Ag; Sn; Pb; (Sr).
2. Pleochroic (orange yellow to colorless) prisms or plates: Mn.
3. Tiny, lemon yellow isometric crystals: As; P.
4. Colorless or white, foliated squares, rhombs, or combined forms: Al; Fe (ferric); Ni. On addition of NH_4OH, Al

and Ni crystals dissolve giving a white to colorless, amorphous precipitate. The ammonium ferric molybdate becomes brown on dissolving.

Hydrochloric Acid

In macroscopical qualitative analysis hydrochloric acid is used as a group reagent to precipitate the Silver Group cations, because they can be immediately and completely carried down into chlorides. Their definite crystal forms are easily recognized under the microscope. The optical characters of the chlorides of Ag, Pb, Hg, and Ba have been discussed in Detection of Individual Elements. Testing for these members with HCl is often valuable as a rapid means of their recognition or elimination. If they are all present in the test drop, they do not interfere seriously with each other, except when mercury is present in large proportions. The following outline may serve as a guide to the identification of common chlorides.

1. A finely-divided, granular material precipitates at first. This is soluble in an excess of HCl. The results are not very characteristic and are generally disappointing from the viewpoint of microscopical qualitative analysis.

Bi Precipitation of basic chloride BiOCl from hydrolysis due to an insufficient quantity of HCl being added.

Sb Precipitation of basic chloride SbOCl from hydrolysis due to an insufficient quantity of HCl being added.

Mo MoO$_3$ with HCl yeilds a blue granular or amorphous precipitate which is soluble in an excess of HCl. Blue coloration results.

W WO$_3$, from ortho- or para- tungstates, yields a yellow granular precipitate soluble in excess of HCl.

2. The following elements do not yield precipitates in dilute HCl, but on evaporation, the residue obtained may constitute isotropic crystals or amorphous masses: Na; K; Sn; Cu (isotropic CuCl and orthorhombic $CuCl_2 \cdot 2H_2O$); Sr (rarely); Zn (rarely).

3. Immediately gives dense, white, granular or amorphous precipitate. Characteristic crystals are observed with a high magnification: Ba; Pb; Hg (mercurous); Ag.

(a) Isotropic grains and cubes, and monoclinic plates: Ba. Sr and Ca do not form crystals that are isomorphous with those of the chlorides of barium. Test for Ba by means of HCl is retarded by Ag, Pb, Hg.

(b) Orthorhombic needles and prisms: Pb; tetragonal rods and grains from dilute test drop: Hg. Pb and Hg do not interfere with each other.

(c) Highly refractive isotropic crystals predominate: Ag. Test for Ag is masked by large amount of Hg, but not by Pb.

(d) If no recognizable crystal separates in the amorphous precipitate, proceed as follows: Wash the precipitate with warm water.

i) Precipitate soluble in warm water. Orthorhombic crystals recrystallize on cooling: Pb.

ii) Precipitate insoluble in warm water. Add NH_4OH. Precipitate soluble in NH_4OH; isotropic crystals separate on gentle warming: Ag.

Precipitate is insoluble and turns black grey in addition of NH_4OH: Hg.

Oxalic Acid

Oxalic acid readily forms colorless to white, crystalline precipitates with many cations. In testing for these cations the appearance of the crystals obtained depends upon the nature of the cations and the concentration of the oxalic acid. Most of them crystallize in elongated monoclinic or orthorhombic prisms and plates, and bear a similar crystal habit. Acid, normal, and double oxalates, in stable or metastable phase, may be abundant, depending on the concentration and temperature conditions. Double oxalates are usually formed when the reagent is added to a test solution which contains alkalies. The oxalic acid is essentially used as a group reagent to indicate the presence or absence of a number of elements.

So far as the writer is aware, the formation of the characteristic crystals of $Ca(C_2O_4) \cdot 3H_2O$ and $Zn(C_2O_4) \cdot 2H_2O$ is not obstructed by the presence of other elements, except when they are present in large proportions.

The monohydrous oxalates of calcium, strontium, and barium, as well as the corresponding carbonates and sulphates, seem to constitute an isomorphous series. This fact is observed from experiments. They are all monoclinic and are capable of complete intercrystallization to form one homogeneous substance. The value of the indices of refraction decrease with variation in composition from $Ca(C_2O_4) \cdot H_2O$ through $Ba(C_2O_4) \cdot H_2O$ to $Sr(C_2O_4) \cdot H_2O$, but the Np of $Sr(C_2O_4) \cdot H_2O$ is shown graphically not to lie on the downward curve. It is probably better to consider this strontium salt as a separate mineral. The monohydrous oxalates of calcium and barium can be miscible in all proportions in a manner similar to the plagioclase feldspars, but the strontium salt has a more limited miscibility with each of the other two. A monoclinic crystal obtained by adding the reagent to the weak acid test solution containing approximately equal amounts of Ca and Ba cations, shows that its three indices are intermediate between the corresponding ones of the pure monohydrated calcium oxalate and monohydrated barium oxalate.

The tests outlined below are performed, at room temperature, by adding the reagent to the acetic or dilute nitric acid test solution.

Ca With oxalic acid immediately produces a precipitate of trihydrated and monohydrated oxalates of calcium. $Ca(C_2O_4)\cdot 3H_2O$ often takes place in a concentrated test solution and has two crystal phases distinguished one from the other by crystal form and refringence. The isometric phase is unstable and crystallizes in octahedrons. Another phase seems to be tetragonal and crystallizes in sub-angular squares (basal section of the tetragonal crystals). These exist even in the presence of other elements. $Ca(C_2O_4)\cdot H_2O$ is monoclinic and has higher indices than the corresponding compounds of barium and strontium.

Ba Yields a precipitate of trihydrated and monohydrated oxalates of barium in dilute, weak acid test drop. $Ba(C_2O_4)\cdot 3H_2O$ abounds when the test solution is concentrated with respect to Ba, and crystallizes in tiny, highly refractive, sharp-edge squares and octahedrons. $Ba(C_2O_4)\cdot H_2O$ crystallizes in fibrous bundles and aggregates of elongated monoclinic prisms.

Sr With oxalic acid strontium forms two oxalates. At first sight the crystals produced develop as rhombic and elongated six-sided plates, having rounded corners of the orthorhombic system. Later, monohydrated oxalate of strontium forms at the expense of the orthorhombic crystals. This resembles the corresponding compounds of barium and calcium in crystal habit.

The formula of the orthorhombic crystals is uncertain. They show positive elongation. Biaxial negative; optic plane normal to 001; Nm (?) = 1.545.

$Sr(c_2O_4)\cdot H_2O$ crystallizes in monoclinic plates. The optic plane and X are normal to 010; the angle between Y and c-axis is about 6°. Biaxial positive with 2V greater than 60°. Ng = 1.543, Nm = 1.539, Np = 1.533.

Ag Silver gives a colorless to white precipitate of tiny rectangular prisms, rods and monoclinic prisms. They are single or in crosses. Biaxial negative; Nm nearly to 1.615.

Co Elongated barrel-shaped rods and needle-like crystals; arrangement of these crystals are similar to those of silver oxalate. Orthorhombic; negative elongation; Nm = 1.613.

Zn Pseudo-octahedra in combination (see Detection of Zinc).

Pb From dilute test drop the crystals separate at the periphery of the drop in the form of large-size, slender and stout monoclinic plates and prisms. Negative elongation, high birefringence and strong pleochroism. Addition of a large amount of concentrated reagent to a concentrated test drop may cause the formation of a dense, granular precipitate which with a high magnification appears as dentritic aggregates and crosses having fern-like branches. These resemble forms of the zinc mercuric thiocyanate crystals.

Cu Gives a granular precipitate of tiny spherulites closely resembling the trihydrated oxalate of calcium in appearance.

Sb Monoclinic plates and prisms resembling those obtained from dilute test solution of lead or silver.

Bi Needle-like crystals and prisms chiefly in clusters or aggregates.

Mn Slender prisms and needles arranged in star-like groups and radiates. Individual crystals resemble those of oxalates of lead, silver, antimony, etc; broad monoclinic plates are rare. It is characterized by the six-rayed twinned crystals. $MnC_2O_4 \cdot 3H_2O$ is biaxially positive; optic plane parallel to 100; Nm = 1.485, Np nearly = 1.43.

Al Colorless, highly refractive, monoclinic tablets and orthorhombic rhombs or prisms.

Sn Short prisms and hexagonal plates. Prisms resemble those formed by antimony and silver. The hexagonal plates are uniaxial negative.

Interference Reactions With Calcium, Strontium, and Barium.

Ag, Cd, Cu, Bi, Pb, Sb, Sn, Zn, Mn, and rare earths. Crystals of the oxalates of these elements are indistinguishable from those of the monohydrous oxalates of calcium, strontium, and barium. Confusion may result if they are present.

Sr Strontium does not interfere with the separation of the trihydrous oxalates of calcium and barium. No tiny cubes and spherulites are obtained from strontium salts. Crystals of monohydrated oxalate of strontium resemble those of barium and calcium; in these cases, sulphuric acid is used as a reagent to test for barium and calcium.

Ba The sharp-edged squares and octahedrons of $BaC_2O_4\cdot 3H_2O$ are distinguished from the spherulites of $CaC_2O_4\cdot 3H_2O$.

Potassium Iodide

The potassium iodide test is extremely sensitive for the detections of lead and mercuric mercury but is less satisfactory for those of antimony, bismuth and arsenic. The iodides of lead, copper, silver, and tin (stannous) are yellow to yellowish white in color, those of mercury, antimony and bismuth are dark red or nearly so, while that of arsenic is yellowish green to yellowish orange. Unless otherwise stated, the reactions given below for comparison are performed by adding a small fragment of potassium iodide to the nitric test solution.

Pb Yellow hexagonal plates of PbI_2 separate from a dilute test drop. This precipitate is soluble in an excess of reagent. The dense, amorphous precipitate of PbI_2 is brilliant yellow by transmitted light; this character affords a means of distinguishing from the other yellow iodide precipitate. In the presence of small amounts of Bi, As, and Sn, crystals of PbI_2 are distinguishable. Ag, Cu, and Hg do not mask the iodide test for Pb.

Hg Mercuric salts give the metastable compound HgI_2 in orange to red squares and rectangular plates. They are soluble in an excess of reagent. Sb and Bi interfere with the iodide test for mercury. In the presence of little Cu, Ag, Pb, As, the crystals of HgI_2 are distinguishable.

Ag Silver with the reagent forms a granular or amorphous precipitate having a yellowish white color. Under certain condition the fine-grained precipitate of AgI appears, under a high magnification, as tiny hexagonal plates and scales. If the yellow precipitate of AgI is heated with dilute nitric acid, $AgIO_3$ precipitates crystallizing as slender prisms or needles. AgI is hexagonal; uniaxial positive, No = 2.218, Ne = 2.229; yellowish white by reflected light and faint yellow or yellowish green by transmitted light; soluble in excess of KI and insoluble in NH_3. $AgIO_3$ is probably orthorhombic; negative elongation; index of refraction lower than that of silver iodide; pleochroic; pale yellowish green by transmitted light; soluble in NH_3 and insoluble in sodium chloride solution.

Sb No precipitates from a strongly acidic test solution. In HCl solution antimony yields a yellow coloration with the reagent. The nitric concentrated test solution of antimony salts with the reagent forms dark red or brownish red crystals of SbI_3. Some of them resemble the rectangular plates and prisms of HgI_2, while some crystallize as hexagonal plates. SbI_3 is uniaxial negative with No = 2.78 and Ne = 2.36. If the reagent is added to a 1% HNO_3 test solution a basic salt $SbIO_3$ in faint yellow rhombs and monoclinic plates is usually obtained. $SbIO_3$ is biaxial negative; the optic plane is normal to 010, X = b, the angle between Z and c-axis is 29°; Nm = 1.602. The basis salt is metastable. The biaxial phase appears first then gradually inverts to another phase which is uniaxial positive with No= 1.647 and Ne = 1.641 - 1.643. In the absence of mercury and bismuth, the coloration of SbI_3 is sufficient to indicate the presence of Sb.

Bi Bi is precipitated as BiI_3 in dark red squares and prisms closely resembling those of HgI_2 and of SbI_3 in appearance. In cold water, BiI_3 is insoluble, while SbI_3 is soluble. If an excess of the reagent is added, the double salt $BiI_3 \cdot KI \cdot 2H_2O$ separates as yellow or orange hexagonal disks. BiI_3 is more easily produced in warm test drop.

As Usually yields a yellowish green to yellow orange, amorphous precipitate. Well-formed crystals of AsI_3 are formed from a dilute hydrochloric (rarely nitric) test solution. AsI_3 is hexagonal and crystallizes in hexagonal and trigonal basal plates. Uniaxial negative with No = 2.59 ±, Ne = 2.23 ±. Color yellow orange. It closely resembles PbI_2 in form but has higher indices and appears dark grey by reflected light.

Cu Cuprous salts give a yellow amorphous precipitate that is soluble in an excess of the reagent and causes the KI set free to crystallize as colorless isotropic crystals.

Sn No precipitate is formed from stannic salts. Stannous salts give a yellow white amorphous precipitate that is soluble in an excess of KI.

Fe No precipitate forms, but the test solution turns yellow or yellowish brown.

Al, Zn, Ni, Mn, Cr, Co, Ca, Sr, Ba, Mo. These elements do not yield precipitates nor do they interfere with the tests for Pb and Hg.

Potassium Mercuric Thiocyanate

This reagent is prepared by dissolving one part of $Hg(SCN)_2$ and 3 to 5 parts of KSCN in a minimum quantity of water. Stir until a complete solution is obtained, and evaporate to crystallization at room temperature. Cool, wash the crystalline residue with alcohol, and dry.

$K_2Hg(SCN)_4$ is monoclinic; crystals in needles or plates. Y nearly = c, Z = b, (-)2V = nearly 90°. Ng = 1.9+, Nm = 1.8, Np = 1.645. White to colorless. This salt can be recrystallized, on gentle warming, in those test solutions with which the reagent gives no reactions.

This salt yields sensitive reactions with a number of common metallic elements and gives delicate crystals especially when it reacts with the salts of Co, Cu, and Zn. Although some crystals produced are metastable, but their characteristic colorations are generally reliable for their identification. If two or more elements are present in the test drop, the crystals separated are slightly different from those obtained by normal reaction with the individual elements and are apt to attain their forms and colors partially identical with those of the normal reaction products. This character may afford a means of estimating the approximate percentage of the cations present in the test drop.

All the reactions cited below are performed by adding a small fragment or a drop of saturated water solution of reagent to the dilute nitric test drop. The figure enclosed in the parenthesis is used to denote the concentration of that cation in the test solution, i.e., Ni(1) represents a 1% test solution of nickel.

Zn White feathery crosses with short branches oblique or perpendicular to the four main arms. From very dilute solution this salt crystallizes in single prisms.

Zn(1) Co(0.1) Co largely masked; all Zn crystals colored blue.

Zn(1) Co(1) Greyish blue dendritic crystals and bundles of prisms.

Zn(0.1) Co(1) Zn crystals are rarely present. Co crystals separate in normal form.

Zn(1) Pb(1) Pb does not give crystals and interferes with the Zn test. Even when the concentration of Pb is much above 2%, there separate a few crystals of $PbHg(SCN)_4$ later than the Zn crystals.

Zn(1), Ag(1), Hg(1), Pb(1) In a test drop containing equal amounts of these 1% test solutions, separate only the Zn crystals.

Zn(1) Cu(1) The greenish grey prisms and needles of Cu salt separate first and a few Zn crystals appear later.

Zn(0.1) Cu(1) Zn crystals are difficultly recognized.

Zn(1) Ag(1) Crystals of both salts are distinguishable.

Zn(1) Ni(0.1) Pale brown to white spherulites of Ni crystals form. Test for Zn not satisfactory.

Zn(0.1) Ni(1) Ni retards the separation of Zn crystals.

Cu Yellowish green needles and prisms, in dendritic or radiating aggregates, separate from concentrated test drop. In 1% test solution this salt crystallizes in single needles, dagger-shaped and arrowhead-shaped crystals.

Cu(1) Pb(1) Cu and Pb do not interfere with each other. When the percentage of Pb is lower than 0.1 in test solution, the test for Pb is often not satisfactory.

Cu(1) Ag(0.1) Cu crystals distinguishable. Ag test not satisfactory.

Cu(1) Ag(1) Cu test masked by the granular precipitate of Ag salt.

Cu(1) Co(0.1) No Co crystals separate.

Cu(1) Co(1) Co does not retard the separation of Cu crystals

Cu(0.1) Co(1) Cu crystals are colored bluish green, and separate later than those of Co salt.

Cu(1) Sn(1) The dense precipitate of Sn salt retards the separation of Cu crystals.

Cu(1), Hg(1), Ag(1), Pb(1) The test for Cu is not satisfactory in the presence of these elements.

Cu(1) Fe(1) Cu crystals colored brownish green.

Co Blue prisms of $CoHg(SCN)_4$ are arranged in radiating masses and star-like groups. The intensity of coloration depends upon the Co concentration in the test solution. Except for Zn, Hg, Ag, and Pb, no other elements give serious interference reactions with the test for Co.

Pb A colorless to white granular precipitate separates in concentrated test drop. In a 1% solution, there is a slow precipitation of colorless, monoclinic plates and stout prisms.

Ag When the concentration of Ag is high, silver may give a granular precipitate or finely divided aggregates. Colorless, tiny leaflets and slender prisms with oblique ends are formed in a 1% test solution.

Ni Nickel is precipitated as spherulites and tiny hexagonal grains which are pale yellow to colorless and are uniaxial negative.

Fe Solution colored reddish brown. The intensity of coloration increases with the rise in Fe concentration.

Hg, Sb, Bi, Cr, Mn, Sn No precipitate.

Sulphuric Acid

Sulphuric acid is the most satisfactory reagent for the detection of alkaline earths. The reagent is applied in low concentration to a cold, neutral or slightly acidic, moderately concentrated test solution unless otherwise noted.

Ca Clusters of acicular crystals of microchemical gypsum separate from HNO_3 or HCl test solution. Recrystallization may give well-formed monoclinic crystals.

Crystals of microchemical gypsum are soluble in warm water and acids.

Sr Yields white to colorless acicular crystals which soon develop to a granular precipitate of minute squares and rhombs. The composition of the acicular crystals is $SrSO_4$, corresponding to the natural substance celesite which is described in great detail in many textbooks of mineralogy. The squares and rhombs are isotropic with an index of refraction greater than 1.78, and are more developed on gentle warming. The formula of this salt is uncertain. All these crystalline precipitates are soluble in acids and insoluble in dilute sulphuric acid and alkalies.

Ba Gives a white, fine-grained amorphous precipitate in which the tiny orthorhombic crystals of $BaSO_4$ can hardly be recognized. $BaSO_4$ is insoluble in water and not appreciably soluble in dilute nitric acid.

Pb Lead sulphate rarely separates as white needle-like crystals or slender prisms, either singly or in crosses. More often it gives a dense, white, granular or amorphous precipitate indistinguishable from barium sulphate. Insoluble in water but will dissolve in HNO_3 with difficulty.

Ag Colorless, highly refractive, rhombs and short prisms separate from the concentrated test drop (Figure 32). These are soluble in water.

Hg Mercuric salts give no precipitate with the reagent. Mercurous salts in a concentrated solution yield aggregates of acicular crystals and slender prisms.

Bi Bismuth produces a precipitate indistinguishable from that of Hg_2SO_4.

Triple Nitrite Reaction

The triple nitrite reaction is dependable for the test of Pb, Cu, Co, and Ni. The formula of the reaction product is $X_2YZ(NO_2)_6$, in which X may be K, Rb, Cs, Tl; Y may be Pb, Ca, Ba, Sr; and Z may be Co, Cu, Ni. The general procedure for detection of Z (metallic elements Co, Cu, Ni) is as follows: To the dried-up test drop add acetic acid, sodium acetate, acetate of Y (usually lead acetate preferable), and a slight excess of solid nitrite of X; tiny cubes of triple nitrite are obtained. The introduction of KNO_2 as a reagent may give large size cubes of potassium triple nitrite $K_2YZ(NO_2)_6$. In the formation of $K_2YCu(NO_2)_6$ crystals, a large amount of copper acetate is often required for the reaction. No crystals separate from a strong acid test drop.

All the potassium triple nitrite salts and their colors are tabulated below. They are isometric, highly refractive, and have the index higher than 1.78. Most of them are yellow to dark brown. However, when the cubic crystals are formed in the preparation, further detection is required for the confirmation of the suspected element.

$K_2PbCu(NO_2)_6$, dark brown to black.

$K_2PbCo(NO_2)_6$, reddish yellow to dark brown.

$K_2PbNi(NO_2)_6$, yellowish brown.

$K_2CaNi(NO_2)_6$, bright yellow.

$K_2SrNi(NO_2)_6$, yellow red.

$K_2BaNi(NO_2)_6$, yellowish brown.

$K_2CaCo(NO_2)_6$, dark grey.

$K_2SrCo(NO_2)_6$, grey.

$K_2BaCo(NO_2)_6$, yellowish green to green.

$K_2CaCu(NO_2)_6$, colorless to white.

$K_2SrCu(NO_2)_6$, light yellowish brown.

$K_2BaCu(NO_2)_6$, yellow.

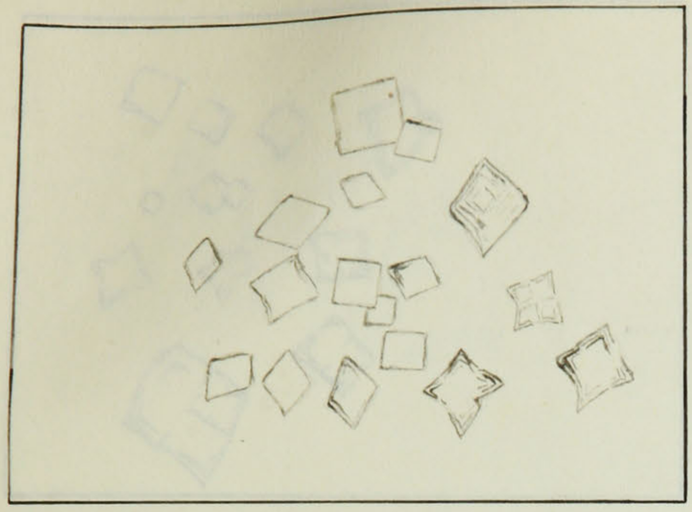

Fig. 1. Ammonium aluminum molybdate. X200.

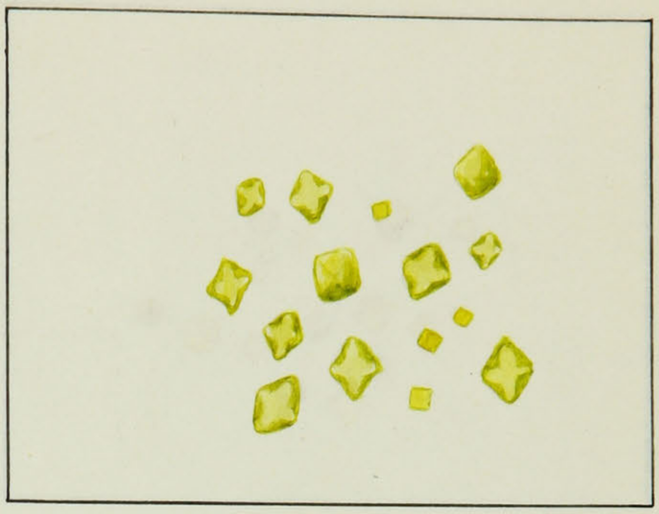

Fig. 2. Ammonium arseno-molybdate. X250.

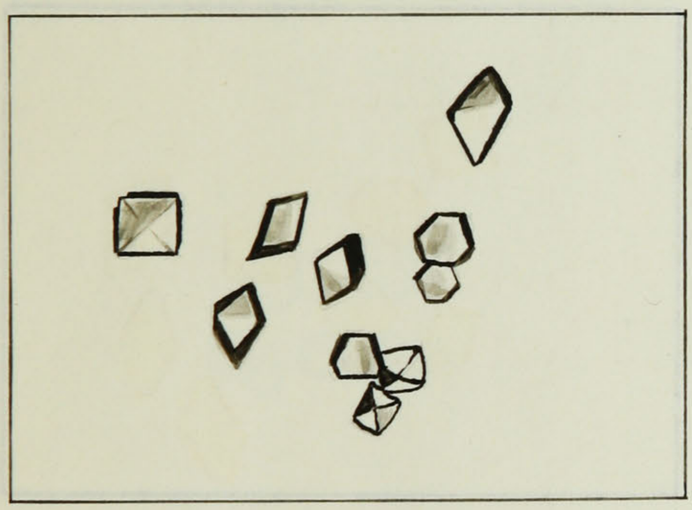

Fig. 3. Ammonium chloro-stannate. X80.

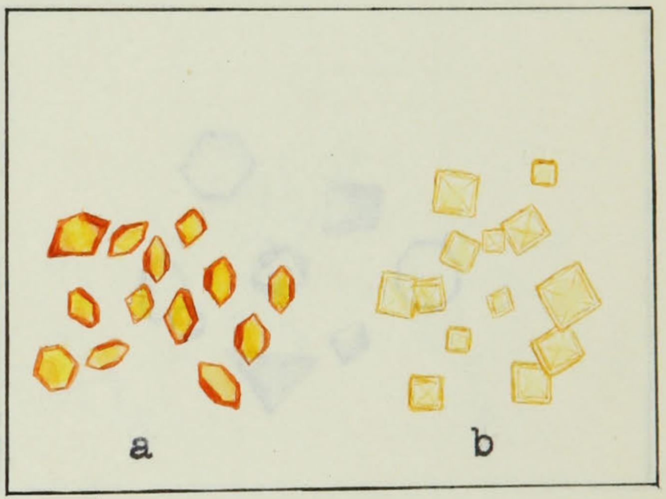

Fig. 4. Ammonium ferric chloride (a) and 'mixed crystals' (b) of ammonium chloride and ferric chloride. X100.

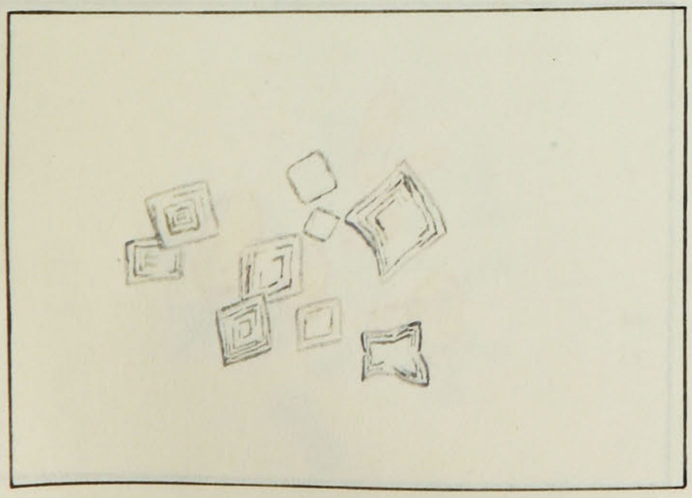

Fig. 5. Ammonium ferric-molybdate. X200.

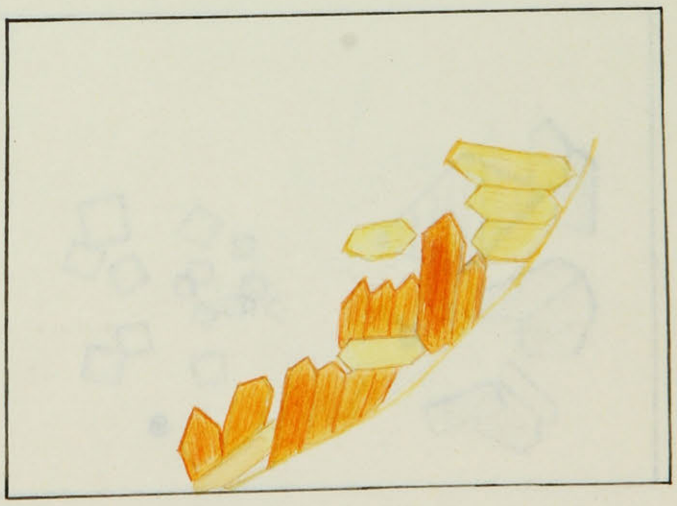

Fig. 6. Ammonium manganese molybdate. X150.

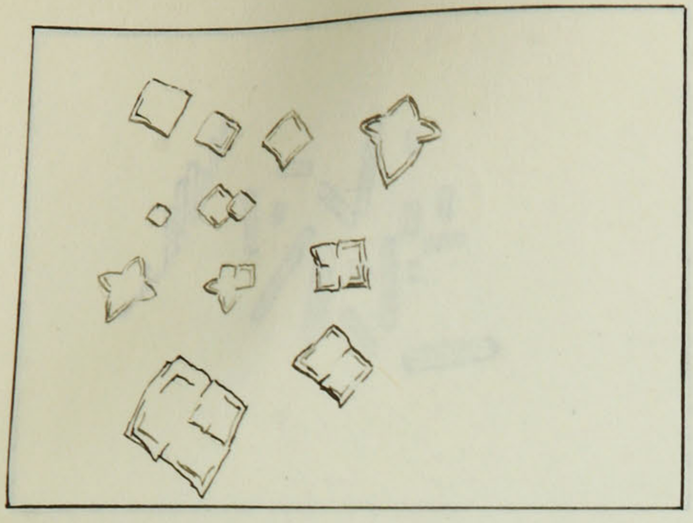

Fig. 7. Ammonium nickel molybdate. X200.

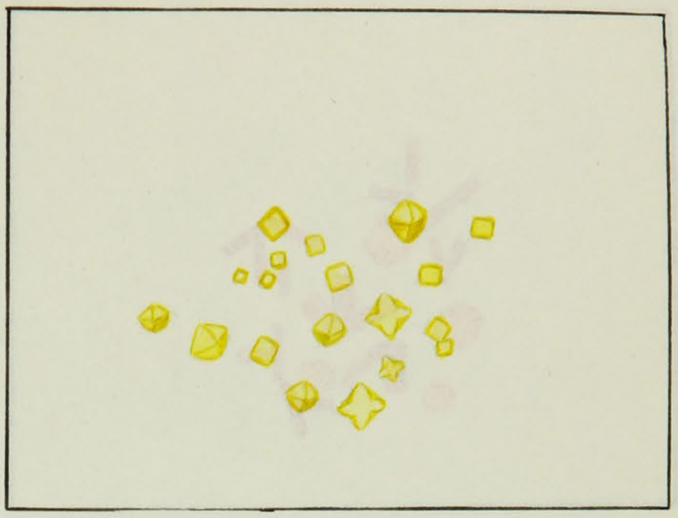

Fig. 8. Ammonium phosphomolybdate. X200.

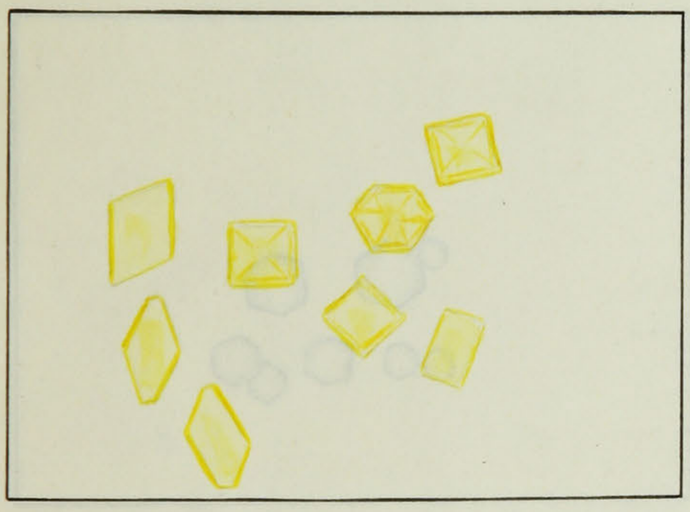

Fig. 9. Antimony oxyiodide. X150.

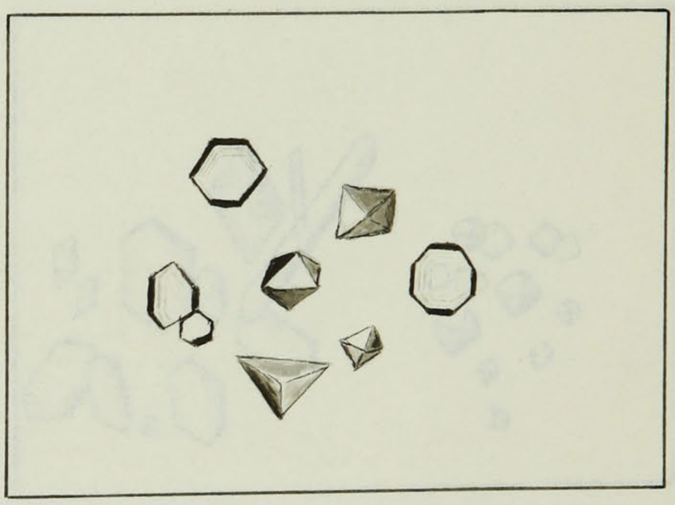

Fig. 10. Arsenic trioxide. X100.

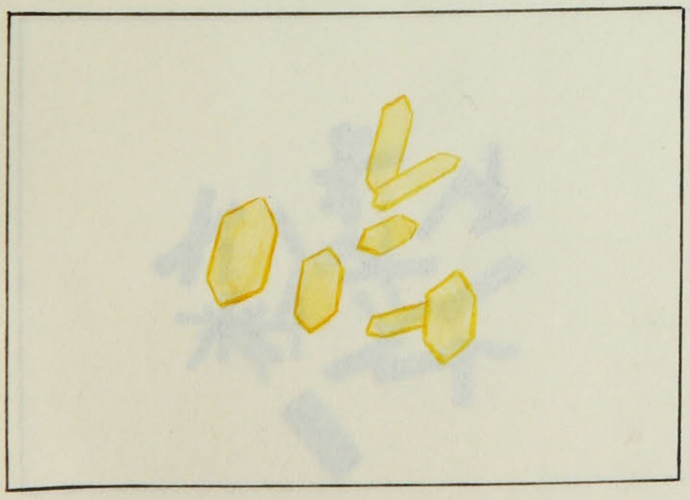

Fig. 11. Barium bichromate. X150.

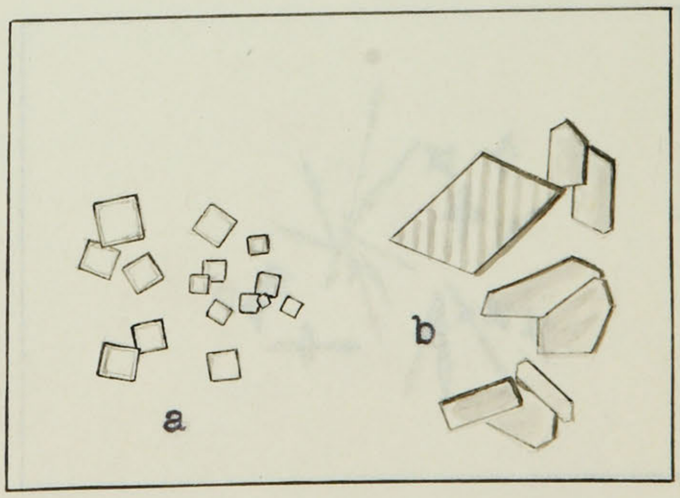

Fig. 12. Barium chloride (a) and dihydrated barium chloride (b). X150.

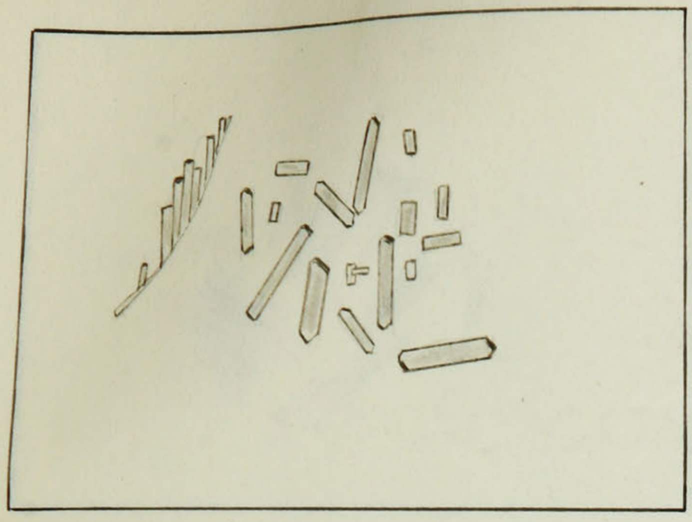

Fig. 13. Barium oxalate monohydrated. X200.

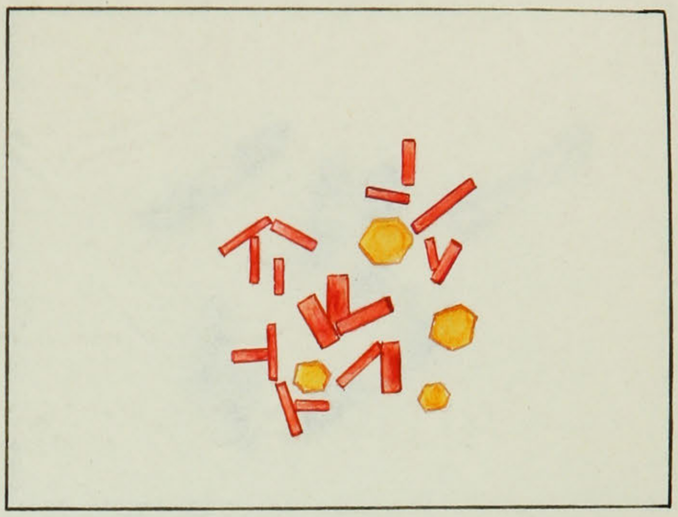

Fig. 14. Bismuth iodide. X200.

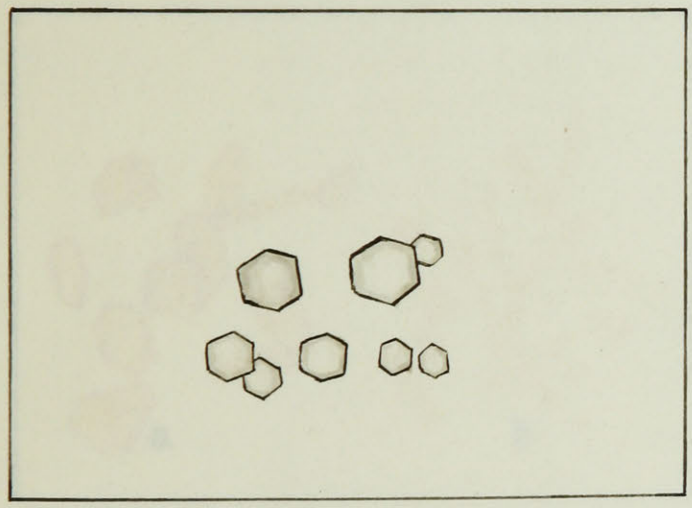

Fig. 15. Bismuth potassium sulphate. X150.

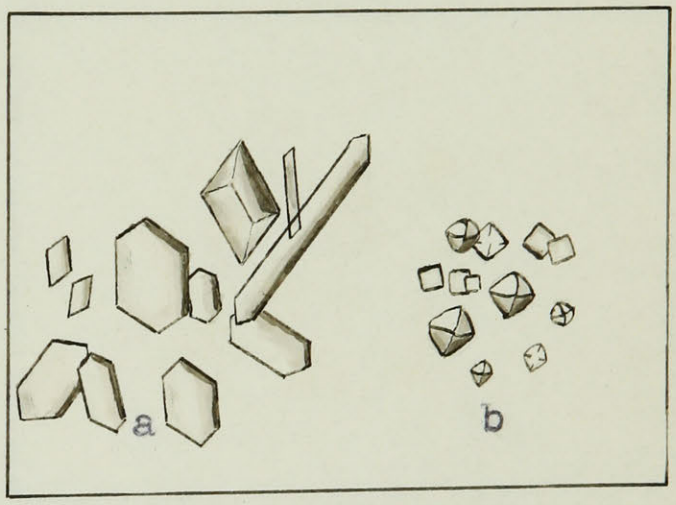

Fig. 16. Calcium oxalates, monohydrated (a) and trihydrated (b). X200.

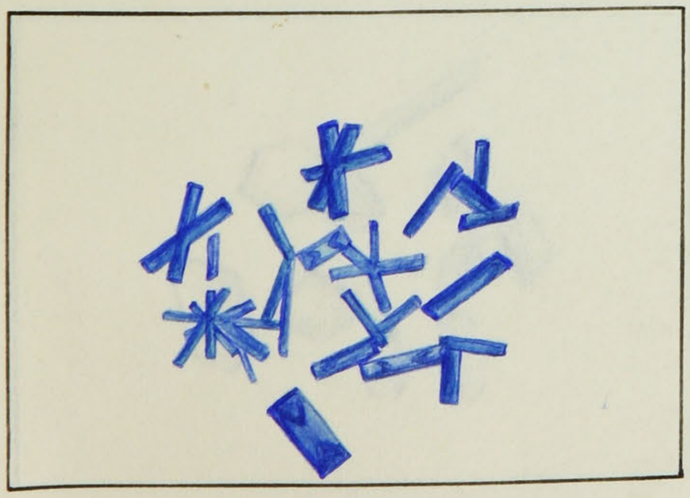

Fig. 17. Cobalt mercuric thiocyanate. X150.

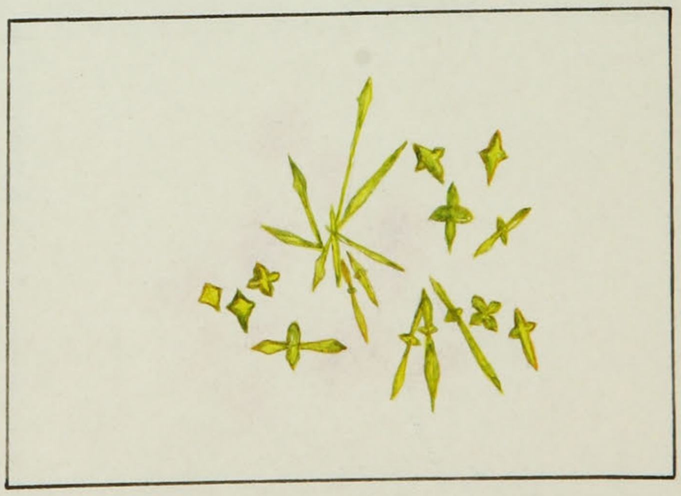

Fig. 18. Copper mercuric thiocyanate. X150.

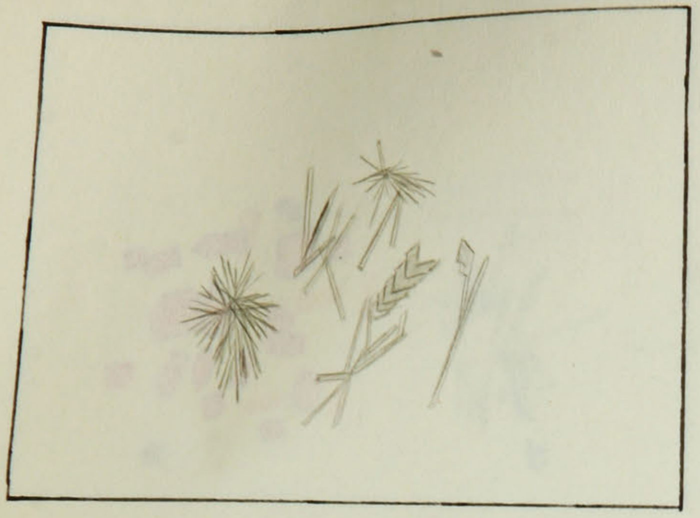

Fig. 19. Crystals of microchemical gypsum. X100.

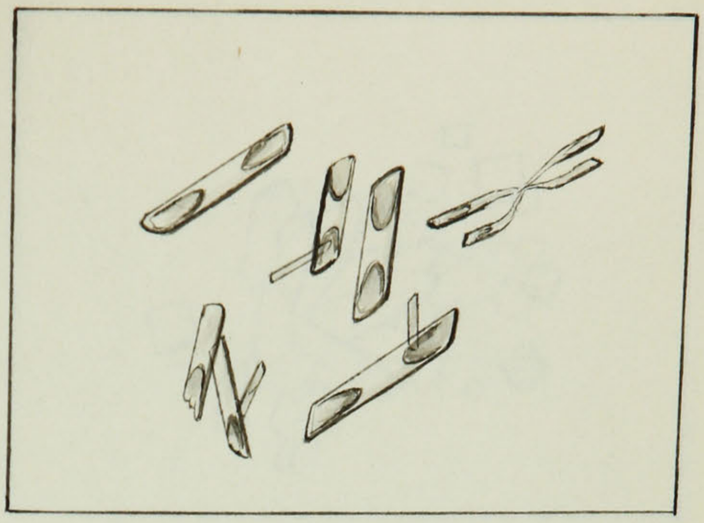

Fig. 20. Lead chloride. X80.

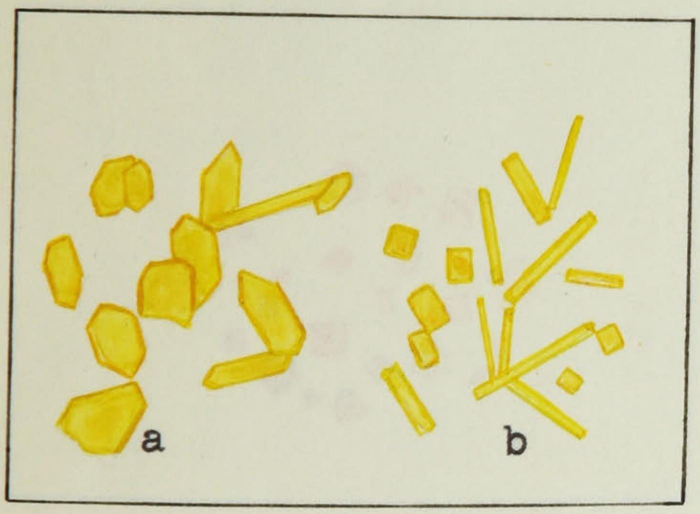

Fig. 21. Lead chromate (a) and basic chromate (b). X250.

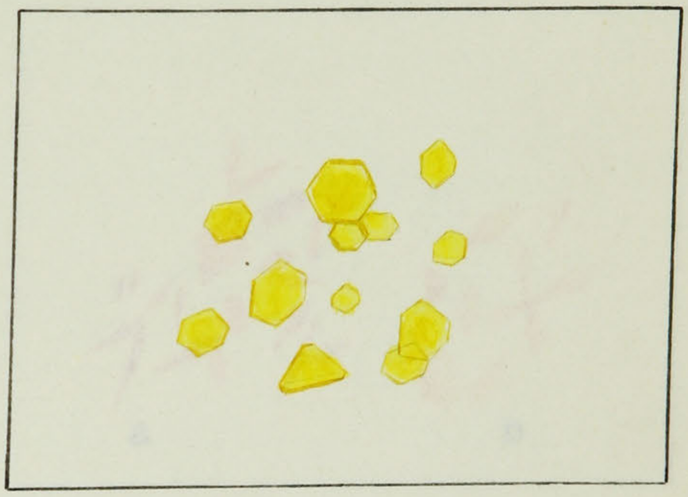

Fig. 22. Lead iodide. X100.

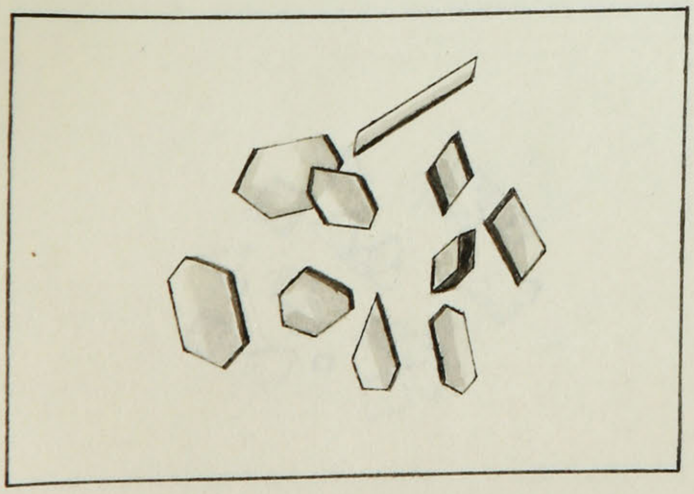

Fig. 23. Lead mercuric thiocyanate. X100.

Fig. 24. Manganese chromate of complex composition. X100.

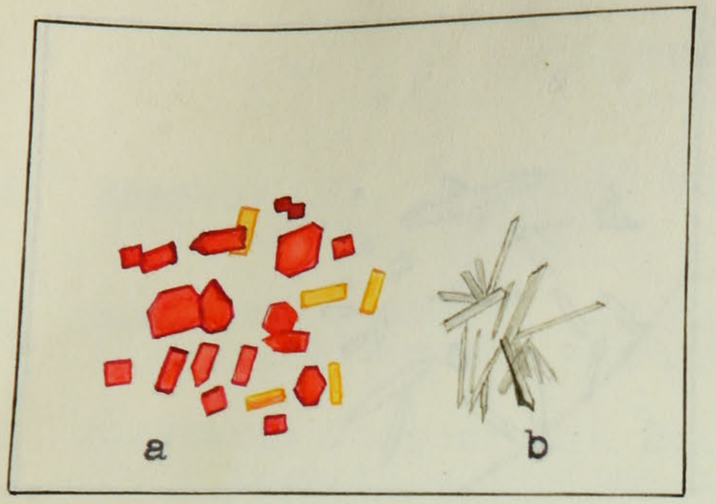

Fig. 25. Mercuric iodide (a) and mercuric potassium iodide (b). X100.

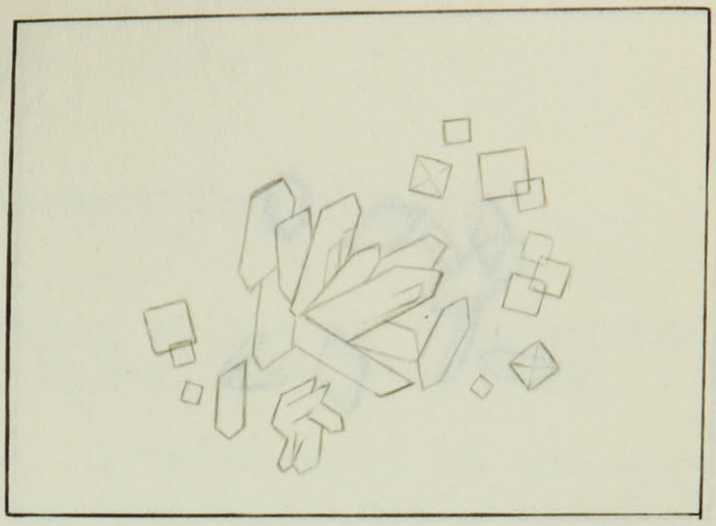

Fig. 26. Potassium alum. X100.

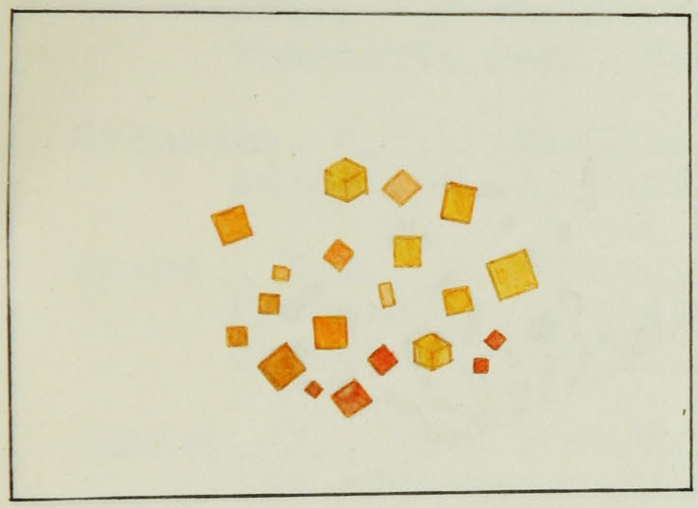

Fig. 27. Potassium-lead-copper nitrite. X80.

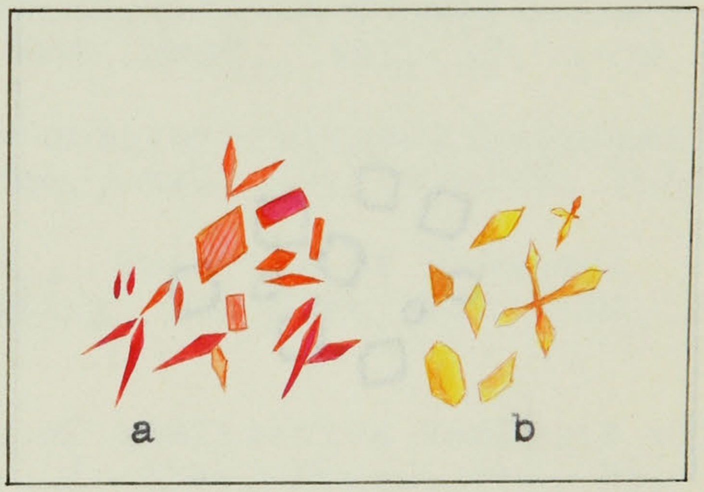

Fig. 28. Silver chromate (a) and bichromate (b). X100.

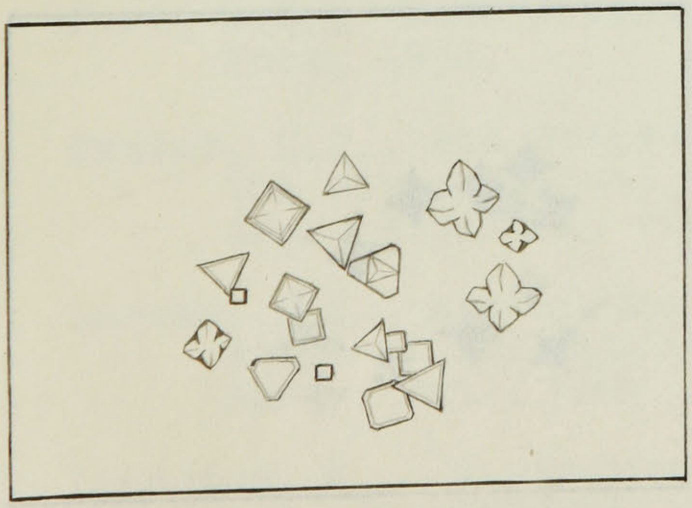

Fig. 29. Silver chloride. X100.

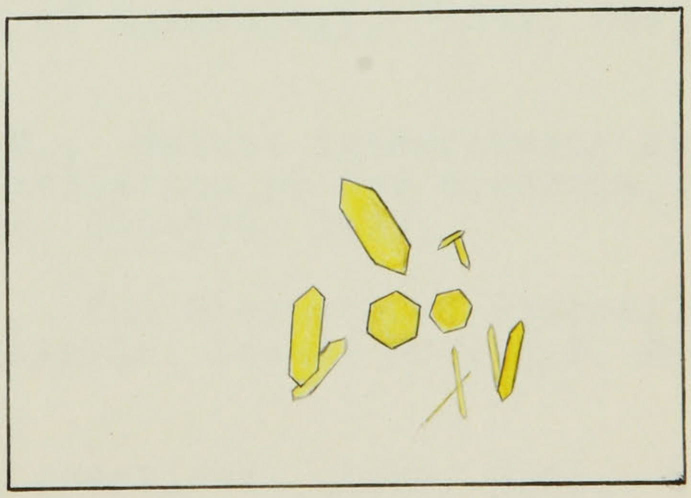

Fig. 30. Silver iodate. X200.

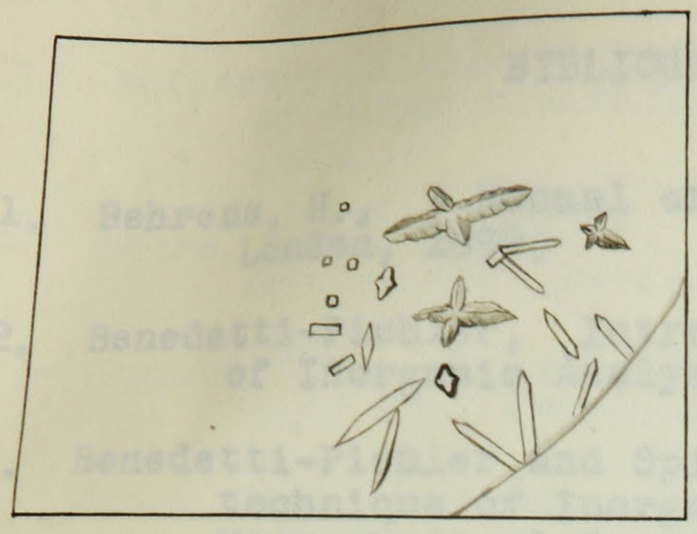

Fig. 31. Silver mercuric thiocyanate. X100.

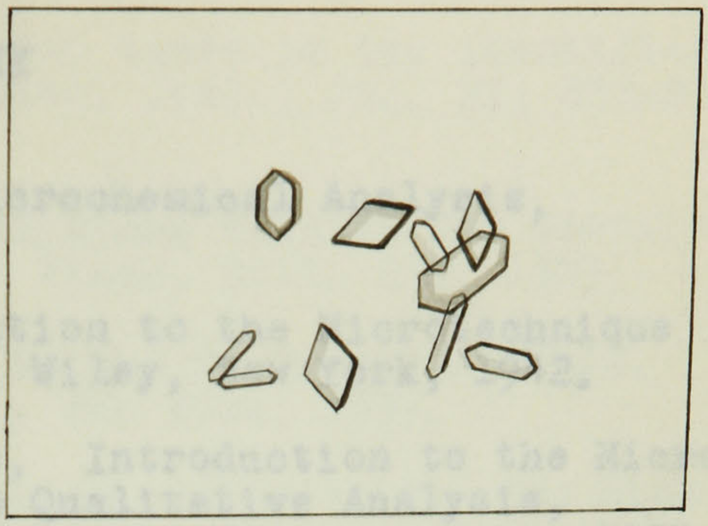

Fig. 32. Silver sulphate. X100.

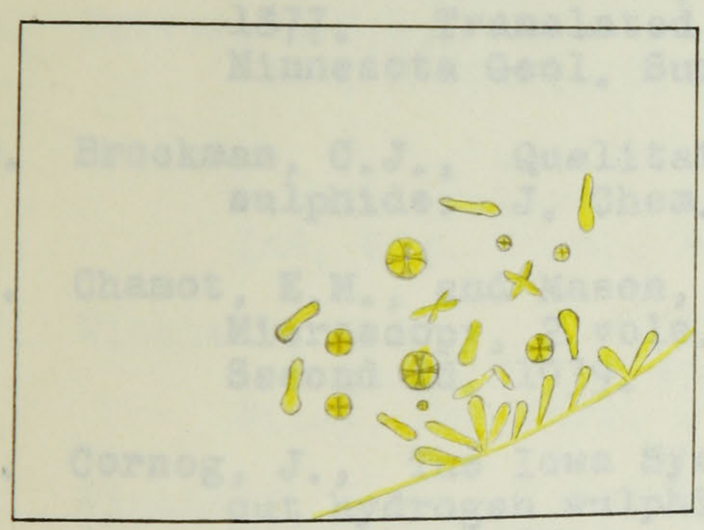

Fig. 33. Strontium chromate. X100.

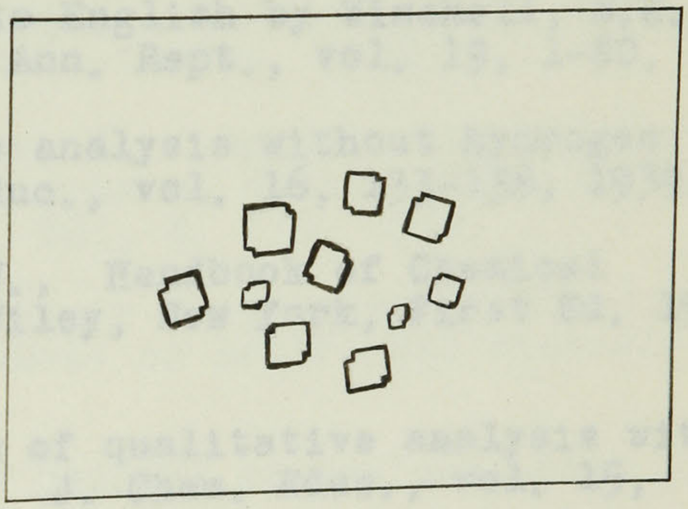

Fig. 34. Zinc oxalate dihydrated. X100.

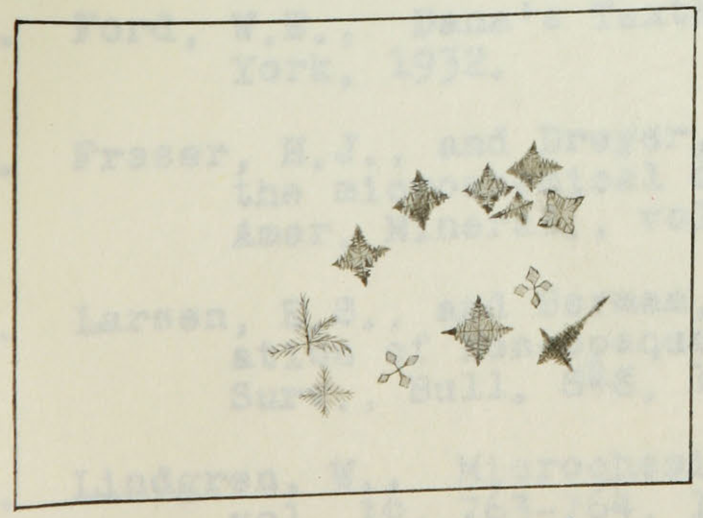

Fig. 35. Zinc mercuric thiocyanate. X150.

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