THE AMERICAN MINERALOGIST
JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 21 OCTOBER, 1936 No. 10

MINERAL DETERMINATION BY MICRO-CHEMICAL METHODS

LLOYD W. STAPLES, *Stanford University, California.*

HISTORICAL INTRODUCTION

The value of the study of chemical reactions under the microscope and the recognition of precipitates by their characteristic geometrical and optical properties has long been known. As early as 1867 Wormley (28) published a treatise on the microchemistry of poisons. Bořický (4) was the pioneer in the application of microchemical tests to minerals. In 1877 he stated his hope of developing a "universal method" for analysis of rock-forming minerals by means of the recognition of the characteristic fluosilicates of the metallic elements. His work gave impetus to a rapid development of microchemistry, which movement lasted until the end of the century. During that period Streng, Haushofer, McMahon, Klement and Renard, Huysse, Behrens, and others made highly valuable contributions. How closely the development of microchemistry was associated with petrography and mineralogy is readily apparent on noting the principal field of interest of the above mentioned workers.

The work of Behrens (1) marked the greatest development of microchemistry up to the last decade. During the first quarter of this century there was a definite lag in interest and it was not without good reason that Lindgren (13) remarked in 1924, "And yet it seems to me that they (microchemical methods) have fallen into a sort of 'innocuous desuetude'; . . . several friends of the geological, yea even of the mineralogical brotherhood . . . have confessed that they never realized the possibilities of reactions on a glass slide, under the microscope, and have become quite enthusiastic."

PRESENT DEVELOPMENT IN MINERALOGY

During the last decade there has been a reawakening of interest in microchemistry. In the field of mineralogy this movement has come principally through the channel of the opaque minerals. McKinstry (14), and Putnam, Roberts, and Selchow (18) made helpful contributions and in 1931 Short (24) published a very complete and satisfactory description of microchemical tests in the limited field of the ore minerals.

Unlike the first rise in interest in microchemical methods, the present movement is welcomed more enthusiastically by chemists. Chamot and Mason's (5) textbook, written chiefly from the chemical viewpoint, is the most valuable general work on the subject in English. Due to the great interest of chemists, a periodical, *Mikrochemie*, has been established. The organization of a microchemical section by the American Chemical Society is further evidence of the growing importance of the subject.

As a result of this interest on the part of chemists it is not surprising that the development of microchemistry should move in a slightly different direction than it did under the influence of mineralogists and petrographers. The latter were well acquainted with the polarizing microscope and the study of crystallography, so they naturally used crystalline precipitates in their work. Under the influence of chemists a departure was taken from the use of crystalline precipitates, and color reactions have become more prominent. It is the writer's belief that since a mineralogist's training fits him so well for the study of crystals, and since a great deal of information may be obtained from them, crystalline precipitates should in general be preferred to color reactions in mineral testing.

In this renewed interest in microchemical methods, the nonopaque minerals have been greatly neglected. There are definite advantages to be gained from the application of microchemical methods to these minerals, and it is the purpose of this paper to pay special attention to tests that are useful in their determination.

Advantages and Difficulties in the Use of Microchemical Methods

The use of microchemical methods in mineral determination frequently results in a saving of material, reagents, and time. Microchemical testing may be used independently of other methods, but its greatest efficiency is most often found when it is used in conjunction with some other determinative method. Because of their dependence on the microscope, immersion methods and microchemical tests work very well when used to supplement each other. This is especially true in the case of minerals with overlapping indices of refraction, or with such good cleavage that complete index determination is made difficult. One can often obtain a quicker and more certain determination of a mineral by finding only one index of refraction and then making one or two simple microchemical tests than by attempting to get accurately all of the indices of refraction.

For the determination of minerals of high index of refraction, above about 1.74, it is difficult to obtain good stable index liquids and many laboratories are without these higher liquids. Consequently microchemical tests become of increasing importance for minerals of high index of refraction. Cerargyrite, for example, can be very simply determined by recrystallizing it in the form of octahedrons from an ammonium hydroxide solution, whereas its high index of refraction might prevent it from being determined by immersion methods in many laboratories.

The value of microchemical methods in the discovery and investigation of new minerals was noted by the writer in his work on the new mineral, austinite (25).

Aside from its value as a tool in determinative work, microchemical study provides excellent training in chemical and geometrical crystallography. The investigator learns to appreciate the phenomenon of isomorphism, and to one who is interested in the still little understood field of crystal growth, ample opportunity is provided for interesting experimentation. Crystals of the type shown in Fig. 6 permit the worker to attack the subject of geometrical crystallography from a viewpoint which is quite different from the conventional one.

Microchemical methods, like all other determinative methods, are not without their attendant difficulties. Failure to obtain satisfactory tests is usually due to one or more of the following causes: lack of technique on the part of the worker, failure to get the mineral in solution, inadequate or indefinite microchemical tests for certain elements, confusion due to interference by elements other than the one for which the test is being made, confusion due to isomorphous precipitates, or difficulty in recognition of crystals because of variation in habit. In spite of these difficulties, the advantages to be gained from microchemical methods are sufficient to recommend them strongly.

Although the application of microchemical methods to minerals has been investigated and developed over a long period of years, there remains ample opportunity for the improvement of tests and technique in this field. It is hoped that this article will prove a stimulus to work in this direction because it seems certain that intensive work will be well rewarded with the discovery of considerable valuable information.

TERMINOLOGY: MICROCHEMISTRY AND CHEMICAL MICROSCOPY

"Microchemistry" is an old term and its original meaning was stated by the pioneer, Wormley (28), in his *Micro-Chemistry of Poisons.* He said: "By the term *micro-chemistry of poisons*, we understand the study of the chemical properties of poisons as revealed by the aid of the microscope . . . ." Because of the introduction of many new micro-methods in which the microscope was not used, Chamot and Mason (5) introduced "chemical microscopy" giving it practically the same meaning originally held by "microchemistry." "Microchemistry" is now taken to mean the chemical investigation of *small amounts* of material, regardless of the apparatus or technique used. "Chemical microscopy" requires the use of the *microscope*, but does not demand the use of small amounts of material or great sensitivity.

In making qualitative tests of the type discussed in this paper, the mineralogist will probably have one or more of the following purposes in mind: (1) to test for small amounts of replacing elements, such as for calcium and barium in strontianite, (2) to determine the mineral present when only a very small amount of material is available, (3) to determine the identity of a mineral with plenty of material available, but using small scale methods in order to save time or to be more certain of the results. According to Chamot and Mason's terminology, only the second of these would necessarily require "microchemical" tests, and if the microscope were used, all three would take advantage of "chemical microscopy." From this it will be evident that the mineralogist's main interest will be in "chemical microscopy" rather than "microchemistry" if the method of crystalline precipitates is used. However, as noted by Benedetti-Pichler (3), it is not always possible in practical work to separate completely these two branches of study.

At present the situation is one in which the term "chemical microscopy" is carefully used by chemists but generally disregarded by mineralogists. Mineralogists may feel that in this instance the degree of refinement required by chemists in their nomenclature is not necessary in the field of mineralogy. In any case, the adoption of a new term in any field will depend on whether that term fills a definite need.

It seems to the writer that the simple word "microchemistry" is to be preferred to the longer, less euphonious "chemical microscopy" when the meaning is clear. Since "microchemistry" is the more general term it includes the other and prevents the necessity of hair-splitting as to which term should be used. In those few cases where a comparison is to be made between various types of microchemical tests, such as between spot-tests[1] (Tüpfelreactionen developed by Feigl and Leitmeier) and chemical microscopic tests, the term "chemical microscopy" serves a real purpose and should be used.

REAGENTS

The number and kind of reagents required for microchemical testing of minerals will depend, of course, on the tests which are selected.

---

[1] This type of reaction, applied to minerals, has recently been discussed by Watson (27).

Since no two workers will agree on which tests are best, and furthermore, since the fields of interest of investigators vary, it is impossible to give a list of reagents which satisfy all demands. There is also likely to be a difference in preference with regard to the use of liquids or solids. This is the case with potassium mercuric thiocyanate, ammonium paramolybdate, and disodium acid phosphate, which may be used either as solids or solutions. For the magnesium test in which magnesium ammonium phosphate is precipitated, all of the reagents may be put into a single solution which will then contain NH_4Cl, Na_2HPO_4, and NH_4OH. Most people prefer to add the reagents separately in this last case. Solid reagents usually keep better than solutions and react more slowly when placed in a test drop. Solutions produce quicker reactions, they permit better control of concentrations, and there remain no undissolved remnants of the reagent to obscure or confuse the test.

For general mineralogical work, more reagents will be required than those listed by Short (24), since he is only concerned with the restricted field of the ore minerals. However it is not necessary to have the great number of reagents suggested by Chamot and Mason (5). The writer uses about 25 reagents in most of his work and keeps these in three groups.

(1) The solvents are kept in small ground-stoppered bottles in a wooden block (22×7×3 cm.), called the solvent block. The most frequently used solvents are HCl (2:3), H_2SO_4(1:4), HNO_3 (1:1), and NH_4OH (conc.). Each reagent bottle has its individual dropping pipette. The pipettes are made out of glass tubing and are superior to glass rods because the quantity of liquid to be delivered can be better regulated.

(2) A wooden block 19 cm. long and 11 cm. wide is constructed to hold the reagent vials. The block is arranged with steps, each step standing about 1 cm. above the one in front of it, and holding 6 vials. Vials which are 45×15 mm. are of a convenient size for this work. The solutions are kept in the vials in the first row and when a drop is needed it is transferred by a platinum wire with a loop in the end of it. The following reagents are kept in the reagent block: ammonium paramolybdate (ordinary "ammonium molybdate"), disodium acid phosphate, chloroplatinic acid, potassium mercuric thiocyanate, potassium iodide, silver nitrate, calcium acetate, sodium dicarbonate, sodium chloride, uranyl acetate, ammonium chloride, ammonium dichromate, cobalt nitrate, cesium chloride, potassium sulfate, dimethylglyoxime, fluorite, sodium bismuthate, iron filings, potassium thiocyanate, and potassium ferrocyanide. The uranyl acetate is wrapped in paper so that it will not come in contact with the glass of the vial.

(3) The less frequently used reagents and solvents should be kept near at hand but not on the desk of the worker, since an overcrowded desk decreases efficiency. In this group are the concentrated acids and some of their commonly used dilutions.

APPARATUS

An advantage of the use of microchemical methods in mineralogy is that very little apparatus ordinarily is required. The apparatus is described in those texts dealing with microchemical methods, and only a few additional remarks will be made here.

A good polarizing microscope should be used for this work. With proper precautions the use of chemicals will not injure the instrument, and consequently it is not necessary to handicap one's self with a poor instrument because of fear of injuring a good one.

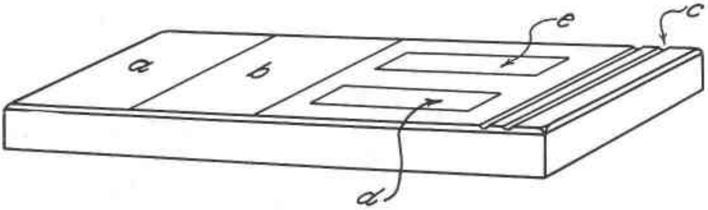

FIG. 1. TESTING BLOCK
(a) Area painted black, (b) area painted white, (c) grooves for holding glass tubes and platinum wire, (d) asbestos pad, (e) mirror.

An alcohol lamp provides the best source of heat for microchemical work. The lamp can easily be made from a drawing-ink bottle, a cork, a piece of string to serve as a wick, and a section about 3 cm. long of an old blowpipe to act as a guide for the wick through the cork. A Bunsen burner should be available for making fusions.

Glass slides of the size used in petrographic work (25×45 mm.) are preferable to the larger slides used in biological work because the latter often extend over the edge of the microscope stage and are likely to be knocked off. The cleaning of slides is important but it is not necessary to be as careful with it as has frequently been recommended. A good scrubbing with soap and water, and rinsing in distilled water is usually sufficient. If they are dried with a paper or cloth towel, any lint deposited may be removed with a silk cloth. The other alternative is to let the water evaporate from them, but this obviously requires a longer time. All of the glassware should be cleaned periodically with sulfuric-chromate cleaning solution.

The writer has found considerable use for what he calls a "testing block." The accompanying illustration shows the general arrangement of the wooden block, which is 20×11cm. in plan and 2 cm. high. It consists of an area (a) painted black, an area (b) painted white, an unpainted portion containing two grooves (c), a rectangular piece of asbestos pad (d), and a mirror (e). The main purpose of the block is to provide a place on which to set slides while adding reagents and from which slides can easily be picked up. Hot slides may be placed on the asbestos pad. The colored areas provide contrasting backgrounds for small amounts of material. If a slide with a drop on it is placed on the mirror the boundaries of the drop and its color are often made more definite. The grooves are used for holding the platinum wire and other pieces of apparatus. By permitting glass tubes to extend out over the edge of the block they are kept from being contaminated by contact with the desk.

A piece of 4 mm. glass tubing with a fine platinum wire extending out of it for about 5 mm. is useful for joining drops on the glass slide. A pointed glass rod may be used for the same purpose but it has the disadvantage that the fine tip breaks off too easily.

SELECT MICROCHEMICAL TESTS

Table 1 presents a summary of those microchemical tests which have been found to yield the most satisfactory results in mineral determinative work. The material in the table is intended to recall some of the important details of these tests, but is not sufficient to act as a guide for the performance of the tests for persons who are not already acquainted with them. For a more complete description of the tests reference should be made to the section on microchemistry by the writer in Rogers' textbook (20), or to the work of the author whose initial follows the reagent, thus (C) refers to Chamot and Mason (5), (S) to Short (24), (B) to Behrens and Kley (2). An asterisk in place of an initial indicates that a description of the test, or new material pertaining to it, is to be found in this paper following the table.

The hydrogen ion concentration of the test drop which will give the best conditions for precipitation of characteristic crystals is not noted in the table. In every case the acid should be dilute. Short recommends the use of 1:7 HNO_3 and 1:5 HCl for all those tests which are marked with his initial (S). All other tests may be performed in 1:1 HNO_3, 2:3 HCl, or 1:4 H_2SO_4. In the case of exception to these rules, the degree of acidity is noted in the table.

Only the most characteristic habits of the precipitates are listed. When no color is given for the precipitate it may be assumed that it is colorless or nearly so.

TABLE 1

Elements	Reagents	Test Drop	Description of Precipitate
Aluminum	NH_4 molyb.*	Neutral	NH_4 alum. molyb. Tab. xls. with sym. extinction.
	CsCl (B)	H_2SO_4	Cesium alum. Octahedra.
Antimony	KI & CsCl (S)	HCl	$SbI_3 \cdot 3CsI$. Orange hexs. or stars.
Arsenic	NH_4 molyb. (S)	HNO_3	NH_4 arsenomolyb. Small yellow octahedra.
	KI *	HCl	AsI_3. Orange hex. plates, stars, powder.
Barium	$K_4Fe(CN)_6$ (C)	NH_4Cl, HAc	$K_2BaFe(CN)_6 \cdot 5H_2O$. Rhombs, sym. extinction.
	HCl *	HCl	$BaCl_2 \cdot 2H_2O$. Mono. xls., polysynthetic twins.
Bismuth	KI & CsCl (S)	HCl	$BiI_3 \cdot 3CsI$. Rose-red hexs., stars.
Borates	HCl *	HCl	H_3BO_3. Pseudo-hex. plates & branching forms.
Calcium	H_2SO_4 (C) *	HCl	$CaSO_4 \cdot 2H_2O$. Mono. xls., length-fast, low biref. $CaSO_4 \cdot \frac{1}{2}H_2O$. Orth. xls., length-slow, higher biref.
Chlorides	$AgNO_3$ (C)	HNO_3	AgCl. Adam. octahedra. (Recrystallize from NH_4OH)
Chromium	$AgNO_3$ (C)	HNO_3 (1%)	Ag_2CrO_4, $Ag_2Cr_2O_7$. Ruby-red pleochroic xls.
Cobalt	$K_2Hg(CNS)_4$ (S)	HNO_3	$CoHg(CNS)_4$. Blue prisms, spherulites.
Copper	$K_2Hg(CNS)_4$ (S)	HNO_3	$CuHg(CNS)_4$. Yellow branching aggregates.
	Iron filings *	Neutral	Copper trees on filings.
Fluorides	NaCl & soluble silicate (B)	HNO_3	Na_2SiF_6. 6-sided xls., low index.
Iron	$K_2Hg(CNS)_4$ (S)	HNO_3	Red coloration.
	NH_4Cl *	HNO_3	Mixed xls., double salt. Brown, isom, orth.

TABLE 1. (*Continued*)

Elements	Reagents	Test Drop	Description of Precipitate
Lead	KI (S)	HAc (0.5%)	PbI_2. Yellow hex. plates.
	HCl (C)	HNO_3	$PbCl_2$. Adam. prisms, aggregates.
Magnesium	Na_2HPO_4 (C)	NH_4OH	$MgNH_4PO_4 \cdot 6H_2O$. Feathery X's, "house tops."
Manganese	NH_4 molyb. *	Neutral	NH_4Mn. molyb. Pleochroic orange laths.
	$NaBiO_3$ (S)	HNO_3	Purple-pink coloration.
Mercury	$Co(NO_3)_2 \cdot 6H_2O$, & KCNS (S)	HNO_3	$CoHg(CNS)_4$. Blue prisms, spherulites.
Molybdenum	Na_2HPO_4 & NH_4Cl (B)	HNO_3	NH_4 phosphomolyb. Small yellow octahedra.
	HCl *	HNO_3	Blue fine-grained ppt. on evap.
Nickel	Dimethylglyoxime (C)	NH_4OH	$Ni(C_4H_7N_2O_2)_2$. Pink acicular xls.
Phosphates	NH_4 molyb. (C)	HNO_3	NH_4 phosphomolyb. Small yellow octahedra.
	$AgNO_3$ (C)	Neutral	Ag_3PO_4. Yellow 3-armed xls.
Potassium	H_2PtCl_6 (C)	HCl	K_2PtCl_6. Yellow octahedra.
	HCl *	HCl	KCl. Isom. xls.
Silicon	CaF_2, H_2SO_4, NaCl *	HNO_3 (1:7)	Na_2SiF_6. 6-sided plates, stars. Low index.
Silver	HCl (S)	HNO_3 (1:1)	AgCl. Adam. octahedra. (Recrystallize from NH_4OH)
	$(NH_4)_2Cr_2O_7$ (S)	HNO_3 (1%)	Ag_2CrO_4, $Ag_2Cr_2O_7$. Ruby-red or yellow xls.
Sodium	Uranyl Ac. (B)	Neutral	Na uranyl Ac. Tetrahedra.
	HCl *	HCl	NaCl. Isom. xls.
Strontium	$(NH_4)_2Cr_2O_7$ (C)	NH_4OH	$SrCrO_4$. Yellow globules, sheaf-shaped groups. Soluble in HAc.
	H_2SO_4 (C)	HNO_3	$SrSO_4$. Rhombs, dagger-shaped xls.

TABLE 1. (*Continued*)

Elements	Reagents	Test Drop	Description of Precipitate
Sulfates	CaAc (C) *	HCl	$CaSO_4 \cdot 2H_2O$. Mono. xls., ext. angle$=37\frac{1}{2}°$ $CaSO_4 \cdot \frac{1}{2}H_2O$. Orth. xls., parallel ext.
Tin	NH_4Cl *	HCl	$(NH_4)_2SnCl_6$. Large octahedra
	CsCl (S)	HCl	Cs_2SnCl_6. Minute octahedra. Sensitive test.
Titanium	H_2O_2 (C)	HCl	Yellow, orange coloration.
Tungsten	Na_2HPO_4 & NH_4Cl (B)	HNO_3	NH_4 phosphotungstate. Small octahedra.
	HCl *	HNO_3	Yellow granular ppt.
Uranium	NaAc (B)	Neutral	Na uranyl Ac. Tetrahedra.
Vanadium	HNO_3 *	HNO_3	V_2O_5. Dense red ppt. on evap.
Zinc	$K_2Hg(CNS)_4$ (S)	HNO_3	$ZnHg(CNS)_4$. Branching aggregates.
	$NaHCO_3$ (C)	Neutral	Double carbonate. Tetrahedra.

DISCUSSION OF CERTAIN TESTS

The tests discussed in the following pages are either new tests, those inadequately described in the literature, or tests concerning which new material has been developed. Only those tests marked with an asterisk in table 1 are described here. They are discussed in alphabetical order, according to the elements for which they are to be used.

Most of the tests discussed here have a limit of sensitivity of about 0.1% of the normal salt of the element. This is a lower sensitivity than that attained in many of the standard reactions, but for mineralogical work it is frequently preferable to use tests that are not too delicate. Also, it is well to have on record several tests of different sensitivities for each element, in order to gain a more accurate idea of concentrations.

A few of the precipitates described are formed on evaporation of the acid solution of minerals. These precipitates are often unexpectedly met when working on unknowns and should be recognized. In this class are sodium chloride, potassium chloride, barium chloride, boric acid, vanadium pentoxide, and the oxides of molybdenum and tungsten. Microchemical gypsum or calcium sulfate hemihydrate may also be formed under these conditions from minerals which contain both calcium and sulfate.

ALUMINUM

Ammonium Paramolybdate.[2] (New test.) If a drop of the acid solution of an aluminum mineral or its fusion is evaporated to dryness and a drop of a saturated water solution of ammonium paramolybdate added, crystals of ammonium aluminum dodecamolybdate will form. According to Hall (9) the formula for this compound is $3(NH_4)_2O \cdot Al_2O_3 \cdot 12MoO_3 \cdot 19H_2O$, but there is some uncertainty as to whether it contains 19 or 20 molecules of water.[3] The crystals (Figs. 1 and 2) are readily recognizable because they occur as rhomb-shaped tabular plates with an angle of 86°. They have symmetrical extinction and their fast ray direction is parallel to the long diagonal. The indices of refraction for the fast and slow ray directions of the plates are $n_s = 1.741$ and $n_f = 1.700$, both ± 0.003, and the birefringence is 0.041 ± 0.006. It is difficult to obtain complete data on the crystals because of their thin tabular habit. By measurement of several plates which were standing on end, the average thickness was found to be about 8μ. This value for the thickness is corroborated by a calculation from the birefringence. The interference color of the single plates is usually white or yellow of the first order and this would indicate a thickness of less than 10μ. The plates when turned on edge seem to have parallel extinction so the crystals probably belong to the orthorhombic system.

As the plates grow they tend to pile up on each other with a slight rotation. Another characteristic is the saddle-shape curvature of many of the plates.

Ferric iron produces a precipitate which is isomorphous with the aluminum compound. Ammonium ferric dodecamolybdate may be distinguished from ammonium aluminum dodecamolybdate by adding an excess of NH_4OH to the drop. Both of the above compounds are soluble in this reagent but the iron compound becomes yellow-brown on dissolving while the aluminum salt remains colorless.

This new test for aluminum has a limiting sensitivity of about 0.1% aluminum chloride and consequently it is not so sensitive as the cesium alum test. It has an advantage over the latter in that a less expensive reagent is used. The difficulty in the isomorphism of the iron and aluminum compounds is shared by both tests, although this has not always been recognized in the case of the cesium test.

---

[2] Since my work with this reagent, I have come across a note in *Chemical Abstracts* of an article by C. van Zijp (*Pharm. Weekblad.*, Band **72**, pp. 414–418, 1935) in which he discussed the use of ammonium molybdate as a microchemical reagent.

[3] Rosenheim and Schwer (23) give the formula $(NH_4)_3H_6[Al(MoO_4)_6] \cdot 7H_2O$ which is equivalent to $3(NH_4)_2O \cdot Al_2O_3 \cdot 12MoO_3 \cdot 20H_2O$.

ARSENIC

Potassium Iodide. The precipitation of arsenic as AsI_3 is a valuable microchemical test because it can be used to distinguish between arsenic and antimony, and between arsenates and phosphates. The latter distinction is especially important in the nonopaque minerals. The best test for arsenates and phosphates is the precipitation of the arsenomolybdate or phosphomolybdate by means of ammonium paramolybdate, but this does not provide a safe distinction between the two, although it usually suggests which is present.

The descriptions of the potassium iodide test for arsenic to be found in the literature are either incomplete or faulty. The lack of uniformity in results obtained by various writers depends chiefly on the concentrations of arsenic salts present and on the strength of the acid used.

The best conditions for obtaining a characteristic precipitate of AsI_3 are produced when about a 1% solution of an arsenic salt is being tested. The salt should be dissolved in 2:3 HCl and a grain of KI added. A stronger concentration of the acid may be used, but very dilute acid should be avoided. The precipitate obtained with the concentrations described above consists of a fine yellow-orange powder from which hexagonal plates roll out (Fig. 3). The plates have the following properties: uniaxial negative, adamantine luster, predominantly yellow by transmitted light and orange by reflected light. Prisms, 3-sided plates, and 6-rayed stars also may form. Occasionally surface films give the plates a greenish color.

With very dilute acids and with low concentrations of arsenic (below about 0.5% K_3AsO_4) the characteristic crystals do not form, but instead a fine granular precipitate is developed. With very dilute acids and high concentrations of arsenic, orange spherulites may develop.

Strong HNO_3 should not be used in place of HCl because the former breaks down the reagent. Black opaque crystals of iodine are frequently encountered in strong acid solutions when using KI as a reagent, but these are easily recognized.

It is evident from the description given above of the plates of AsI_3 that they closely resemble the hexagonal plates of PbI_2 which are used as a test for lead (compare Figs. 3 and 4). Unless the conditions of precipitation are studied, confusion of lead and arsenic may result. The precipitation of PbI_2 should be made only in very dilute HNO_3 or acetic acid solutions and under these conditions typical crystals of AsI_3 are not easily formed. On the other hand, AsI_3 should be precipitated in strong HCl solutions and under these conditions good crystals of PbI_2 will not develop. The formation of $PbCl_2$ will indicate the presence of lead. Although an experienced worker may prove the presence of both lead and arsenic, as in mimetite, by using KI and noting the difference in the color of the crystals of the precipitate and the different conditions under which precipitation is obtained, it is usually well to use other tests for these elements when they occur together.

A yellow coloration is obtained on adding KI to solutions of antimony, bismuth, and tin salts. Copper gives a crystalline precipitate with KI but the crystals are not likely to be confused with the typical plates of AsI_3.

BARIUM

Hydrochloric Acid. Crystals of barium chloride ($BaCl_2 \cdot 2H_2O$) may be obtained on evaporating HCl solutions of barium salts. The crystals, which are monoclinic, usually show polysynthetic twinning in more than one direction and consequently are easily recognized. The chlorides of strontium or calcium do not give isomorphous precipitates.

The use of barium chloride as a microchemical test for barium was first discussed by McMahon (15) in 1893. The test has been used for many years by Professor A. F. Rogers (19) who discovered it independently and has found it very useful.

BORATES

Hydrochloric acid. Acid solutions of borates produce crystals of boric acid when evaporated. The crystals (Fig. 5) belong to the triclinic system and have two different aspects depending on the orientation. Both are characteristic and usually occur together. The crystals appear either as pseudo-hexagonal plates with low birefringence, or branching tree-like forms with striations transverse to their length and higher birefringence. The branching aspect represents a side view of an aggregate of plates.

CALCIUM AND SULFATE

Sulfuric acid or calcium acetate. The precipitation of microchemical gypsum ($CaSO_4 \cdot 2H_2O$) is one of our most satisfactory microchemical tests. In spite of the frequency with which it is used and the great detail with which it is described in textbooks, there has been no mention of a modification of it which frequently occurs. In the presence of a high concentration of sodium ions, orthorhombic pseudo-hexagonal prisms form either along with microchemical gypsum or alone. The crystals (Fig. 12) have parallel extinction and when they are lying on a prism face show higher birefringence than microchemical gypsum. They are length-slow, while microchemical gypsum is length-fast. The hexagonal cross-sections of the prisms show twinning under crossed nicols. These crystals are probably the hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) which has recently

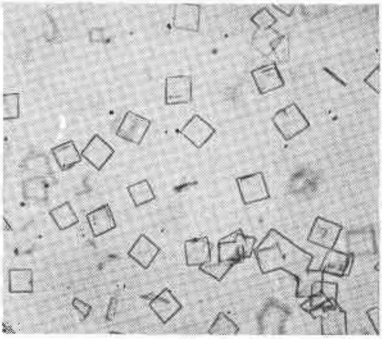

FIG. 1. Ammonium aluminum molybdate. Single crystals. ×220.

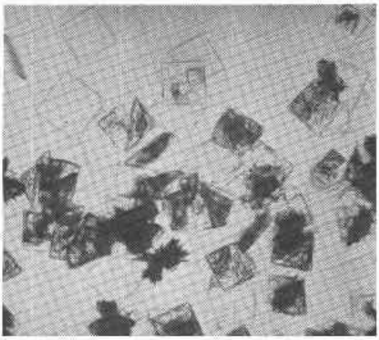

FIG. 2. Ammonium aluminum molybdate showing the manner in which crystals group themselves. ×110.

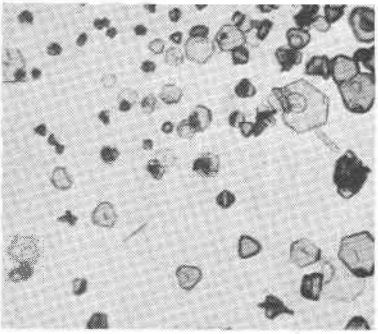

FIG. 3. Arsenic iodide. The orange hexagonal plates are the most characteristic. ×110.

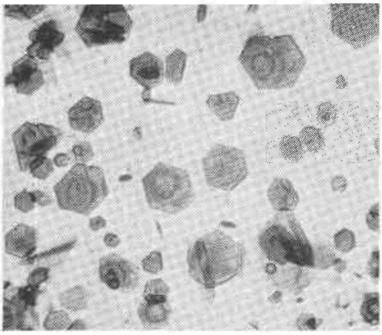

FIG. 4. Lead iodide. Note similarity to crystals in Fig. 3, formed by same reagent. ×220.

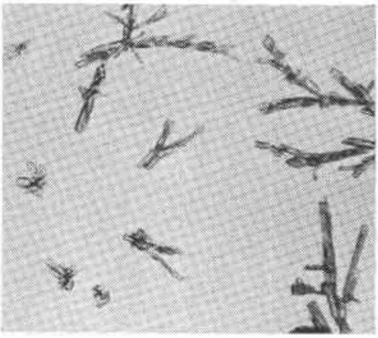

FIG. 5. Boric acid. The plates show low birefringence while the branching forms have higher birefringence. ×40.

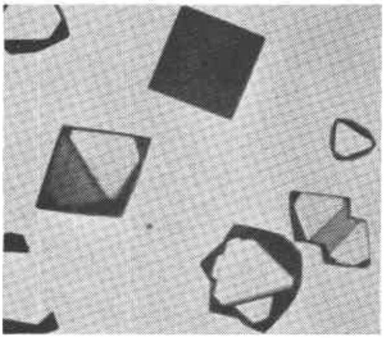

FIG. 6. Ammonium chlorostannate. The single crystals lie almost perpendicular to 2-, 3-, and 4-fold axes of symmetry. A spinel twin and a parallel growth are also present. ×110.

been discussed by Gaubert (7). The hemihydrate may be produced even in the absence of sodium from the HCl solutions of some minerals on the addition of dilute H_2SO_4. It is also formed directly in the dilute HCl solution of minerals, such as wilkeite, which contain both calcium and sulfate. The hemihydrate produced under these conditions may look very much like typical microchemical gypsum until it is tested optically.

Grengg (8) has noted the transformation of gypsum to the hemihydrate in concentrated solutions of NaCl or $MgCl_2$, but the presence of chlorine ions is not necessary for the direct precipitation of the hemihydrate. Magnesium ions do not seem to be so important in inducing the precipitation of the hemihydrate as are sodium ions, and generally the influence of magnesium is not noticeable.

COPPER

Iron filings. The formation of copper "trees" provides a spectacular and convincing test for copper. One or two very small filings (less than 1 mm. in length) taken from an ordinary nail, are placed in the test drop. The drop should be neutral or only very slightly acid, since concentrated acids attack the iron too rapidly. If copper is present it will coat the iron filings and sprout out from them in dendrites and trees. The color of the copper is best observed by shutting out the transmitted light either with the hand or by tilting the mirror.

The potassium mercuric thiocyanate test for copper is very satisfactory but under certain conditions, such as when considerable iron is present, the copper-trees test has been found useful. The limiting concentration under which this test works is about 0.05% copper sulfate. The precipitation of copper may be hindered or even completely prevented if considerable lead is present.

The precipitation of metallic trees may be used for many elements as has been shown by Chamot and Mason (5), but the test described here is the only one of this type used by the writer. Dr. A. F. Rogers worked out this test independently and has used it successfully for many years.

IRON

Ammonium chloride. (New test.) The following test for iron was discovered in an attempt to find one that would be somewhat less sensitive than the thiocyanate test and would yield a crystalline precipitate instead of giving a color reaction. The test satisfies both of these requirements and in addition is somewhat quantitative. It works under either acid or neutral conditions and the only reagent needed is NH_4Cl.

The iron mineral should be dissolved in HNO_3 in order to oxidize all iron to the ferric state. On addition of a drop of HCl to the solution there is produced a coloration which is yellow to brown, depending on the concentration of ferric ions. A large grain of NH_4Cl is placed in the test drop and allowed to dissolve. The drop is then heated until evaporation produces a precipitate at the border of the drop. Depending on the concentration of the ferric ions in the drop and also on the speed and extent to which evaporation has taken place, various characteristic results will be obtained. With high concentrations of iron, brown orthorhombic highly birefringent crystals (Fig. 7), usually composed of two rhombic prisms and often pseudo-octahedral, will form. This is the double salt $FeCl_3 \cdot 2NH_4Cl \cdot H_2O$ which was discovered almost a century ago by Fritzsche (6).

The second type of crystals, which will be called "anomalous mixed crystals of ammonium chloride and ferric chloride", are more characteristic of solutions containing low concentrations of iron. They frequently occur as individual malformed yellow or orange cubes and octahedrons.[4] The octahedrons usually show a blue or green anomalous interference color under X-nicols, and in some cases they develop directly from cubes. The cubes often have rounded edges and are most characteristic when they show a pleochroism in quadrants (Fig. 8). When octahedrons develop from cubes, the lines separating the pleochroic quadrants become octahedron edges. If only a very little iron is present in the solution, instead of individual crystals developing there will be a thickening and yellow coloration of the tips of the usual NH_4Cl lattice-like precipitate. Also characteristic of this test is the segregation of the yellow coloration of the solution to the vicinity of growing crystals, leaving the rest of the solution colorless.

Concentrations as low as 0.1% ferric chloride can be tested in this way. With concentrations above about 1%, crystals of both the double salt and anomalous mixed crystals frequently are obtained in the same drop.

The anomalous mixed crystals of ammonium chloride and ferric chloride have been known for a long time and although a great deal of work has been done on them, especially by chemists, there still remains considerable uncertainty regarding them. Lehmann (12) was the pioneer in the study of these crystals and he expressed the opinion that they represent a crystallization of the double salt with NH_4Cl. He also published a good colored plate showing the gradation in the forms of the crystals. Roozeboom (21) did not agree with Lehmann that the coloration was due to a crystallization of the double salt with NH_4Cl, but thought that it was due to a crystallization with a hydrated ferric chloride. He did not know the type of mixture. Mohr (16) agreed with

---

[4] For the sake of convenience the isometric form names are used, although it is realized that the optical properties are not in accordance with these names.

Lehmann that the double salt was mixed with NH_4Cl and he also stated that the crystals do not represent a mechanical mixture of the two compounds, but that they are a homogeneous chemical mixture. Johnsen (10) decided against the color being due to the double salt and called these anomalous mixed crystals. He says that according to phase law the crystals are homogeneous mixtures and possibly form a transition between an isomorphous mixture and a microscopic intergrowth. Neuhaus (17) recently worked on these crystals and came to the conclusion that they are not double salts or mixed crystals, but rather represent the inclusion of foreign matter along certain faces of the NH_4Cl crystals. He also recommended calling them anomalous mixed crystals.

Similar anomalous mixed crystals are formed by NH_4Cl with cobalt, nickel, manganese, copper, and cadmium. None of these causes confusion with the iron test and the writer would not recommend any but the mixture with the iron salt to be used as a microchemical test.

MANGANESE

Ammonium Paramolybdate. (New test.) The following test for manganese is valuable in that it gives a readily recognized crystalline pleochroic precipitate, it can show the presence of both manganese and iron simultaneously, and the reagent is common and inexpensive.

A drop of the solution of the mineral or its fusion should be evaporated to dryness to remove all free acid. A little solid ammonium paramolybdate is placed in the center of the dried-up area and a drop of water added. If manganese is present, characteristic crystals will form at the edge of the drop in a few minutes. Very good tests may be obtained from solutions of 1% manganese chloride and the limit of the reaction is about 0.1% of the salt.

The crystals produced in this test (Fig. 9) are colorless in the direction of the fast ray, and yellow to reddish-orange, depending on the thickness, in the direction of the slow ray. They are length-slow and have parallel extinction. Parallel growths, producing reentrant angles and swallow-tail terminations are common, but twinning has not been observed. Frequently, in addition to the crystals a yellow granular precipitate is formed. No other element gives similar precipitates and since ammonium ferric dodecamolybdate is not isomorphous and forms under the same conditions as the manganese salt, it can be precipitated simultaneously (Fig. 10).

The formula of the ammonium manganese molybdate which is precipitated in this test is $(NH_4)_3H_7[Mn(MoO_4)_6]\cdot 3H_2O$ according to Rosenheim (22) who prepared and analyzed crystals which are probably the same as those produced in this test.

MOLYBDENUM AND TUNGSTEN

Hydrochloric Acid. The precipitation of the yellow phosphomolybdate or white phosphotungstate is useful as a group reaction but it cannot always be used to distinguish between molybdenum and tungsten compounds because the color difference may not be marked. One reason for the difficulty frequently encountered in obtaining precipitates of the phosphosalts, especially the phosphotungstate, is that insoluble oxides are formed on treating the mineral with acid. These oxides are soluble in NH_4OH and therefore the test may be made by dissolving the acid residue in this base, adding Na_2HPO_4 and then acidifying with HNO_3.

The following procedure is a quick one for distinguishing between molybdenum and tungsten minerals. The mineral is dissolved in HNO_3 and the drop evaporated to dryness. A drop of HCl is added and this is likewise evaporated. If the mineral is a tungsten compound the yellow oxide, WO_3, will quickly be formed. If molybdenum is present, a dark greenish-blue oxide will appear after stong heating. In the case of molybdates soluble directly in HCl, the molybdenum-blue coloration of the powder can be quickly brought out by the addition of a drop of H_2O_2 to the residue obtained by evaporating the HCl solution to dryness.

POTASSIUM (see SODIUM)

SILICON

Fluorite, Sodium Chloride, and Sulfuric Acid. A description of the details of this test has recently been published by the writer (26). The materials needed for the silicon test are a small platinum spoon, a block of charcoal, a small tripod, and a celluloid slide. The reagents required are sulfuric acid, nitric acid, sodium chloride, and pure fluorite. The test employs the well-known precipitate of sodium fluosilicate which was originally described by Bořický as a test for sodium. This precipitate is interesting in that it has the lowest index of refraction of any crystalline substance with the exception of ice.

The test gives good results on all silicon-bearing minerals in 10 minutes or less, and the only element known to give an isomorphous precipitate under the conditions of the test is germanium. Because of the rarity of germanium minerals, this isomorphism causes no difficulty.

SODIUM AND POTASSIUM

Hydrochloric Acid. Evaporation of HCl solutions of sodium and potassium salts produces isometric crystals of NaCl and KCl. The most common habits are the cube and skeletal growths. These are so frequently encountered in the testing of unknowns that it is well to recognize them.

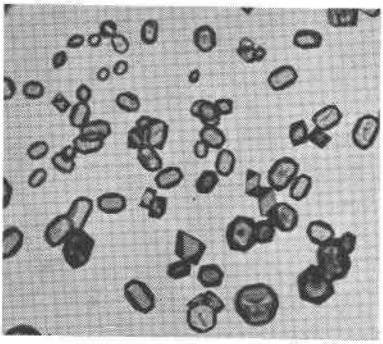

FIG. 7. Orthorhombic crystals of the double salt of ammonium chloride and ferric chloride. ×110.

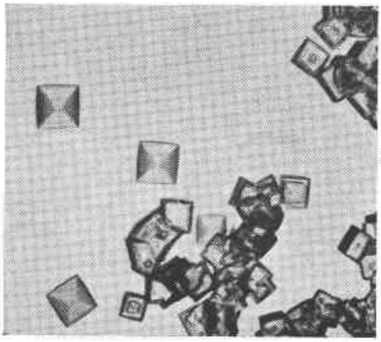

FIG. 8. Anomalous mixed crystals of ammonium chloride and ferric chloride showing cubes with pleochroism in quadrants, and octahedrons. ×110.

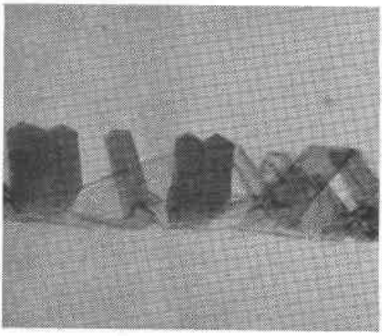

FIG. 9. Ammonium manganese molybdate developed at edge of drop. Strong pleochroism is apparent. ×110.

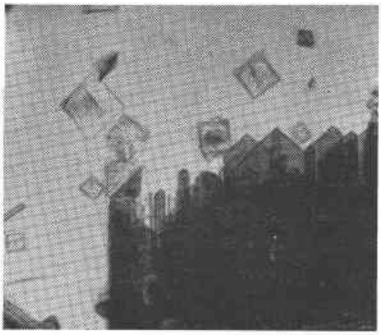

FIG. 10. Simultaneous precipitation of plates of ammonium ferric molybdate and red prisms of ammonium manganese molybdate. ×110.

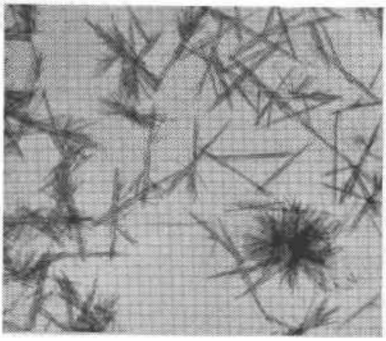

FIG. 11. Typical crystals of microchemical gypsum ($CaSO_4 \cdot 2H_2O$). ×110.

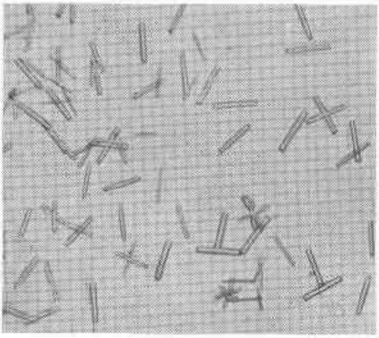

FIG. 12. Crystals of calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$). Compare with the more common crystals of microchemical gypsum in Fig. 11. ×220.

The precipitation of NaCl is fairly sensitive, giving definite results in solutions containing 0.05% of the salt. Dilute HCl is used as the precipitant.

It is interesting to note that from solutions containing about equal amounts of sodium and potassium, the chlorides of these elements will be precipitated separately, not as isomorphous mixtures. The chlorides can be distinguished from each other by removing the liquid by evaporation, dislodging the crystals, and adding a drop of clove oil. The crystals of NaCl have a slightly higher index of refraction than clove oil while those of KCl have a lower index than the oil.

SULFATES (see CALCIUM)

TIN

Ammonium Chloride. The precipitation of tin using CsCl or RbCl is a very good test but with either reagent the octahedrons of the chlorostannate which form are very small. Large crystals (Fig. 6) may be obtained by the use of the more common and less expensive reagent, NH_4Cl, following the same procedure as though CsCl were used. This test gives excellent results with solutions containing about 0.5% or more stannic chloride. For lower concentrations one must resort to the less satisfactory precipitate of cesium or rubidium chlorostannate.

Cassiterite, the most common tin mineral, can easily be tested by following a method similar to the one used in ordinary mineral determinative work. A small grain or some of the powder of the mineral, preferably the former, is placed on a small piece of zinc and this is put in HCl for a few minutes. After the zinc has dissolved, the solution is evaporated to dryness, a drop of HNO_3 added and evaporated for the purpose of oxidizing and dissolving the tin, and the test drop is then again acidified with HCl. On addition of a grain of NH_4Cl, large octahedrons of $(NH_4)_2SnCl_6$ are formed. The second most common tin mineral, stannite, may be dissolved directly in HNO_3 and the evaporated drop tested with HCl and NH_4Cl.

TUNGSTEN (see MOLYBDENUM)

VANADIUM

Nitric Acid. The presence of vanadium can readily be shown by dissolving the mineral in HNO_3 and evaporating the solution to dryness. A dense red precipitate of vanadium pentoxide (V_2O_5) is formed. This test is not so satisfactory as a good crystalline precipitate would be, but in the absence of other easily performed and definite tests it frequently serves a valuable purpose. The precipitation of V_2O_5 was used many years ago by Lacroix (11).

ACKNOWLEDGMENTS

The writer wishes to acknowledge his indebtedness to Professor A. F. Rogers for the many valuable suggestions he has offered during the course of this work and for a helpful criticism of the manuscript.

REFERENCES

1. Behrens, H., *A Manual of Microchemical Analysis*, London, **1894.**

2. Behrens, H., and Kley, P. D. C., *Mikrochemische Analyse*, 4th ed., Leipzig, **1921.**

3. Benedetti-Pichler, A., Unterricht in Mikrochemie und chemischer Mikroskopie: *Mikrochemie*, Band **17,** pp. 320–331, 1935.

4. Bořický, E., Elemente einer neuen chemisch-mikroskopischen Mineral- und Gesteins analyse: *Archiv. d. naturwiss. Landesdurchforsch, von Böhmen*, Band III, Prag, **1877.**

5. Chamot, E. M., and Mason, C. W., *Handbook of Chemical Microscopy*, 2 vols., **1930, 1931.**

6. Fritzsche, J., Ueber die Verbindungen des Eisenchlorids mit Wasser, Chlorkalium, und Chlorammonium: *Jour. prakt. Chemie*, Band **18,** pp. 479–486, 1839.

7. Gaubert, P., Hémihydrate de sulfate de calcium obtenu par voie humide et polymorphisme du sulfate anhydre: *Bull. Soc. Fran. Min.*, tome **57,** pp. 252–267, 1934.

8. Grengg, R., Die Entwässerungsprodukte des Gipses: *Zeit. anorg. Chemie*, Band **90,** pp. 327–360, 1915.

9. Hall, R. D., Combinations of the sesquioxides with the acid molybdates: *Jour. Am Chem. Soc.*, vol. **29,** pp. 692–714, 1907.

10. Johnsen, A., Die anomalen Mischkrystalle: *Neues Jahrb.*, Band 2, pp. 93–138, **1903.**

11. Lacroix, A., *Minéralogie de la France*, tome 4, p. 411, Paris, **1910.**

12. Lehmann, O., *Molekularphysik mit besonderer Berücksichtigung mikroskopischer Untersuchungen usw.*, 2 Bde., Leipzig, **1888, 1889.**

13. Lindgren, W., Microchemical reactions: *Econ. Geology*, vol. **19,** pp. 762–764, 1924.

14. McKinstry, H. E., Microchemical tests in the identification of opaque minerals: *Econ. Geology*, vol. **22,** pp. 830–843, 1927.

15. McMahon, C. A., Notes on the micro-chemical analysis of rock-making minerals: *Mineralog. Mag.*, vol. **10,** pp. 79–122, 1893.

16. Mohr, E. C. J., Gleichgewichtsstudien über das System: Wasser, Salmiak, Eisenchlorid: *Zeit. physikal. Chemie*, Band **27,** pp. 193–221, 1899.

17. Neuhaus, A., Über anomale kristallisierte Mischsysteme von Typus des sogenannten Eisensalmiaks: *Chemie der Erde*, Band **5,** pp. 554–624, 1930.

18. Putnam, P. C., Roberts, E. J., and Selchow, D. H., Contributions to determinative mineralogy: *Am. Jour. Sci.*, (5), vol. **15,** pp. 89–102, 253–261, 423–430, 455–460, 1928.

19. Rogers, A. F., The determination of minerals in crushed fragments by means of the polarizing microscope: *The School of Mines Quarterly*, vol. **27,** pp. 340–359, 1906.

20. Rogers, A. F., *The Study of Minerals*, 3rd ed., New York, **1936.**

21. Roozeboom, H. W., Die Löslichkeitskurve für Salzpaare welche sowohl Doppelsalz als Mischkrystalle bilden, speziell für Salmiak mit Eisenchlorid: *Zeit. physikal. Chemie*, Band **10,** pp. 145-164, 1892.

22. Rosenheim, A., Über die Konstitution der Polymolybdänate, Polywolframate und Polyvanadinate: *Ziet. anorg. Chemie*, Band **96,** p. 149, 1916.

23. Rosenheim, A., und Schwer, H., Über neunbasische Heteropolysäuren: *Zeit. anorg. Chemie*, Band **89,** p. 228, 1914.

24. Short, M. N., *Microscopic Determination of the Ore Minerals, U. S. Geol. Survey Bull.* **825,** 1931.

25. Staples, L. W., Austinite, a new arsenate mineral, from Gold Hill, Utah: *Am. Mineral.*, vol. **20,** pp. 112–119, 1935.

26. Staples, L. W., A simple microchemical test for silicon: *Am. Mineral.*, vol. **21,** pp. 379–383, 1936.

27. Watson, J. A., Colour reactions in the micro-chemical determination of minerals: *Mineralog. Mag.*, vol. **24,** pp. 21–34, 1935.

28. Wormley, T. G., *Microchemistry of Poisons*, New York, **1867.**