Microchemical aids to the identification of minerals developed in the zone of oxidation, together with certain other non-opaque species, of hardness less than 5, which are of economic importance

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Abstract During the search for hard-rock ore deposits, and when such deposits are being evaluated and exploited, it is necessary to identify those species that have developed in the zone of oxidation. Expert mineralogists in a well-appointed laboratory can do this very easily, but it is often desirable, or necessary, for others, such as mining engineers, extraction metallurgists, and field geologists, who are generally not *expert* mineralogists, and who usually lack, in any case, the specialist modern equipment of the mineralogist, to effect such identifications.

The chemicals and apparatus that are needed are cheap, and the techniques required to carry out the tests are easily and quickly mastered. The tests, which are essentially an extenion of those devised by Short (1940) cover all the radicals likely to be encountered in important concentrations in species developed in the zone of oxidation and in certain other non-opaque ones of hardness less than 5 which are of economic importance. In addition, a number of tests for specific minerals is included.

INTRODUCTION

Many developing countries that have relied and are relying on placer mining to provide them with a considerable portion of their income are now giving ever-increasing attention to the potential of their hard-rock deposits, because they are aware that their placers cannot last for ever.

During exploration and evaluation of hard-rock deposits it is essential to recognize and identify any products of supergene alteration, both secondary sulphides and the others, that may be present, yet in many of the developing countries 'the others' have received but scant attention.

It is true that in a laboratory suitably equipped with modern and expensive apparatus, and staffed by the appropriate experts, identification of any of the species in question can usually be effected reasonably rapidly. However, such centres are still thin on the ground in most developing countries. Furthermore, it is often necessary or desirable for such species to be identified as presicely as circumstances allow in temporary field laboratories, in mine and mill assay offices, etc., where elaborate equipment is lacking, and where those who have to make the identifications are mining engineers, extraction metallurgists and geologists, none of whom may be expert analysts or

mineralogists. So the following tests have been devised primarily to facilitate identification of the species under discussion (together with certain non-opaque minerals of hardness less than 5 that are of economic importance) by such people, although it is also believed that the tests may be of assistance to others.

The tests, which have been largely devised by the writer, for the identification of small quantities of material are termed microchemical ones, although they are not confined to tests conducted on a microscope slide, as are those developed by Short (1940), nor do they include chromographic contact printing and etch tests. They are of value when examining scrapings of minerals taken from thin and polished sections, mineral grains isolated from mill and similar products, fragments collected during diamond-drilling, small encrustations on hand-specimens, and hand-specimens which for aesthetic or other reasons should not be obviously defaced.

Because the minerals under discussion embrace a larger number of radicals — some of which are not easily nor rapidly identifiable — than is encountered in the primary ore-minerals, and because there are many examples of different species which contain the same, or almost the same, elements, the tests described below must be used in conjunction with simple physical tests. When the results of these chemical tests are consideed in conjunction with the colour, hardness and form of the mineral under examination, together with the identities of other species with which it is associated, a reliable diagnosis can often be made. There are, of course, many species which can only be identified as members of a given group by these methods, and should an absolute identification be desirable, such minerals must be subjected to the more elaborate optical, X-ray, etc., methods of examination and/or to quantitative analysis, if enough material is available. Even when dealing with such cases, the results of simple chemical tests often assist in the orientation of the later, more precise work.

The examination of minerals developed in the zone of oxidation by the tests described below possesses one marked drawback in that it is often necessary to have a quantity of test-substance available which is fairly large when compared with that required to conduct similar investigations on most of the primary ore-minerals.

Finally, as the present work is, in essence, an extension of the work carried out by Short (1940) on what is essentially the identification of the primary ore-minerals, tests advocated by him are employed by the present writer whenever they are suitable.

Methods of obtaining a powder sample of the mineral to be tested.

Regardless of the type of test employed, the mineral powder utilised for the examination is obtained by gouging it out from the parent specimen by means of a needle ground to a chisel-point and mounted in a wooden handle. This is precisely the method advocated by Short (1940, pp. 176—177). This operation is carried out under a low-power·microscope when the mineral to be examined is a component of a thin or polished section. The powder, so produced, is collected on the point of a match which has been

2

pointed by means of a razor-blade and slightly damped. The sample is then transferred to a drop of reagent on a microscope slide by dipping the point of the match in the liquid.

In order to obtain a powder-sample from a hand-specimen, the gouging operation is controlled either by conducting the work under a mounted lens, such as is sometimes used by zoologists when dissecting small creatures, or by using a watch-maker's lens. Depending on the shape of the specimen, the powder is either collected directly by means of a damped match, or first allowed to fall on to a microscope slide from which it is subsequently collected by employing a damped watch.

The quantity of powder which it is necessary to collect varies consideerably, and is dependent on the number, type and delicacy of the tests to be conducted.

The types of tests employed.

Most of the tests described in the subsequent pages of this paper are microchemical tests in the sense that Short uses the phrase: that is to say, they are conducted on a microscope slide, and are concerned essentially with the development of solid reaction products of characteristic shape and/or colour. A number of other types of test are also employed, but as these are all very easily carried out they need not be dealt with at this stage.

The methods of conducting tests on microscope slides which are employed by the writer are fundamentally the same as those advocated by Short. However, as the writer's procedures vary somewhat from Short's it is pertinent that they should be given prominence at this stage. The basic procedures employed by the writer are incorporated in the following notes:

(i) Liquid reagents are transferred to slides by means of test-pipettes with capillary terminations rather than by employing platinum loops as used by Short.

(ii) Either a micro gas-burner (made by removing the barrel from a Bunsen burner) or a home-made alcohol lamp with a string wick is used for heating material on a glass slide. Regardless of the source of heat, the flame should not be more than 1.5 cm. high. Heating is commenced at about 10 cm. above the flame, but the slide is gradually lowered to within about 1 cm. of it. During the entire heating process the slide is rotated.

(iii) In order to develop characteristic crystals, liquid reagents are normally merged with test drops by drawing a channel between the two (which should only be 0.5 cm apart) by means of a pointed match. Solid reagents, on on the other hand, are picked up on a piece of capillary tube whose ends have been closed and which has been previously damped by breathing upon it, are transferred, directly to the test drops.

(iv) A liquid is transferred from one part of the slide to another by taking it up in a capillary tube and blowing it out where it is required.

3

(v) Filtrations are effected by the employment of capillary tubes drawn out to hair-like terminations. On placing the hair-like tip of one of these tubes into a solid/liquid mixture the liquid fraction only passes into the tube. The latter is then removed, the fine tip broken off, and the filtrate blown out on to an appropriate portion of the slide.

(vi) After a capillary tube has been used for filtration or for the transference of solution the contaminated part is broken off and rejected, whilst the remaining portion is used for subsequent operations.

DETAILS OF TESTS FOR SPECIFIC RADICALS

As the majority of the tests described below have been conducted a number of times on each of the appropriate species and have yielded consistent results, they are probably reliable. Doubtless most of the tests can be used, with little or no modification, to identify radicals in many other species which have not been examined during this investigation because they have not been available.

ALUMINIUM

The Pontachrome Blue Black R. Test (White, and Lowe, 1937, p. 430.)

Aluminium Minerals Tested: – Alunite, $(KAl_3(SO_4)_2(OH)_6)$. Alunogen, $Al_2(SO_4)_3.18H_2)$. Anthoinite, $AlWO_4OH.H_2O$. Bauxite – various oxides and hydroxides of Al. Chalcophyllite, $(Cu_{18}Al_2(AsO_4)_3(SO_4)_3(OH)_{27}. 36H_2O)$. Childrenite, $8((Fe,Mn)AlPO_4(OH)_2.H_2O)$. Cryolite, $2(Na_3AlF_6)$. Liroconite, $4(Cu_2Al AsO_4(OH)_4.4H_2O)$. Plumbogummite, $(PbAl_3(PO_4)_2(OH)_5.H_2O)$. Potash Alum, $4(KAl(SO_4)_2)$. $12H_2O)$. Rashleighite, $(Cu(Al , Fe)_6(PO_4)(OH)_8.5H_2))$. Turquoise, $(CuAl_6(PO_4)_4(OH)_8.5H_2O)$. Vauxite, $Fe^{..}Al_2 (PO_4)_2(OH)_2.5H_2O$. Wavellite, $2(Al_6(PO_4)_4(OH)_6.9H_2O)$.

Procedure and Results

Fuse a minute quantity of the powdered mineral with potassium bisulphate in a small platinum loop. Crush the cold bead and dissolve the resultant powder in a little water. Add a volume of solid sodium hyrdroxide approximately equal to that of the bead and stir until it dissolves. Filter off a drop of the solution and transfer it to a depression on a black spot-plate. Acidify with acetic acid and then add a few drops of a 0.1 per cent. aqueous solution of Pontachrome Blue Black R. Add distilled water until the depression is almost full, then mix well. In an adjoining depression prepare a "blank" containing the same quantity of organic reagent, acetic acid and water as is in the test solution. Examine the two solutions under either long- or short– wave ultraviolet light. The presence of aluminium in the test solution is indicated by the latter fluorescing a strong orange-red.

The presence of aluminium in all the above minerals may be proved by this method.

Other Notes

(i) The test is specific for aluminium.

(ii) A saturated solution of Morin in methanol may be used instead of Pontachrome Blue Black R, when the presence of aluminium is indicated by a green flourescence. (Goppelsroeder, 1868, p. 195, and Eegriwe, 1929, p. 440). Be, Zn, Ga and Sc also form fluorescent compounds with Morin (Beck, 1937, p. 287).

(iii) The preliminary fusion is best conducted in the flame of a Bunsen burner.

(iv) When dealing with the more soluble minerals such as potash alum and alunogen, the preliminary fusion is unnecessary, but as a general rule the writer considers it best to employ a method which will always give a positive test for a given element regardless of the species in which it occurs. This is particularly important when only a small quantity of material is available for examination.

(iv) Having filtered off sufficient solution for the aluminium test, the remainder may be examined in order to determine some or all of the other components of the mineral.

Thus, for example, to confirm the presence of copper and arsenate ions in the residue from the examination of liroconite for aluminium, a drop of the alkaline solution containing abundant suspended solids is evaporated to dryness on a microscope slide. The resulting deposit is dissolved in 1:1 HNO_3 and a little of the solution is transferred to another part of the slide where a drop of ammonium molybdate solution is merged with it. The test drop is then gently warmed, when a yellow crystalline precipitate slowly develops which confirms the presence of arsenate ions. A drop of ammonium mercuric thiocyanate is then merged with the same drop: the formation of yellowish-green crystal aggregates and moss-like dendrites confirms copper. (These tests are discussed fully on subsequent pages.)

(v) Several crystal-tests and spot-tests for aluminium have been described by Chamot and Mason (1948, Vol. 2, pp. 175–184) and by Feigl (1947, pp. 142–147), but in the writer's opinion only the fluorescent tests described above are entirely satisfactory.

ANTIMONY

The Double Iodide Test. (Short, 1940, pp. 214–218.)

Antimony Minerals Tested: — Senarmonite, 16(Sb_2O_3). Stibiconite Sb_3O_6(OH)?
Valentine 4 (Sb_2O_3)

Procedure and Results

Break down the mineral with concentrated HCl. Leach the residue with 1:5 HCl and transfer a drop to another part of the slide. Place a small fragment of KI into one side of this drop and when it has dissolved insert a fragment of caesium chloride into the opposite side. The presence of antimony is indicated by the liquid becoming yellow immediately around the KI fragment and by the subsequent development of orange hexagons and stars.

All the above species react positively to this test.

Other Notes

(i) When a solution containing bismuth ions is subjected to the same test the liquid around the KI fragment also becomes yellow, but rose-red crystals — largely hexogons — develop after the caesium chloride has been added. With experience, no difficulty is found in differentiating between the crystals due to antimony and those

due to bismuth, but if there is any doubt the folloiwng sodium sulphite test should be applied:— Allow the solution containing the crystals to evaporate almost to dryness, then add a drop of sodium sulphide to it. The antimony-containing crystals dissolve rapidly, but a black residue — due to the presence of extraneous elements — may appear. On the other hand, the bismuth-caesium double iodide crystals are converted to black pseudomorphs of bismuth sulphide. (Short, 1940, pp. 217—218.)

(ii)) When the double iodide test is applied to a solution containing arsenic, a yellow to orange precipitate develops on introducing the KI. This precipitate is usually amorphous, but with a high concentration of arsenic, yellow hexagons appear which are similar to those which form when solutions containing lead are similarly treated. On the addition of caesium chloride a deep orange-coloured precipitate is thrown down. This precipitate is usually amrophous, but if the concentration of arsenic is high, orange-coloured hexagons are developed which are physically identical with those due to antimony. However, as antimony and arsenic react differently with KI, there should be no confusion.

(iii) Several other ions react with KI, or KI and caesium chloride, in 1:5 HCl with the consequent production of crystals of diagnostic value, but only those likely to cause confusion during the testing of secondary antimony minerals have been discussed. (See, however, Short, 1940, pp. 261—263.)

The detection of kermesite, $8(Sb_2S_2O)$.
This red antimony mineral could be mistaken for the variety of cuprite termed chalcotoichite and, therefore, methods of establishing its identity must be included.

(a) *The KOH Tests, (Short, 1940, p. 128.)*
Warm a little of the powdered mineral with 40 per cent. KOH. Grains of kermesite, but of no other red mineral, become yellow.

(b) *The Double Iodide Test*
To establish the presence of antimony in kermesite decompose the powdered mineral with aquaregia and leach the residue with 1:5 HCl. Transfer a drop of the solution to another part of the slide and subject it to the double iodide test noted above.

(c) *The Sodium azide/Iodine Test*
This test for sulphide sulphur enables rapid differentation to be made between kermesite and chalcotrichite. Apply a drop of sodium azide/iodine reagent to a little of the powdered mineral. Trains of nitrogen bubbles emanate from kermesite but not from chalcotrichite.

(For futher details of the test see the Sulphur and Sulphate Section.)

ARSENIC, ARSENATES AND PHOSPHATES

The Double Iodide Test.
Arsenic Minerals Tested:— Arsenolite, $16(As_2O_3)$. Claudetite, $4(As_2O_3)$.

6

Procedure and Results

Decompose the powdered mineral by warming it *very gently* with concentrated HCl, but do not take to dryness because the arsenious chloride which is formed is very volatile. When some, or all, of the sample has dissolved, allow the slide to cool somewhat and then add a small drop of water directly to the test-drop. Subject this solution to the double iodide test described in the Antimony Section.

The presence of arsenic in both the above minerals, when their powders are subjected to the above treatment, is indicated by the development of a yellow to orange amorphous or crystalline precipitate on the addition of the KI, and a deep-orange amorphous or crystalline precipitate on the addition of the caesium chloride.

Other Notes

Elements which react in a manner similar to arsenic to this test are discussed in the Antimony Section.

The identification of Orpiment, 4(AsS) and Realgar, 16(AsS).

With the possible exception of some varieties of sphalerite and greenockite, 2(CdS), no other common sulphide-containing minerals resemble orpiment and realgar. Therefore, the identities of these arsenic species can usually be established by considering their simpler physical properties — especially their colour — and by confirming the presence of sulphide sulphur.

The sulphide radical is most easily proved by conducting the sodium azide/iodine test noted earlier.

Alternatively, as suggested by Short (1940, pp. 284 and 286) the presence of arsenic in either of these species may be indicated as follows:— "Decompose mineral with five drops of 1:1 HNO_3 followed by one of aqua-regia. Leach residue with 1:7 HNO_3, transfer drop, and evaporate slowly over microflame. When nearly dry add drop of ammonium molybdate solution and again evaporate slowly over microflame, this time to dryness. Cool and add drop of 1:7 HNO_3 to dissolve excess of ammonium molybdate. Tiny yellow isometric crystals prove arsenic."

Other Notes

In suggesting the above tests Short pre-supposes that phosphates and arsenates —which would react in a similar manner to the sulphides of arsenic-are absent. Probably the safest procedure would be to apply both the sodium azide/iodine test and the one suggested by Short.

The detection of Arsenate and Phosphate Ions

Probably all phosphates and arsenates can be broken down by warming them with 1:1 HNO_3, although in some cases an aqua-regia attach is likely to prove more effective.

7

Whether the one or the other reagent is used, it may be necessary to attack the mineral powder with several successive drops of acid before a sufficient quantity of the solid is decomposed for purposes of examination.

The Ammonium Molybdate Test for Phosphates and Arsenates

The most suitable test for phosphate and/or arsenate ions involves the use of ammonium molybdate and is best conducted in the manner suggested by Short (1940, p. 209), (who — incidentally — uses it almost exclusively for identifying arsenic in minerals with a metallic lustre). The powdered mineral is decomposed on a glass slide by warming it with successive drops of 1:1 HNO_3 (or in very difficult cases with aqua regia). The residue is leached with 1:7 HNO_3 and a drop is transferred to another part of the slide where it is slowly evaporated over a microflame. When the drop is nearly dry a drop of a 1.5 per cent. solution of ammonium molybdate in 1:7 HNO_3 is added to it. This drop is very slowly, but completely, evaporated and then a drop of 1:7 HNO_3 is added to dissolve the excess ammonium molybdate. In the presence of arsenate and/or phosphate ions tiny, lemon-yellow, isometric crystals are seen. (Octahedra pre-dominate, but other isometric crystals are seen. (Octahedra pre-dominate, but other isometric forms and twins are usually present.)

Silicate ions react with a nitric acid solution of ammonium molybdate forming a yellow *solution* of ammonium silico-molybdate which on evaporating *to dryness* yields yellow crystals which are identical with those noted above. However, interference by silicate ions is overcome by the initial evaporation of the test solution with nitric acid as this causes any soluble silicate to be deposited as insoluble silicon dioxide.

Other Notes

(i). It is comparatively rare to encounter a mineral containing the phosphate radical which is devoid of the arsenate radical, and vice versa. Therefore, on many occasions, if the above test yields positive results, no further information of diagnostic value can be obtained by applying the specific phosphate and arsenate tests described below. However, consideration of the simpler physical properties of the mineral — notably colour — will sometimes enable a more precise diagnosis to be made. Thus, an orange mineral which contains no other cations but lead and which reacts positively to the molybdate test is doubtless a member of the mimetite-pyromorphite series, with a constitution in which the percentage of arsenate exceeds that of phosphate.

(ii). The ammonium mercuric thiocyanate test for iron, cadmium, zinc, copper, cobalt and nickel (described later) can be applied directly to the filtrate from the test-drop containing the yellow phospho-molybdate and/or arseno-molybdate crystals. Indeed, Short (1940, p. 210) states that under such conditions better crystals of copper and cobalt mercuric thiocyanate are obtained than when the test is conducted on the original solution.

The Ammonium Molybdate/Tartaric Acid Test for Phosphates

Feigl (1929, p. 299 and 1947, p. 252) has shown that in the presence of tartaric acid a solution of ammonium molybdate in nitric acid reacts with the phosphate radical forming phospho-molybdate ions. Under the same conditions arsenates and silicates do not react.

Feigl, therefore, recommends testing for phosphates by placing a drop of the test-solution on a filter-paper; adding a drop of ammonium molybdate/tartaric acid solution; warming over a hot wire-gauze to accelerate the reaction, and finally adding a drop of benzidine reagent and holding the paper over ammonia. The development of a blue spot proves the presence of the phosphate radical.

The writer has shown that if the ammonium molybdate/tartaric acid solution is substituted for ammonium molybdate reagent in the crystal test discussed above, that in the presence of phosphate ions the normal yellow crystals develop, but if only arsenate ions are present yellow crystals are not formed, even when the solution approaches its boiling-point.

Reagent. The ammonium molybdate/tartaric acid reagent is prepared by dissolving 15g. of tartaric acid crystals in a 100 ml. of a 3 per cent solution of ammonium molybdate in $1:4$ HNO_3.

Other Notes

The application of this crystal test to a considerable number of minerals has confirmed the statement made earlier that it is comparatively rare to encounter a so-called arsenate which is entirely devoid of phosphate ions. Pharmacolite, however, often lacks a phosphate component, as does erythrite: indeed, about 20 samples of the latter mineral, from a number of different localities, have been examined by the above phosphate test and all reacted negatively.

The Silver Nitrate Test for Arsenates

The test is based on the fact that both soluble and insoluble arsenates react with silver nitrate forming rust-red silver arsenate which is insoluble in acetic acid solution.

$$Metal_3 AsO_4 + 3 AgNO_3 = Ag_3 AsO_4 + 3\ Metal\ NO_3$$
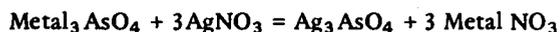
Chromates and ferricyanides also form silver salts which are insoluble in acetic acid and, therefore, the test is only specific for arsenates in the absence of these two anions (Feigl, 1947, p. 82). However, with the possible exception of crocoite, $4(PbCrO_4)$, chromate minerals are extremely rare, and ferricyanides do not occur naturally.

To test for the presence of the arsenate radical, the writer adds a drop of silver nitrate/acetic acid solution to a little of the powdered mineral on a microscope slide and carefully evaporates the liquid to a small bulk over a microflame. Having allowed the slide to cool somewhat, the treated sample is examined under a microscope. If a reddish-brown

precipitate is observed, either on the slide and/or partially or entirely coating the sample, then the arsenate radical is present. If, however, the characteristic precipitate cannot be seen, arsenate ions cannot be said with certainty to be absent, and another drop of the reagent must be added and the above procedure repeated. Whilst, in fact, no arsenate minerals yet tested have failed to react positively after the third application of the reagent — and many react positively after the first or second — the arsenate ion is not regarded as being absent by the writer unless no precipitate develops after the fifth application of reagent.

In order to illustrate the fact that the number of applications of silver nitrate/acetic acid reagent necessary to obtain satisfactory results varies from species to species, it can be stated that whilst erythrite reacts satisfactorily to one application, clinoclasite, bayldo‑nite, liroconite and mimetite often require two, and olivenite and pharmacosiderite three applications.

Reagent. The reagent is prepared by mixing equal volumes of 2 per cent. silver nitrate and 5N. acetic acid just before the test.

Other Notes

The portion of sample subjected to this test is not used for further examination.

The Double Iodide Test for Arsenates

The essentials of this test have been described above in connection with the identi‑fication of arsenolite, etc. When using it to identify the arsenate radical the mineral under examination is decomposed with 1:1 HNO_3 (or aqua-regia) and the residue leached with 1:5 HCl. A drop of this solution is transferred to another portion of the slide and KI and caesium chloride are added. The presence of the arsenate radical is indicated, essentially, the development of an orange amorphous or crystalline precipitate.

Other Notes

The test has been carried out on a considerable number of arsenates with success, but the results obtained from copper and lead arsenates are not always quite as convincing as might be desired: this is chiefly due to the precipitation of the iodides of lead and copper whose colours are not unlike those of arsenic-caesium double iodide ($AsI_3.3CsI$), and arsenic tri-iodide (AsI_3), respectively. Thus, when mimetite (essentially lead chlor‑arsenate) is decompsoed with 1:1 HNO_3, the residue leached with 1:5 HCl and the filtrate transferred to another part of the slide, colourless needle-like crystals of $PbCl_2$ develop. On the addition of a fragment of KI, yellow hexagons of PbI_2 appear, together with an amorphous yellow-orange precipitate which is probably AsI_3. On the addition of a fragment of caesium chloride, a deep-orange precipitate forms near the edge of the drop (probably $AsI_3.3CsI$), together with yellow-orange needle-like crystals (probably a lead-caesium compound).

When olivenite, $4(Cu_2AsO_4.OH)$, is decomposed with 1:1 HNO_3, the residue leached with 1:5 HCl, a drop of the solution transferred to another part of the slide and a

fragment of KI is added to it, a brownish-yellow amorphous precipitate develops. This is probably a mixture of the iodides of arsenic and copper. If, then, a fragment of caesium chloride is added, an orange precipitate — indicating arsenic — appears near the edge of the drop, whilst the darker-coloured precipitate persists near the centre.

General Procedure for the Examination of Arsenates and Phosphates

By utilising the results obtained by employing the general chemical procedure out-lined blow, in conjunction with the more obvious physical characteristics — notably colour — of the test-substance, the writer has shown that it is possible to identify the following species with a degree of accuracy which cannot be exceeded unless they are subjected to extensive physical examination or to quantitative analysis:

Adamite, $4(Zn_2AsO_4OH)$. Amblygonite, $2((Li,Na)AlPO_4(F,OH))$. Annabergite, $2(Ni_3 (AsO_4)_2.8H_2O)$. Apatite, $2(Ca_5(PO_4)_3F)$. Autunite, $Ca(UO_2)_2(PO_4)_2.8H_2O$. Bayldonite, $(Pb,Cu)_7(AsO_4)_4(OH)_2.H_2O$. Carminite, $PbFe_2(AsO_4)_2(OH)_2$. Chalcophyllite, $(Cu_{18}Al_2 (AsO_4)(SO_4)_3(OH)_{27}.36H_2O)$. Chenevixite, near $CuFeAsO_4(OH)_2.½H_2O$. Clinoclasite, $4(Cu_3AsO_4(OH)_3)$. Cornwallite, $Cu_5(AsO_4)_2(OH)_4.H_2O$. Erythrite, $2(Co_3(AsO_4)_2.8H_2O)$. Hopeite, $4(Zn_3(PO_4)_2.4H_2O)$. Libethenite, $4(Cu_2PO_4OH)$. Liroconite, $4(Cu_2AlAsO_4 (OH)_4.4H_2O)$. Mimetite, $2(Pb_5(AsO_4)_3Cl)$. Olivenite, $4(Cu_2AsO_4OH)$. Parahopeite, $(Zn_3(PO_4)_3.4H_2O)$. Pharmacolite, $8(CaHAsO_4.2H_2O)$. Pitticite, an arsenate and sulphate of iron. Pseudomalachite, $Cu_3PO_4(OH)_3$. Pyromorphite, $2(Pb_5(PO_4)_3Cl)$. Scorodite, $8(FeAsO_4.2H_2O)$. Tarbuttite, $8(Zn_2PO_4OH)$. Vivianite, $2(Fe_3(PO_4)_2.8H_2O)$.

PROCEDURE

Note:– Full details of the cation tests mentioned below appear in the appropriate sections.

1A. Decompose the powdered mineral on a slide with 1:1 HNO_3 or aqua-regia.

If 1:1 HNO_3 is used examine the residue for the characteristic lead nitrate lattice.

2A. Leach the residue with 1:7 HNO_3 and transfer a drop to another part of the slide. Apply the ammonium molybdate/nitric acid test to this drop.

Yellow crystals indicate arsenate and/or phosphate.

3A. Merge a drop of ammonium (or potassium) mercuric thiocyanate with the drop containing the yellow crystals and note if the solution becomes red — indicating iron — and/or if crystals indicative of one or more of the following develop:– Cu, Co, Ni, Cd, Zn.

4A. Leach the original residue with 1:7 HNO_3, and having transferred a drop to another part of the slide, apply the ammonium molybdate/tartaric acid test to it.

Yellow crystals indicate phosphate.

5A. Add a drop of water to the original residue and warm. Add a fragment of KI to the cooled solution.

Yellow hexogonal plates prove lead.

(If copper is present the residue must be leached with ammonia before conducting the lead test.)

1B Decompose a second portion of the powdered mineral in the manner indicated in 1A. Leach the residue with 1:5 HCl and transfer a drop to another part of the slide. Test this drop for Pb, Cu, Bi, Sb and As by applying the double iodide test.

1C Apply the silver nitrate/acetic acid test to a third portion of the sample in order to establish the presence or absence of the arsenate radical.

1D If there is any reason to believe that any of the following elements are present then further tests must be conducted on fresh portions of samples:— uranium, aluminium, alkali elements, alkaline earth elements, magnesium. Appropriate tests are described in the relevant sections.

Other Notes

(i) It is obviously never necessary to conduct all the tests noted in the above scheme, and a given species can usually be dealt with in a few minutes.

(ii) Naturally occurring phosphates and/or arsenates containing bismuth, barium, strontium, magnesium and the alkali metals exist, but most of them are exceedingly rare, and apart from amblygonite have not been subjected to microchemical tests by the writer.

(iii) Tests for the chloride ion in pyromorphite and mimetite, and for the sulphate ion in pitticite and chalcophyllite can be ignored, because they would not materially assist in identifying the species in question.

BARIUM, CALCIUM and STRONTIUM

When examining material derived from ore-deposits, the species most likely to be encountered which contain alkaline earths are the following, about which discussion will largely be centred:—

Anhydrite, $4(CaSO_4)$. Ankerite, $(Ca(Mg,Fe)(CO_3)_2)$. Apatite, $2(Ca_5(PO_4)_3F)$: the fluoride component may be partially replaced by chloride. Barite, $4(BaSO_4)$. Barytocalcite, $2(BaCa(CO_3)_2)$. Bromlite, $2(BaCa(CO_3)_2)$. Calcite, $2(CaCO_3)$. Celestite, $4(SrSO_4)$. Dolomite, $(CaMg(CO_3)_2)$. Fluorite, $4(CaF_2)$. Gypsum, $4(CaSO_4)$. Strontianite, $4(SrCO_3)$. Witherite, $4(BaCO_3)$.

Although crystal tests for the alkaline earths exist (see, for example, Chamot, and Mason, 1948, vol. 2, pp. 101—130) these are not, in the writer's experience, generally satisfactory, simple or rapid when applied to mineralogical problems. With few exceptions, therefore, spot and flame tests are recommended for identifying the components of the above species.

Practical Details

Initially the above species may be divided into 3 groups according to how they behave when treated with 1:1 HCl. The carbonates all dissolve with effervescence: anhydrite, gypsum and apatite dissolve reasonably readily in the hot acid: the other sulphates and fluorite are, practically speaking, unattacked. In practice this test is carried out by placing a drop of 1:1 HCl on a small portion of the powdered sample on a microscope slide and warming, if necessary, over a microflame.

The alkaline earth components of the soluble minerals are usually easily identified by dipping a platinum loop into the above solution and holding it in a flame. The characteristic brick-red, olive-green and crimson flames due respectively to calcium, barium and strontium are readily recognised, and even when more than one alkaline earth is present the flame coloration due to each may often be seen. However, the examination of the flames through a hand spectroscope sometimes facilitates identification.

The presence of iron in ankerite (and in any of the other soluble species in which it may occur as an impurity) is readily indicated by adding a drop of 1:7 HNO_3 to the 1:1 HCl solution of the mineral and then a drop of ammonium (or potassium) thiocyanate: ferric thiocyanate is thus formed which causes the solution to become red or pink.

If the HCl solution of gypsum or anhydrite is allowed to cool, typical crystals of $CaSO_4.2H_2O$ appear, which enable differentiation to be made between the calcium sulphate minerals and the other members of the above group. The crystals which develop first are needle-like; later they become thin monoclinic prisms with obliquely truncated ends. These needles and prisms occur singly, in rosettes, sheaves and crosses. With continued growth the prisms become plates, which appear piled over one another like shingles. According to Chamot and Mason (1948, vol. 2, p. 106) this change from acicular crystals to plates is specific for calcium.

Means of detecting magnesium in some of the above species are discussed in the Magnesium Section.

Apatite

The writer identifies the anionic components of apatite by applying the following crystal tests which are modifications of those recommended by Holmes (1930, p.283).

A little of the powdered mineral on a slide is decomposed by 1:1 HNO_3. The residue is leached with 1:7 HNO_3, a drop of the filtrate is transferred to another part of the slide and is subjected to the ammonium molybdate/tartaric acid test for phosphates which is described earlier.

To detect the chloride radical, a further drop of the 1:7 HNO_3 solution is first mixed with a drop of a 1 per cent solution of silver nitrate and then a drop of photographic developer is added. The presence of chloride is indicated by the formation of a white precipitate of silver chloride, which becomes brown to black on the addition of the developer.

To identify the fluoride component, a little of the powdered mineral is heated in a microcrucible with a drop or two of concentrated sulphuric acid in which some sodium silicate has been previously dissolved. A drop of the solution is transferred to a slide and observed under a microscope. The presence of fluoride ions is indicated by the development of pale pink, hexagonal rosettes, stars and plates, and short prisms of sodium fluosilicate.

An alternative and simpler test is noted below, but, unfortunately soluble sulphates, and phosphates and arsenates, react similarly to it.

Fluorite

The fluoride radical in fluorite (and in certain other minerals — notably fluorapatite and cryolite) may be established by stirring a little of the powdered mineral in a drop of zirconium-alizarin reagent with a platinum wire. The fluoride component causes the purple reagent to become yellow almost immediately.

Preparation of the Reagent

Dissolve 0.05 g of zirconium nitrate in 60 ml. of 1:5 HCl and add this to a solution of 0.05 g. of sodium alizarin sulphonate in 50 ml. of water.

The Alkaline Earth Sulphates

(1) Gypsum and anhydrite.

The hydrochloric acid test (described above) enables differentiation to be made between the calcium sulphate minerals and the other alkaline earth sulphates.

The sulphate radical, both in these species and in the other alkaline earth sulphates, is best established by reducing them to sulphide and applying the sodium azide/iodine test as described in the Sulphur and Sulphate Section.

Distinction between gypsum and anhydrite is most easily effected by Feigl and Demant's test (Feigl, 1947, p. 447) which is based on the fact that gypsum is much more soluble in water, even at room temperature, than is anhydrite. A few mg. of the powdered sample is placed in a depression on a spot-plate and moistened with a few drops of a 4 per cent. solution of sodium carbonate which has been reddened by the addition of 3 drops of a 2 per cent. alcoholic solution of phenolphthalein. On stirring with a platinum wire, gypsum causes an appreciable lightening of the colour in 1 to 2 minutes and complete decolorisation in 4 to 5 minutes, whilst anhydrite takes 15 and 45 minutes respectively to produce the same results.

(2) Barite and Celestite

A means of detecting the sulphate radical in these species is described above.

The best procedure for identifying the cations of these species is as follows:— Mix a

little of the powdered mineral with 3 to 4 times its volume of fusion mixture and fuse in a platinum loop. Digest the melt by heating it with water in a micro-centrifuge-tube and centrifuge. Withdraw the supernatant liquid with a capillary tube, then add a little water; break up the residue in the tube with a glass rod and centrifuge again. Remove the supernatant liquid and repeat the washing process several times. Finally, dissolve the residue in dilute HCl and subject it to a flame test. (See Feigl, 1947, p. 302) Barite, thus treated, yields an olive-green flame, and celestite a crimson.

BISMUTH

The Double Iodide Test. (Short, 1940, pp. 214–218).

Bismuth Minerals Tested — Bismite, $4(Bi_2O_3)$. Bismutite, $2((BiO)_2CO_3)$. Bismuth ochre: a group name for undertermined oxides and carbonates of bismuth.

The double iodide test — which has already been discussed in the Antimony Section — is all that is required for the certain identification of bismuth in the species noted above, and probably in all secondary bismuth minerals.

Procedure and Results

Decompose a little of the powdered mineral by warming it on a slide with a drop of $1:1$ HNO_3. Take the drop just to dryness, then leach the residue with $1:5$ HCl. Transfer a drop of the solution to another part of the slide and place a small fragment of KI in the drop and then a fragment of caesium chloride. Bismuth is indicated by the formation of red hexagons and — on occasion — stars.

Other Notes

(i). The writer has never had difficulty in distinguishing between the antimony and bismuth double iodides, but should there by any doubt then either the sodium sulphide test (noted in the Antimony Section) should be employed or the cinchonine/iodide test.

The cinchonine/iodide test is conducted as follows:— Place a drop of the $1:5$ HCl solution (obtained in the manner noted above) on a piece of filter-paper impregnated with cinchonine/iodide reagent. The development of an orange ring indicates bismuth. (Lead causes the development of an outer yellow ring and copper a brown one.)

Preparation of the Reagent

1. *Chinchonine/iodide reagent.* Dissolve 1 g. of cinchonine by warming in a 100 ml. of water containing a little nitric acid. After cooling, add 2 g. of potassium iodide.

2. The strengths and methods of preparation of the reagent solutions used to confirm copper and lead are given in the appropriate sub-sections.

CADMIUM, COBALT, COPPER, IRON, NICKEL AND ZINC

It is convenient to deal with the above elements in the same sub-section, as they can all be identified in those secondary minerals in which they occur in appreciable amounts by employing the ammonium (or potassium) mercuric thiocyanate test. Furthermore, the

test is superior to all others when examining secondary minerals for the presence of all the above elements excepting nickel.

Preparation of the Reagent

Short (1947, pp. 185—186) recommends using potassium mercuric thiocyanate and gives elaborate instructions for preparing a solution of the necessary strength and degree of purity. The present writer prefers to use a solution of ammonium mercuric thiocyanate as it is quickly prepared and gives entirely satisfactory results. This solution is prepared, in accordance with Vogel's directions (1947, pp. 156—157), by dissolving 9g of ammonium thiocyanate and 8g. of mercuric chloride in a 100 ml. of water. (Both reagents should be A.R. grade.)

General Procedure for Conducting a Test

Decompose a little of the powdered mineral under test on a microscope slide by warming it with one or more drops of 1:1 HNO_3 or aqua regia. (In the overwhelming majority of cases 1:1 HNO_3 is perfectly adequate.) Evaporate the solution just to dryness and leach the residue with either 1:7 HNO_3 or 1 per cent. HNO_3. Transfer a drop of this solution to another part of the slide and merge a drop of the thiocyanate reagent with it. Note the colour and shapes of any crystals which develop and any change in the colour of the solution.

As stated earlier in this section, if the mineral is suspected of being an arsenate or phosphate, first carry out the ammonium molybdate/nitric acide test and then test for copper, cobalt, etc., by merging a drop of the thiocyanate reagent with the molybdate — treated test-drop.

Characteristics of the products formed when a drop of ammonium mercuric thiocyanate is merged with a test-drop consisting of certain metallic ions in 1 per cent. or 1:7 HNO_3

Cadmium.

Cadmium mercuric thiocyanate separates as brilliant, colourless, orthorhombic prisms. One end of a given crystal is usually pyramidal and the other beveled or truncated. Almost invariably conical cavities are to be seen near each end of the crystal. Sometimes the cavities almost meet so that the crystal is reminiscent of an hour-glass.

As crystals of cadmium mercuric thiocyanate are quite unlike those of any other double thiocyanate, they enable cadmium to be readily recognised.

Although secondary cadmium minerals are very rare, it is probable that small quantities of cadmium occur quite often in secondary zinc species. In such circumstances the test under discussion enables both cadmium and zinc to be detected simultaneously. The writer has detected cadmium in tarbuttite from Broken Hill, Northern Rhodesia, by this method.

Cobalt

Cobalt mercuric thiocyanate usually separates as indigo-blue prisms, but if the solution is very dilute blue spherulites may also form. Occasionally, crystals do not appear until evaporation of the drop is well advanced.

Iron, which forms a red solution with the reagent under discussion, does not interfere with the test for cobalt unless present in high concentration: then the crystals are not blue, but purple to black.

Appreciable amounts of zinc modify the characteristics of the crystals but do not normally prevent cobalt from being detected.

Copper does not interfere, and both copper and cobalt can be detected simultaneously.

Copper

Copper mercuric thiocyanate is precipitated as greenish-yellow, mosslike aggregates from fairly concentrated solutions and as greenish-yellow or olive-green acicular prisms from dilute solutions. Extraneous elements generally interfere, but in the presence of zinc purple crystals may appear.

Iron

Having decomposed a mineral with nitric acid, any iron present will be in the ferric state and will react with the thiocyanate reagent forming a pink to red solution. If the test solution is very dilute, the pink colour may not be apparent until the drop is almost dry.

Other elements do not interfere.

Many minerals which do not contain essential iron give a positive iron reaction to this test.

Nickel

Nickel mercuric thiocynate is deposited — usually when the drop has partially evaporated — as spherulites which are light brown in transmitted light and white in reflected light. If iron is present they are tinged pink.

This test for nickel is much inferior to the dimethylgloyxime test described below.

Zinc.

In the absence of iron, copper and cobalt, zinc mercuric thiocyanate is precipitated as white feathery crosses — or if the solution is dilute — simple crosses.

If iron is present, some of the zinc crosses in the red solution may be light lavender to purplish-red.

Copper markedly affects the nature of the product and causes the development of crosses and prisms of shades of violet which vary with the Cu: Zn ratio. If zinc is greatly in excess of copper, normal white crosses develop in addition to the violet crosses, and if the reverse holds greenish-yellow copper mercuric thiocyanate appears with the violet crystals.

Cobalt and zinc also form mixed crystals. As the Co:Zn ratio increases the proportion of blue to white crosses also increases, and when it reaches 10:1 the only indication of the presence of zinc is a few deep-blue crosses and V-shaped crystals scattered amongst normal deep-blue cobalt prisms.

Other Elements

Gold, lead, selenium and silver also form precipitates with ammonium mercuric thiocyanate under the above-mentioned conditions but they do not interfere with the detection of the elements under discussion and need not be dealt with further at this stage.

Antimony, arsenic, bismuth, manganese, mercury, tellurium and tin neither form precipitates nor coloured soluble compounds when the above test is applied.

(For a detailed discussion of the test under review see Short, 1940, pp. 185—199 and 259—260.)

Certain Other Useful Tests for Some of the Elements Under Discussion.

(1) The Potassium Ferrocyanide Test for Iron. (See Short 1940, pp. 198—199.)

Potassium ferrocyanide reacts with ferric iron in either nitric or hydrochloric acid forming a prussian-blue precipitate. The objection to using this reaction as a test for iron is that several other elements also form insoluble, coloured ferrocyanides under the same conditions and thus, if present, might mask the iron compound.

Short (1940) recommends its use when testing for iron in goethite (pp. 277—278), limonite (p. 181), and hematite (p. 278). As each of these minerals is somewhat resistant to chemical attack, they are broken down by repeated applications of aqua-regia. The residue is leached with 1:5 HCl and a drop of the solution is transferred to another part of the slide where a fragment of potassium ferrocyanide is added to it. An amorphous blue precipitate proves iron.

Other Notes

Whilst the test may be conducted equally well in either 1:5 HCl or 1:7 HNO_3 solutions, if more concentrated acid solutions are used, iron may be liberated from the ferrocyanide radical and so vitiate the results.

(2) The Dimethylglyoxime Test for Nickel. (See Short, 1940, pp. 192—193.)

The dimethylglyoxime test is the best for nickel and is carried out as follows:— A

little of the powdered mineral under test is broken down with 1:1 HNO_3, or aqua-regia, and the residue is leached with 1:7 HNO_3. A little of the solution is transferred to another part of the slide where it is evaporated. A drop of 20 per cent. NH_4OH is added to the residue in order to precipitate any iron present and the filtrate is transferred to another part of the slide. A drop of a 2 per cent. alcoholic solution of dimethylglyoxime is added to the test-drop. The development of a pink amorphous precipitate proves the presence of nickel. This amorphous precipitate soon changes into a mass of small pink needles which under high-power are seen to be markedly pleachroic between colourless and pink.

Minerals Tested

The folloiwng minerals have been subjected by the writer to the tests noted above with wholly satisfactory results. Methods of identifying radicals which cannot be detected by the ammonium mercuric thiocyanate test and which occur in the species below, are described in appropirate sectons. However, it is usually necessáry to conduct tests on fresh samples to detect these other radicals.

Cobalt

Asbolane: hydrated oxide of Mn and Co. Bieberite, $8(CoSo_4.7H_2O)$. Erythrite, $2(Co_3(AsO_4)_2.8H_2O)$.

Copper

Atacamite, $4(Cu_2Cl(OH)_3)$. Azurite, $2(Cu_3(CO_3)_2(OH)_2)$. Bayldonite, $(Pb,Cu)_7(AsO_4)_4(OH)_2.H_2O$. Brochantite, $4(Cu_4SO_4(OH)_6)$. Chalcanthite, $2(CuSo_4.5H_2O)$. Chalcophyllite, $(Cu_{18}Al_2(AsO_4)_3(SO_4)_3(OH)_{27}.36H_2O)$. Chenevixite, near $CuFeAsO_4(OH)_2.\frac{1}{2}H_2O$. Chrysocolla, near $CuSiO_3.2H_2O$. Clinoclasite, $4(Cu_3AsO_4(OH)_3)$. Connellite: sulphate and chloride of copper. Cornwallite, $Cu_5(AsO_4)_2(OH)_4.H_2O)$. Cuprite, $2(Cu_2O)$. Cuprodescloizite, $4(Pb(Cu,Zn)VO_4OH)$. Delafossite, $(CuFeO_2)$. Herrengrundite, $CaCu_4(SO_4)_2(OH)_2.3H_2O$. Krohnkite, $2(Na_2Cu(SO_4)_2.2H_2O)$. Langite, $Cu_4SO_4(OH)_6.H_2O$. Libethenite, $4(Cu_2PO_4OH)$. Linarite, $(Pb,Cu)SO_4(OH_2)$. Liroconite, $4(Cu_2AlAsO_4(OH)_4.4H_2O)$. Malachite, $4(Cu_2CO_3(OH)_2)$. Melaconite, $4(CuO)$. Olivenite, $4(Cu_2AsO_4OH)$. Pseudomalachite, $Cu_3PO_4(OH)_3$. Turquoise, $(CuAl_6(PO_4)_4(OH)_8.5H_2O)$. Torbernite, $Cu(UO_2)_2(PO_4)_2.8H_2O$. Aurichalcite, $(Zn,Cu)_5(CO_3)_2(OH)_6(?)$.

Iron

Ankerite, $(Ca(Mg,Fe)(CO_3)_2)$. Carminite, $PbFe_2(AsO_4)_2(OH)_2$ Chachosiderite, $(CuFe_6(PO_4)_4(OH)_8.4H_2O)$. Chenevixite, near $CuFeAsO_4(OH)_2.\frac{1}{2}H_2O$. Coquimbite, $4(Fe_2(SO_4)_3.9H_2O)$. Delafossite, $(CuFeO_2)$. Hematite, $2(Fe_2O_3)$. Limonite: unidentified oxides or hydroxides of iron. Melanterite, $8(FeSO_4.7H_2O)$' Pharmacosiderite, $(Fe_5(AsO_4)_3(OH)_6.6H_2O)$. Pitticite: arsenate and sulphate of iron. Scorodite, $8(FeAsO_4.2H_2O)$. Siderite, $2(FeCO_3)$. Vauxite, $Fe^{..}Al_2(PO_4)_2(OH)_2.5H_2O$. Vivianite, $2(Fe_3(PO_4)_2.8H_2O)$.

Nickel

Annabergite, $2(Ni_3(AsO_4)_2.8H_2O)$. Garnierite, $(Ni,Mg)_3 Si_2O_6(OH)_4$. Morenosite, $4(NiSO_4.7H_2O)$.

Zinc

Aurichalcite, $(Zn,Cu)_5(CO_3)_2(OH)_6(?)$. Cuprodescloizite, $4(Pb(Cu,Zn)VO_4OH$. Goslarite, $4(ZnSO_4.7H_2O)$. Hemimorphite, $2(Zn_4Si_2O_7(OH)_2.H_2O)$. Hopeite, $(Zn_3(PO_4)_2.4H_2O)$. Hydrozincite, $2(Zn_5(CO_3)_2(OH)_6)$. Parahopeite, $(Zn_3(PO_4)_2.4H_2O)$. Smithsonite, $2(ZnCO_3)$. Tarbuttite, $8(Zn_2PO_4.OH)$.

CARBONATES

The ready evolution of bubbles of colourless, odourless gas when a little of the powdered sample is treated with 1:1 mineral acid, either in the cold or after very slight warming, is a certain indication of the presence of a carbonate. It is quite unnecessary to confirm the identity of the gas by chemical methods.

Sulphides react much less readily than carbonates with the above acids and in any case if the mineral under test is a fairly reactive sulphide the fact that it is so is almost certain to be apparent because of the odour of the H_2S evolved. However, if very small quantities of mineral are being detected it is just possible that there may be some uncertainty as to whether the gas evolved does, or does not, possess an odour. In such cases it is wise to test for the sulphide radical by applying the sodium azide/iodine test described elsewhere in this section. Furthermore, unlike the carbonates, most sulphide-containing minerals possess a metallic lustre, and of the few that do not, only greenockite, $2(CdS)$, is likely to be mistaken on visual examination for one. Greenockite is not unlike some samples of rutherfordite, $UO_2.CO_3$. However, apart from chemical tests, differentiation between these two species can easily be made because rutherfordite, unlike greenockite, fluoresces a strong yellow under either long- or short-wave ultraviolet light.

CHROMIUM (AS CHROMATE)

Of the few secondary minerals containing chromium, the only comparatively important species is *crocoite*, $4(PbCrO_4)$. The radicals of this species may be established as follows:—

Decompose a little of the powdered sample by warming it with a drop of 1:1 HNO_3 on a microscope slide. Examination of the residue under the microscope reveals the typical lead nitrate lattice. Leach the residue with a drop of water and transfer a drop of this solution to another part of the slide. Add a small fragment of KI to it. The development of yellow hexagonal crystals confirms lead. (This test is discussed fully in the Lead Subsection.) Evaporate the original drop to dryness and add a drop of a 1:1 mixture of 5N. H_2SO_4 and a 1 per cent. alcoholic solution of diphenylcarbazide. A violet colour, which usually appears immediately, but which intensifies on standing, indicates the presence of the chromate radical.

Other Notes

Molybdates and vanadates form blue to violet compounds with diphenylcarbazide in mineral acid solutions and therefore independent tests (described later) should be made for these anions before evaluating the results of the above test. However, interferences due to molybdate can be overcome by employing a saturated solution of oxalic acid instead of sulphuric acid. It is, however, then necessary to conduct the test as follows:— Leach the original residue with oxalic acid and having transferred a drop of the solution to another part of the slide add a drop of diphenylcarbazide solution to it In the absence of vanadate ions, a violet colour appearing immediately, or after slight warming, indicates the presence of the chromate radical. (See Feigl, 1947, p. 305.)

HALIDES

Halides formed in the zone of oxidation

Minerals species containing halide ions. and which are developed in the zone of oxidation may be divided into the two following groups:—

(A) Minerals in which the halide radicals are, for purposes of identification, of considerable importance.

(B) Minerals in which the halide radicals are, for purposes of identification, of little importance.

The identification of the halide radicals in Group A Species.

Fortunately, the presence of halide radicals in these species can be established — even when only a very small quantity of material is available for examination — by the folloiwng simple spot tests.

1. Calomel, $2(Hg_2 Cl_2)$.

This is the only white mercury mineral likely to be encountered, though a few rare white oxy-chlorides of mercury exist) and is characterised by the fact that if a little of it — in powdered form — is warmed on a slide with 0.880 ammonia, the powder becomes black.

2. Silver Halides

(a) The addition of a drop of potassium nickel cyanide/dimethylglyoxime/ammonia reagent to a small quantity of silver halide causes the immediate development of a precipitate of rose-red nickel dimethylglyoxime (Feigl, 1947, pp. 302—303).

A positive reaction to this test, together with the colour of the sample, usually enables a reasonably correct identification to be established.

(b) Chlorargyrite, $4(AgCl)$, may be identified as follows (Short, 1940, p. 271):— Place a fragment of the mineral in a drop of 0.880 ammonia on a microscope slide. In a few seconds crystals of AgCl separate out of the solution. These are often skeletal and

opaque, and in obliquely reflected light are white. The prevalent forms are right-angle crosses and stars in which 3 arms 120° apart radiate from a centre. Further treatment with ammonia usually results in the development of well-formed transparent cubes and other isometric forms.

(c) Silver species containing iodide ions are best recognised by applying the palladium chloride test (Orlow, 1906, p. 630). A small quantity of the test-substance is placed on a piece filter-paper, damped with a drop of water and held in steam for about two minutes. A drop of a 1 per cent. solution of palladium chloride is then added to the spot and the paper is subjected to further steaming. Silver species containing appreciable iodide ions become black by this treatment.

(d) Chloride, bromide and iodide ions in silver minerals may be detected by the following proce ure which is a modification of one suggested by Briscoe and Holt (1950, p. 22) for the general detection of halides:—

Attack a little of the mineral (in powder form, if possible) with 0.880 ammonia and then allow the drop to evaporate to dryness. Leach the residue with a drop of a solution composed of 1 part of 0.880 ammonia in 100 parts of water, and transfer as much of the solution as possible to another part of the slide. As this solution evaporates, colourless cubes and other isometric forms will be deposited if the sample contains a silver chloride component.

Leach the residue with several successive drops of 1:4 ammonia and discard the solution. Treat the residue with 2 drops of 0.880 ammonia and transfer a half of the resultant solution to another part of the slide. In due course hexagonal or triangular crystals will appear if silver bromide is present.

Treat the remainder (together with any residue) with a drop of pyridine. The development of stellate clusters of rods indicates that the original sample contains silver iodide.

3. Copper species containing halide ions.

Both the flame and the silver nitrate tests described below have been applied success-fully to the identification of chloride ions in atacamite, $4(Cu_2Cl(OH)_3)$, and connellite (a sulphate and chloride of copper): other copper species containing halide ions (e.g., nantokite, $4(CuCl)$, and antofagastite, $2(CuCl_2.2H_2O))$ would doubtless also react positively to these tests.

(a) The Flame test.

Take up a little of the powdered sample on a damped platinum wire and place it in the flame of a micro-burner. The development of an intense azure-blue flame of short duration is a certaain indication of the presence of copper chloride.

(b) The Silver Nitrate test

Decompose a little of the powdered mineral on a slide by warming it with 1:1 HNO_3.

Do not, however, evaporate to dryness, and if after decomposition the bulk of solution is small add a further drop of 1:1 HNO_3 and mix with a platinum wire. Transfer a drop of this solution to another part of the slide and merge a drop of a 1 per cent. solution of silver nitrate with it. The development of a white precipitate indicates the presence of chloride ions.

4. *Lead species containing halide ions*

Generally, halide ions in lead species can only be satisfactorily detected by the tests described below. Cotunnite, 4 $(PbCl_2)$, can be detected, however, by heating a little of tthe powdered mineral with a drop of water on a slide. The mineral dissolves, and on cooling the resultant solution, characteristic crystals of $PbCl_2$ separate. These are described in the Lead Section.

The identification of the halide radicals in Group B species

Although , as indicated above, the detection of halide ions in these species is normally unnecessary for purposes of identification, it can be acchieved by applying the following tests.

(a) The Flame Test

Fuse cupric oxide in a microcosmic salt bead in a platinum loop until the melt no longer colours the flame green. Then take up a little of the substance under test on the bead and introduce it into the flame of a micro-burner. The appearance of a transient azure-blue flame indicates the presence of chloride.

This test shows the presence of the chloride radical in pyromorphite, $2(Pb_5(PO_4)_3$ Cl), for example, extremely well.

(b) The Silver Nitrate Test

A small portion of the powdered sample is fused with fusion mixture in a platinum loop and the bead aso produced is cooled and decomposed by warming it with a few drops of water in a micro-crucible. A drop of the filtrate is placed in a depression on a microscope slide, neutralised by the addition of 1:1 HNO_3 and a drop of a 1 per cent. solution of silver nitrate is added. The development of a white precipitate indicates the presence of chloride ions in the original sample.

The test is applicable to most, but not all species containing a chloride radical. Silver halide minerals, for example are not decomposed when heated with fusion mixture.

Other notes

Methods of identifying the halide components of apatite, fluorite and cryolite have been described in the Alkaline Earths Section.

LEAD

Lead Minerals Tested: Anglesite, $4(PbSO_4)$, Bayldonite, $(Pb,Cu)_7 (AsO_4)_4(OH)_2.H_2O$. Caledonite, $Cu_2Pb(SO_4)_3CO_3(OH)_6$. Carminite, $PbFe_2(AsO_4)_2(OH)_2$. Cerussite, $4(PbCO_3)$. Cotunnite, $4(PbCl_2)$. Crocoite, $4(PbCrO_4)$. Descloizite, $4(PbZnVO_4OH)$. Laurionite, $4(PbCl OH)$. Leadhillite, $Pb_4SO_4(CO_3)_2(OH)_2(?)$. Linarite, $(Pb,Cu)_2SO_4(OH)_2$. Litharge, $2(PbO)$ Mendipite, $4(Pb_3Cl_2O_2)$. Mimetite, $2(Pb_5(AsO_4)_3Cl)$. Plattnerite, $2(PbO_2)$. Plumbogummite, $(PbAl_3(PO_4)_2(OH)_5H_2O)$. Pyromorphite, $2(Pb_5(PO_4)_3Cl)$. Raspite, $PbWO_4$. Stolzite, $8(PbWO_4)$. Vanadinite, $2(Pb_5(VO_4)_3Cl)$. Wulfenite, $8(PbMoO_4)$. Minium $4(Pb_3O_4)$, Phosgenite $2(Pb_2Co_3Al)$.

(1) *The Potassium Iodide Test.* (See Short, 1940, pp. 220—222.)

The following method of detecing lead is applicable to all the above species except cotunnite.

A little of the powdered mineral is decomposed by warming it with a drop of 1:1 HNO_3 on a microscope slide. The resultant solution is evaporated just to dryness by warming it very gently: this prevents the relatively insoluble basic nitrate from forming. Examination under the microscope reveals the highly characteristic lead nitrate lattice. (Only mercuruy compounds which have been decomposed by aqua-regia give a similar residue on evaporation.)

In the absence of copper and bismuth the residue is leached with water and a drop of the solution is transferred to another part of the slide where a small fragment of KI is added to it. The development of lemon-yellow crystals, which may take the form of hexagonal plates, stars, discs, or which may be of irregular shape, confirms lead.

The colour of the sample usually indicates when copper is present and then either of the two following tests should be used to detect lead:—

Test (1A). Decompose a little of the powdered sample on a slide by treating it with 1:1 HNO_3 then leach the residue with successive drops of 0.880 ammonia in order to remove the copper. Add a drop of 1:1 HNO_3 to the copper-free residue and gently evaporate to dryness. Leach with a drop of water, then transfer a little of the solution to another part of the slide and continue with the KI test noted above.

Test (1A). Decompose a little of the powdered sample on a slide by treating it with 1:1 leach the residue with successive drops of 1:5 HCl to remove the copper. (This treatment will convert lead to $PbCl_2$ which is practically insoluble in 1:5 HCl.) Leach the copper-free residue with successive drops of water. Transfer the filtrate from each leaching operation to another part of the slide and add a small fragment of KI to each portion. Typical crystals of lead iodide may not develop in the first or second drops because of the presence of HCl, but they will appear in subsequent drops.

As far as the writer is aware there is only one secondary lead-bismuth mineral. namely boksputite, $Pb_6Bi_2O_6(CO_3)_3(?)$, and even its status is suspect (see Hey, M.H., 1950, p. 75). However, when such minerals as aikinite, $4(CuPbBiS_3)$, alaskaite, $Pb(Ag, Cu)_2 Bi_4S_8(?)$, and cosalite, $2(CuPb_7Bi_8S_{22})$, undergo oxidation there is a distinct possibility that the resulting lead bismuth and copper minerals may be mechanically admixed. It is,

therefore, clearly desirable to be able to detect lead rapidly in a sample which also contains bismuth and copper: this can be effected by employing the chloride test described below.

The Chloride Test (Short, 1940, p. 222)

Decompose a small sample of the powdered test-substance by warming it on a slide with a drop of 1:1 HNO_3. If copper is present, remove it by the ammonia treatment noted above, then leach the residue with water. Transfer a drop of the solution to another part of the slide and merge a drop of 1:5 HCl with it. The presence of lead is indicated by the development of long, colourless, acicular, orthorhombic crystals of $PbCl_2$.

The presence of lead may be confirmed by evaporating the drop containing the $PbCl_2$ crystals to dryness, leaching with water and applying the KI test to the filtrate.

A test for Cotunnite, 4($PbCl_2$)

Dissolve a little of the powdered imineral by boiling it with a drop of water on a miscroscope slide. As the test-drop cools highly characteristic crystals of lead chloride develop. The presence of lead may then be confirmed by applying the KI test in the manner noted immediately above.

MAGNESIUM

The Miscrocosmic Salt Test

Magnesium Minerals Tested:—Ankerite, (Ca(Mg,Fe)(CO$_3$)$_2$). Brucite, (Mg(OH)$_2$). Dolomite, (CaMg(CO$_3$)$_2$). Hydromagnesite, 2(Mg$_5$(CO$_3$)$_4$(OH)$_2$.4H$_2$O). Magnesite, 2(MgCO$_3$). Periclase, 4(MgO).

The above, which are the commonest of the acid-soluble magnesium minerals, may all be shown to contain magnesium by applying the following modification of a test recommended by Holmes (1930, pp. 259—260):—

Decompose a small portion of the powdered mineral under test on a microscope slide by arming it with a drop of 1:1 HNO_3. Leach the residue with water and transfer a drop of the solution to another part of the slide. Add a fairly large fragment of ammonium chloride to the drop and when it has dissolved add a drop of 5N. ammonium hydroxide. Place a drop of a fairly concentrated solution of microcosmic salt near the test-drop and heat the latter until the glass beneath it is just uncomfortably hot to the touch, then merge the drops. On cooling, x-shaped skeletal crystals, or tabular orthorhombic crystals with pyramidal truncations develop, of composition $Mg(NH_4)PO_4.6H_2O$: these prove the presence of magnesium.

25

Other Notes

(i) As ferrous iron forms a phosphate under the conditions of the test which is isomorphous with magnesium ammonium phosphate, the writer recommends that whenever this particular test for magnesium is employed that the sample should be decomposed whenever possible with nitric acid, as this converts any iron present to the tri-valent state. Holmes overcomes the difficulty by allowing any ferrous iron to oxidise in the air before completing the test. Chamot and Mason (1948, vol. 2, pp. 130–131), who conduct the microcosmic salt test in a somewhat different manner from that which is recommended above, prevent ferrous iron from interfering by complexing it with critric acid.

(ii) Holmes (1930, p. 260) suggests using the test to differentiate between muscovite mica and talc (having first decomposed the sample with hydrochloric acid).

MANGANESE

1. The Sodium Bismuthate Test

Minerals tested:— Braunite, $8(Mn^{..}Mn_6{}^{...}SiO_{12})$. Chalcophanite, $(Zn,Mn) Mn_2O_5.2H_2O(?)$. Hausmannite, $8(Mn_3O_4)$. Manganite, $8(MnO.OH)$. Psilomelane, $2((Ba, Mn^{..})Mn_4O_8 (OH)_2)$. Pyrolusite, $2(MnO_2)$. Rhodochrosite, $2(MnCO_3)$.

1

All the above species, with the exception of rhodochrosite, have been examined by Short (1940, pp. 270, 271, 281, 285 and 286) who recommends the following procedure for establishing the presence of manganese in them:— Dissolve a little of the powdered mineral by warming it with aqua-regia on a microscope slide. (Several successive drops of acid may be necessary to effect solution.) Leach the residue with a drop of 1:7 HNO_3 and transfer a portion of the filtrate to another part of the slide. Add a few fragments of sodium bismuthate to this drop. The presence of manganese is proved by the solution becoming pink to purple near the bismuthate fragments.

Essentially the same test may be employed to prove the presence of manganese in rhodochrosite, but 1:1 HNO_3 should be employed to decompose the mineral.

2. The Sodium Peroxide Test

The presence of manganese can be established in any mineral in which it occurs in appreciable quantity — even when only a comparatively small quantity of material is available for examination — by fusing it with sodium peroxide. By this treatment manganese is converted into readily recognisable blue-green sodium manganate. The writer recommends the following procedure when examining small quantities of material:— Take up a little of the powdered mineral to be examined with the damped point of a sharpened match, and transfer the powder to a drop of water on a piece of silica glass. (A portion of the wall of a broken Pyrex beaker is admirable for this test.) Evaporate to dryness, then cool to room temperature and cover the sample with 3 to 4 times its volume of sodium peroxide. Carefully heat the charge over a microflame until fusion is effected and the blue-green manganate develops.

Sometimes it is advantageous to examine the product under the microscope.

MOLYBDENUM and MOLYBDATE

1. The Potassium Ethyl Xanthate Test (Mallowan, 1914, p. 73).

Solutions of molybdates in phosphoric, acetic, or dilute mineral acids react with potassium ethyl xanthate forming a soluble complex which, according to its concentration, colours the solution pink, red or violet. This constitutes a specific reaction for the molybdate radical and is the most satisfactory test for detecting molybdates (or molybdenum if it is first converted to molybdate) in small quantities of material.

It has proved most satisfactorily when applied to the detection of molybdenum in scheelite, molybdic ochre and wulfenite, and doubtless it would be equally suitable for detecting the element in such rare species as lindgrenite, $4(Cu_3(MoO_4)_2(OH)_2)$, and koechlinite, Bi_2MoO_6.

Of the following procedures, that suggested for the examination of scheelite by application of the xanthate reaction has been developed by Feigl and Braile (1943, p. 56), whilst the other two are due to the writer.

(a) The detection of molybdenum in scheelite

Scheelite, $8(CaWO_4)$, is isomorphous with powellite, $8(CaMoO_4)$ and primary scheelite is rarely found which is completely devoid of molybdenum.

On the other hand, scheelite which has been derived from wolframite by supergene or hypogene alteration is often, for all practical purposes, free from molybdenum contamination.

It is well-known that the simplest way of obtaining information concerning the powellite content of scheelite is to examine the mineral under short-wave ultraviolet light. (See, for example, De Ment, and Dake, 1946, p. 208). However, should a short-wave lamp not be available, satisfactory information may be obtained by conducting the following chemical test:— Digest a little of the powdered sample in a small crucible with the minimum of concentrated sodium hydroxide solution, then acidify with phosphoric acid. Add a few fragments of potassium ethyl xanthate. The development of a dark violet to red colour indicates the presence of molybdenum.

(b) Molybdic ochre: probably hydrated iron molybdate with oxide of molybdenum.

Decompose a little of the powdered sample by warming it with a drop of 1:1 HNO_3 on a slide. Leach the residue with a drop of 1:7 HNO_3. Transfer a portion of the filtrate to another part of the slide and merge a drop of ammonium mercuric thiocyanate with it. The development of a red or pink colouration proves iron.

Evaporate the original drop to dryness, then cool, add a drop of 1:5 HCl to the residue and again evaporate to dryness. Examine the residue under the microscope. The rim of the residue will appear dark gray and metallic in reflected light, but fox-brown,

greenish and bluish areas will also be apparent near the periphery. (The bluish areas are most clearly seen in trasmitted light.) These colours are some indication of the presence of molybdenum, but to confirm the presence of the element, add a drop of 5N. acetic acid to the residue, warmly slightly and stir in a few fragments of potassium ethyl xanthate. The development of a pink, red or violet colour confirms molybdenum.

(c) Wulfenite, $8(PbMoO_4)$

Decompose a little of the powedered mineral on a microscope slide by warming it with a drop of 1:1 HNO_3. Cool somewhat and examine under the microscope. The presence of the typical lead nitrate lattice indicates lead. Leach the residue with a drop of water, transfer a little of the solution to another part of the slide and add a fragment of KI to it. The development of yellow lead iodide crystals confirms lead.

Evaporate the original solution to dryness, then add a drop of 1:5 HCl and continue the test for molybdenum in the manner indicated above. In this case, if the 1:5 HCl residue is examined under the microscope, only the characteristic gray rim and isolated, blue peripheral patches are seen.

THE DETECTION OF MONAZITE, $4((La,Ce)PO_4)$.

This mineral has been included in this section, not only because it is of considerable economic importance, but also because it is often encountered in tin-bearing and other alluvials which have been derived from areas consisting of granite or its metamorphic equivalents.

The following little-known test for monazite, which was developed by Ohly (1907, p. 169) and which can be conducted on a comparatively small quantity of material, is based on the fact that the mineral is readily soluble in warm concentrated H_2SO_4 and that as the resulting solution evaporates characteristic ceric sulphate crystals are deposited.

The test is conducted as follows:— A grain of the mineral is placed on a microscope slide, damped with a drop of concentrated sulphuric acid and heated until all the acid has evaporated. After cooling, the slide is examined under the microscope. The presence of double ball-shaped clusters of radiating acicular crystals, or isolated crystals shaped like cucumber seeds, indicates that the substance under test is monazite.

If the crystal development is not satisfactory add a drop of water to the product and allow recrystallisation to take place in a desiccator.

Other Notes

Monazite usually displays a marked green pseudo-fluorencence when exposed to short wave ultraviolet light from a lamp from which the purple glass filter has been removed. However, if the surface of the monazite has been modified by weathering, or other processes, the reaction may be disappointing. Thus discoidal monazite that had weathered out from Central African metasediments only reacted normally to the test when fresh surfaces, obtained by breaking the grains, were examined.

SILICON (AS SILICATE)

The Ammonium Molybdate/Benzidine Test

Silicates Tested:— Chrysocolla, near $CuSiO_3.H_2O$. Dioptase, $6(CuSiO_2(OH)_2)$. Hemimorphite, $2(Zn_4Si_2O_7(OH)_2.H_2O)$ Rhodonite, $10(MnSiO_3)$. Willemite, $6(Zn_2SiO_4)$.

The most satisfactory·method of identifying the silicate radical in a comparatively small quantity of material is to employ a test described by Feigl (1947, p. 470). This test depends on the fact that when a silicate (regardless of its solubility) is heated with a fluoride and concentrated sulphuric acid, volatile silicon tetrafluoride is liberated which reacts with water forming silicic and hydrofluosilicic acids. These two acids are converted by ammonium molybdate into silicomolybdic acid which may be identified by the well-known benzidine test.

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$
$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6$$
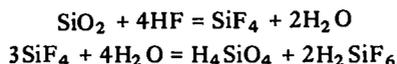
Procedure

Place 1 or 2 mg. of the powdered mineral under test, together with a few mg. of *pure* calcium fluoride and two drops of concentrated H_2SO_4, in a small platinum crucible. Cover the crucible with a piece of filter paper on which has been placed a drop of ammonium molybdate solution. Heat the crucible over a microburner for a minute and then allow it to cool for 5 minutes. Remove the paper. Treat the molybdate spot with a drop of benzidine solution and develop over ammonia. The appearance of a blue fleck indicates the presence of the silicate radical.

Reagents. Ammonium Molybdate Solution. Dissolve 5g of ammonium molybdate in 100 ml of water and pour into 35 ml. of concentrated nitric acid.

Benzidine Solution. Dissolve 0.05g. of benzidine in 10 ml. of concentrated acetic acid and dilute with water to 100 ml. (*CAUTION*, Considerable care should be taken when preparing and using this reagent as it has carcinogenic properties.)

Other Notes

(i) The minerals listed at the head of this subsection — which are amongst the most well-known silicates of the heavy metals — all react excellently to this test. However, the presence of silicate in hemimorphite can be demonstrated quite simply by warming a little of the powdered mineral on a slide with concentrated HCl, when silica gel separates. (The acid must not be evaporated to dryness.) The gel is normally quite recognisable as such, but may be stained for better identification as follows:— Wash the gel with several successive drops of water and then cover it with a 0.1 per cent. aqueous solution of Malachite Green.

After a few seconds wash with several successive drops of water to remove the "free" dye. This treatment causes the gel to become blue.

SILVER

Chemical aids to the identification of the silver halide minerals have been described in an earlier subsection. However, silver may also occur as a secondary product in the zone of the oxidation as native silver, as an "impurity" in certain lead species, and as a major component of certain rare minerals of which the most notable is argentojarosite, $(AgFe_3O_4)_2(OH)_6)$.

(1) Native Silver

Short (1940, p. 288) recommends the following test for native silver:—

Bring a little of the test-substance into solution by warming it with 1:1 HNO_3 on a microscope slide, then evaporate just to dryness.

Leach the residue with a drop of 1 per cent. HNO_3. Transfer a drop of the solution to another part of the slide and add a fragment of ammonium dichromate to it. The development of red crystals, which may show a considerable variety of forms, indicates silver.

When the drop has largely evaporated it is good practice to add a drop of 1 per cent. HNO_3 to it: this will dissolve the ammonium but not the silver dichromate (and chromate) crystals.

(2) Silver "Impurities" in Secondary Lead Minerals.

If secondary lead minerals are to be examined for silver it is advisable to employ the very sensitive p-dimethylaminobenzylidene rhodanine test (see Feigl, 1928 p. 380) as the silver content may well be insufficient to react convincingly to the ammonium dichromate test.

The rhodanine test is conveniently conducted as follows:— Decompose a portion of the powdered mineral by warming it with a few successive drops of 1:1 HNO_3 on a microscope slide. Gently evaporate to dryness and leach the residue with 1 per cent. HNO_3. Transfer a drop of the solution to a piece of spot-reaction paper which has been previously impregnated with a drop of the reagent and dried. The presence of silver is indicated by the development of a violet-red fleck which, if the silver content is low, may not be apparent until the paper has been bathed in. acetone to remove the unused yellow-brown organic reagent.

Reagent. p-dimethylaminobenzylidene rhodanine. A saturated solution of the reagent in acetone.

Other Notes

(i) Although several other elements react with the organic reagent in acid solution forming compounds whose colours are similar to that of the silver compound, they are not likely to interfere in this instance.

(ii) By the employment of this test the writer has established, for example, the presence of silver in cerussite from Western Australia.

(iii) Argentojarosite has not been available for examination, but probably either of the above tests could, without modification, be employed to establish the presence of silver in this mineral.

SELENIUM, SELENITES, SELENATES, TELLURIUM, TELLURITES, AND TELLURATES

Secondary selenium and tellurium minerals are very rare and none have been available for examination. It is, however, probable that most, if not all, of these species are decomposed when they are warned with 1:1 HNO_3. Whenever decomposition by 1:1 HNO_3 can be effected the following microchemical tests will prove satisfactory:—

(a) Selenium-containing Minerals

(1) The Stannous Chloride Test (See Short, 1940, p.204).

Procedure and Results

Break down the powdered mineral on a microscope slide with 1:1 HNO_3 and leach the residue with 1:5 HCl. (A reddish-tinged residue indicates selenium.) Transfer a little of the filtrate to another part of the slide and merge it with a 2 per cent. solution of stannous chloride in 1:5 HCl. The precipitation of a brick-red powder (elemental selenium) proves the presence of selenium.

(2) The Potassium Iodide Test. (See Short, 1940, pp. 204–205.)

Procedure and Results

Decompose a litle of the powdered mineral on a microscope slide by warming it with öne, or several successive drops, of 1:1 HNO_3. Leach the residue wíth 1:5 HCl and transfer a portion of the filtrate to another part of the slide. Place a fragment of KI in the centre of the drop. The immediate development of a reddish-brown amorphous precipitate proves selenium. However, under the same circumstances tellurium forms a chocolate-brown amorphous precipitate, and therefore, it may be difficult to decide whether a given precipitate is due to tellurium or selenium. If in doubt, either the stannous chloride test for selenium must be carried out, or the following caesium chloride test for tellurium.

(b) Tellurium-containing minerals.

The Caseium Chloride Test (See Short, 1940, pp. 206–207).

Procedure and Results

Decompose a little of the powdered mineral by warming it with one, or several successive drops, of 1:1 HNO_3. Leach the residue with a drop of 1:5 HCl and transfer a drop of the filtrate to another part of the slide. Add a fragment of caesium chloride to

this drop. The development of lemon-yellow isometric crystals which, depending on the concentration of the element under test, may be largely octahedra, pseudohexagonal plates or triangles, is a reliable indication of the presence of tellurium.

Further Tests for Selenium and Tellurium

Should a mineral which is believed to contain selenium or tellurium prove to be too insoluble in 1:1 HNO_3 for the above tests to be applied, then the following tests, which require larger quantities of sample, should be resorted to.

(a) Selenium-containing minerals

The Sodium Sulphite Test. (Rose, 1862, and Keller, 1897.)

Procedure and Results

Heat a few mg. of the powdered sample in a microcrucible with a drop of concentrat :d HNO_3. Add 3 or 4 drops of a satuturated solution of sodium carbonate and boil. Filter, and place a drop of the filtrate on spot-reaction paper. Add a drop of a saturated solution of sodium sulphite and then a drop of concentrated HCl. The development of an orange-red spot proves selenium.

(b) Tellurium-containing Minerals.

The Tin and Sulphuric Acid Test

Place a little of the powdered mineral in a microcrucible and add several drops of concentrated H_2SO_4 to it. Heat to boiling, then remove from the heat and add a small piece of tin foil. The development of a carmine-red solution, the colour of which disappears on dilution, is a certain indication of the presence of tellurium.

Other Notes

(i) When selenium-containing minerals are similarly treated, brick-red selenium is precipitated which dissolves in the acid, forming a green solution. When this solution is diluted, red selenium is again precipitated.

(ii) Schoeller and Powell (1940, p. 182) confirm that tellurium dioxide and oxidised tellurium minerals react positively to this test.

Secondary Selenium and Tellurium Minerals

The secondary selenium and tellurium minerals recorded by Hey (1950, pp. 49 and 267–268) are noted below in order to indicate for which other elements tests should be made if either selenium or tellurium is detected in a given mineral.

Oxides:– Selenolite, SeO_2. Tellurite. $8(TeO_2)$.
    Selenites:– Ahlfeldite: selenite of nickel. Chalcomenite, $CuSeO_3.2H_2O$. Cobalto-
    menite: selenite of cobalt. Kerstenite: selenite of lead. Molybdomenite: selenite of
    lead. Onofrite: selenite of mercury.

Selenates:– Selenojarosite, $(KFe_3(S,Se)O_4)_2)(OH)_6$.

Tellurites:— Blakeite: tellurite of iron. Dunhamite, $PbTeO_3$. Emmonsite, $Fe_2(TeO_3)_3.2H_2O$. Ferrotellurite: tellurite of iron (?). Mackayite: probably $Fe_2(TeO_3)_3.nH_2O$. Magnolite: tellurite of mercury.

Tellurates:— Montanite, $Be_2TeO_6.2H_2O$. Teineite, $Cu(Te,S)O_4.2H_2O$.

SULPHUR AND SULPHATE

(1) The Identification of elemental sulphur

Not only does elemental sulphur occur in vast quantities in certain parts of the world, but small amounts have been noted in the oxidation zone overlying sulphide ore-bodies and, indeed, in some of the primary sulphide minerals (Feigl, 1947, pp. 482—483). It is also well-known that the reduction of sulphates to sulphur by bacteria is taking place in certain of the North African lakes, and recently the writer has identified sulphur in material from the Mountfield Gypsum Mines (Sussex) which also probably owes its origin to reduction by bacteria. Therefore, a microchemical test capable of identifying elemental sulphure is of value.

There are several allotropic forms of sulphur, but the sulphur occurring in the commercial deposits is the orthorhombic variety which is, unlike the other varieties, soluble in carbon disulphide and benzene. Sulphur which is sometimes found on the dumps of Lambriggan Mine (Cornwall) associated with oxidising galena, sphalerite, pyrite and chalcopyrite, has been examined by the writer who established that it is soluble in the above reagents: it is, therefore, probably the orthorhombic form. Similarly, elemental sulphur occurring in certain primary sulphides, is also soluble in these two liquids.

Short (1940, pp. 27—228) tests for naturally — occurring elemental sulphur as follows:— A little of the powdered substance to be investigated is placed on a glass slide and is covered with a small cover-glass. A drop of benzene is so placed on the slide that it flows under the cover-glass and dissolves some of the sulphur present. As the liquid evaporates — which takes only a minute — crystals of sulphur are precipitated which may be identified under the microscope.

"The crystals (of sulphur) are large and tend to agglomerate. Recognizable forms are not common, but straight edges are seen at the boundaries of the mass. The best in-dication of crystalline sulphur is the very high birefringence of the mass. The inter-eference color is white of a high order similar to that of carbonate crystals. In oblique reflected light crystalline sulphur is yellow."

Fiegl (1947, pp. 482—483) recommends the following sensitive test for detecting elemental sulphur in certain sulphide minerals. The test depends on the fact that if black thallous sulphide, which is finely dispersed in the capillaries of filter-paper, is brought into contact with a solution of sulphur, reddish-brown, acid-resistant thallium poly-sulphide ($2\,Tl_2S.Tl_2S_3$) is deposited.

Several mg. of the powdered sample are placed on freshly-prepared thallous sulphide paper and the mass is moistened by applying several successive drops of pure carbon disulphide to it. After the solvent has evaporated the powder is brushed off and the black thallous sulphide is removed by bathing the paper in 0.5N. HNO_3. In the presence of soluble sulphur a fleck is seen which varies in colour — according to the quantity of soluble sulphur present in the original sample — from reddish-brown to light-brown.

Preparation of Thallous Sulphide Paper. Bathe Whatman 42 filter-paper in a 0.5 per cent. solution of thallous carbonate or acetate. After a few minutes remove the paper, allow it to drain, and dry it in a blast of hot air. Hold the paper over a beaker containing ammonium sulphide heated to $80^{\circ}C$. Within a short space of time the salt in the paper is converted into black thallous sulphide.

Other Notes Concerning the Above Tests

(i) Carbon disulphide decomposes slowly, liberating sulphur, and, therefore, before using it in either of the above tests, a little of it should be evaporated on a glass slide. Should a residue be observed, the reagent should be rejected.

(ii) Pyridine may be used to dissolve the sulphur in either of the above tests. It differs from carbon disulphide and benzene in that it is capable of dissolving all allotropes of sulphur, but none very readily.

(iii) Selenium behaves analogously to sulphur when subjected to the thallous sulphide test. The fleck due to selenium is, however, dark brown to black. (See Feigl, 1947, pp. 279—280.)

(iv) By employing the thallous sulphide test, Feigl (1947, pp. 482—483) was able to demonstrate that "considerable quantities" of soluble sulphur were present in pyrite, marcasite and galena, whilst only traces could be detected in sphalerite. These results have been confirmed by the writer. In view, however, of the important role which elemental sulphur might play in determining the flotation characteristics of certain sulphide minerals, the test might well prove to be of paramount importance to research-workers in the sphere of mineral-dressing, especially as it is obviously capable of being adapted to yield semi-quantitative results.

(2) The Detection of the Sulphate Radical.

Various crystal tests for detecting the sulphate radical have been described by Chamot and Mason (1948, vol. 2, pp. 349—350) but they have been rejected by the writer as they are less rapid and less easy to conduct than the following test which depends on reducing the sulphate to sulphide and establishing the identity of the latter by means of the sodium azide/iodine test. Furthermore, the results of the crystal tests are often less convincing than those of the reduction test.

Procedure and Results

Pick up a little of the powdered material under examination by means of a small globule of "Gloy" adhesive paste attached to the closed end of a capillary tube, and introduce the charge into the reducing zone of a Bunsen burner flame. Rotate the tube twice in the flame so that the goobule becomes charred, then remove it and allow it to cool. Holding the tube horizontally, place the "charred end" into a drop of sodium azide/iodine reagent on a slide and observe it through a microscope. The presence of sulphate ions in the original sample is indicated by the rapid evolution of bubbles of nitrogen from the charred mass.

Reagent. Dissolve 3g. of sodium azide in 100 ml. of 0.1 N. iodine solution.

Other Notes

(i) During the reduction phosphates and arsenates may be converted to phosphides and arsenides which react with water liberating hydrides of phosphorus and arsine respectively. It is, therefore, wise to apply the ammonium molybdate/nitric acid test for these radicals before conducting the sodium azide/iodine test. Should the arsenate and/or phosphate radical be present, the sulphate test should be modified as follows:— Break off the "charred end" of the tube and place it in a depression on a microscope slide. Add 2 or 3 drops of water and warm gently. Cool somewhat, and whilst observing the assay under the microscope, add two drops of sodium azide/iodine reagent and stir with a platinum wire..The sudden rapid evolution of bubbles of nitrogen indicates the presence of the sulphate radical in the original sample.

(ii) The advantage of using "Gloy" is twofold: as it is sticky, a portion of sample is easily taken up and retained during the test, and as the adhesive is essentially organic, the development of carbon during the heating facilitates reduction.

(iii) This test depends on the fact that although solutions of sodium azide and iodine react exceedingly slowly under normal circumstances, the reaction is catalyzed by sulphide ions and there is then an immediate, and usually vigorous, evolution of bubbles of nitrogen.

Although thiosulphates and thiocynates also catalyse this reaction, it is of little consequence to the mineralogist as they do not occur naturally.

TUNGSTEN AND TUNGSTATE

Tungsten Minerals Tested:— Anthoinite, $AlWO_4OH.H_2O$. Raspite, $PbWO_4$. Scheelite, $8(CaWO_4)$. Stolzite, $8(PbWO_4)$. Tungstite, H_2WO_4. Wolframite, $2((Fe,Mn)WO_4)$.

(1) The Ammonium Hypophosphite Test

The detection of tungsten in small quantities of material can be carried out quite satisfactorily by applying the ammonium hypophosphite reaction which has been discussed in earlier sections. The following procedure is suitable:— Heat a 1:4 mixture of the powdered test-material and ammonium hypo-

phosphite on a piece of silica glass (a portion of the wall of a broken Pyrex beaker is admirable for this purpose). When the charge has fused, remove it from the flame, and whilst it is still warm add a few drops of water to it. The development of an intense blue to violet solution proves tungsten.

All the above minerals react positively to this test

(2) The Stannous Chloride/HCl/Thiocyanate Test

If a small quantity of any of the above species, with the exception of wolframite, is warmed with a mixture composed of stannous chloride, HCl and ammonium (or potassium) thiocyanate, the powder becomes blue.

In practice, one drop of a hydrochloric acid solution of stannous chloride and one drop of thiocyanate are added to the sample on a microscope slide and after warming the product is examined under the microscope. If no blue colouration is apparent in obliquely reflected light, a further drop of each of the two solutions is added and warming is continued. Often after one or two treatments the blue colour is quite strongly developed, but only after five treatments have been given without a blue colour appearing should tungsten be assumed to be absent.

Reagents. (a) Stannous chloride/HCl. This reagent is prepared immediately before the test by boiling about 1g. of tin with 5 ml. of concentrated HCl for 5 minutes.

(b) Ammonium (or potassium) thiocyanate. An 8 per cent. solution.

Other Notes

(i) The presence of aluminium in anthoinite may be demonstrated by the tests described in the Aluminium Section.

(ii) Lead may be·detected in raspite and stolzite by applying the Potassium Iodide Test described in the Lead Section.

(iii) Scheelite always fluoresces under short-wave ultraviolet light, the colour being blue, white or yellowish according to its MoO_4 content. This fact constitutes a great aid to the identification of the species, but it must be remembered that other minerals [particularly hydrozincite and pabsite (blue fluorescence) and malayaite (yellow fluorescence)] behave similarly, so confirmatory tests are often necessary.

URANIUM

Fluorescence Tests

Secondary uranium minerals can usually be identified as such because the majority of them are not only brightly coloured (orang,e yellow and green) but also exhibit strong yellow, yellowish-green, or green fluorescence under either long- or short-wave ultra-violet light. The less spectacular gummite, which varies in colour from reddish-yellow to reddish-brown, is unique amongst uraniam minerals in that it may fluoresce violet under

ultraviolet light. (See De Ment, and Dake, 1946, p. 239.) However, of the three most important uranium minerals — from an economic point of view — uraninite, UO_2, and carnotite, KUO_2VO_2, are non-fluorescent, whilst torbernite, $Cu(UO_2)_2(PO_4)_2.8H_2O)$, may or may not fluoresce under ultraviolet light. Nevertheless, these may be established as uranium-bearing species — even when only a small quantity of material is available — by means of the following, extremely sensitive test:— Make a bead of A.R. sodium fluoride on a platinum wire and introduce a little of the finely powdered mineral under examination into it. Heat the bead strongly for a few minutes, then cool it and examine it under long-wave ultraviolet light. The presence of uranium is indicated by a bright lemon-yellow or yellow-green fluorescence.

Other Notes

i) After completing the test, the test-bead is discarded and the wire is cleaned by building up successive sodium fluoride beads on it until one is developed which is non-fluorescent in ultraviolet light.

(ii) When the method is applied as a general test for uranium in samples of ore, it is important to realise that columbium-bearing minerals which are devoid of uranium may cause the bead to fluoresce a dull-yellow, that rare-earths and calcium fluoride tend to quench the fluorescence due to uranium markedly, and that silicon, iron, titanium and the sulphate radical quench it to some extent (Groves, 1951, p. 251).

(iii) The above test is preferred to strictly chemical tests because none of the latter are conclusive unless the uranium is first isolated from interfering elements.

(iv) The value of the Geiger or Scintillation Counter for establishing the presence of radio-active minerals is, of course, realised, but the fluorescence tests are obviously often more useful when it is desirable to establish which component of a composite sample is radio-active.

(v) Radicals other than uranium (or uranyl) which occur in the commoner secondary uranium minerals can usually be identified with little difficulty by crystal tests. (In most cases they can be decomposed by warming with 1:1 HNO_3.)

VANADIUM

Short (1940, p. 238) states that all vanadium minerals are soluble in 1:1 HNO_3 with the exception of sulvanite, (Cu_3VS_4), with is only decomposed on boiling with concentrated HNO_3. He also notes that if a small portion of powdered vanadium mineral is broken down on a glass slide by treatment with concentrated HNO_3 that V_2O5 is liberated as a reddish-brown amorphous precipitate. This precipitate is soluble in 1:1 and more dilute HNO_3 but reappears on evaporating the solution to dryness. This precipitate, in the opinion of Short (1940, p. 238), "furnishes a good indication of the presence of vanadium but is not absolute proof."

Short, who did not know of a good test for vanadium which could be carried out on a microscope slide, recommended that if the element were suspected, that the well-known hydrogen peroxide test should be performed in a porcelain crucible (1940, pp. 238—239). In essence, this entails dissolving a comparatively large quantity of the mineral in 1:1 HNO_3, doubling the volume of the resulting solution by the addition of water and adding a few drops of hydrogen peroxide to it. If vanadium is present the solution becomes orange. When minerals containing molybdenum and/or tungsten, which are soluble in HNO_3, are similarly treated, the solution becomes pale-yellow. Therefore, on occasion it may be difficult to interpret the results of this test.

The writer has shown that the presence of vanadium in the minerals available to him for testing can be demonstrated quite conclusively by conducting the ferrocyanide test (described below) on a microscope slide.

The Ferrocyanide Test

Vanadium Minerals Tested:— Calciovolborthite, $CuCaVO_4.OH$. Descloizite, 4 ($PbZnVO_4$ OH).. Turanite, Cu $(VO_4)_2(OH)_4$. Vanadinite, $2(Pb_5(VO_4)_3Cl)$. *

Procedure and Results

To a little of the powdered mineral on a microscope slide add 3 to 4 times its volume of powdered zinc followed by a large drop of 1:5 HCl. After about 10 seconds add a drop of a 1 per cent. solution of potassium ferrocyanide and warm gently. The development of a pink colouration proves the presence of vanadium. This colour is normally apparent when the product is examined with the naked eye or through a lens. When viewed under the microscope, and in reflected light, a pale pink gelatinous mass containing numerous bubbles with deep pink rims is seen.

Other notes

(i) The presence of lead, zinc and copper in secondary vanadium minerals can be established by the following mans:— Decompose a little of the powdered mineral by warming it with 1:1 HNO_3 on a microscope slide and evaporate just to dryness. (A reddish-brown residue indicates vanadium.) Leach the residue with a drop of 1 per cent. HNO_3, transfer a portion of the filtrate to another part of the slide, and merge a drop of ammonium (or potassium) mercuric thiocyanate with it. Yellowish-green mosslike aggregates and prisms prove copper, white feathery crosses prove zinc, and purple feathery crosses, etc., prove zinc and copper together.

If copper is present, leach the original residue with a drop of 1:5 HCl, then removed the drop and reject it. Leach the acid-cleaned residue with two or three successive drops of water, transfer each drop, and test for lead by adding a fragment of KI to each. The presence of lead is established by the development of the characteristic yellow lead iodide crystals which usually appear in the second or third drop.

To test for lead in the absence of copper, it is sufficient to leach the original residue with water, transfer a drop of the filtrate to another part of the slide and apply the KI test to it.

38

THE ROLE OF THE MICROCHEMICAL TESTS UNDER DISCUSSION TO PROBLEMS OF MINERAL IDENTIFICATION

In order to establish the identity of a small quantity of one of the minerals under review, microchemical tests are invariably preceded by physical tests. The physical tests employed, and the types, vary with the nature of the sample, the apparatus and time available, and the skill of the investigator. Therefore, depending on circumstances, much or little information of diagnostic value is obtained by the application of such tests. It follows, then, that the role of microchemical tests during such investigations is also variable. Microchemical tests are often employed either to confirm the identity of a given species which has been provisionally established by physical methods, or to determine the identity of a mineral when physical tests have eliminated all but a few alternatives. Under such circumstances an analytical chemical scheme is quite unnecessary. However, on rarer occasions when, as the result of comparatively small amount of information of diagnostic value having been obtained by the application of physical tests, microchemical tests assume a dominant role, an analytical guide is obviously desirable in order to obtain the maximum information with a minimum effort. The guide below has been devised for this reason.

Finally, it must be reiterated that it is by no means always possible to establish the complete identity of a given mineral which has developed in an ore-body in the zone of oxidation by the application of simple physical and microchemical tests.

A GUIDE FOR USE DURING THE PRELIMINARY STAGES OF MICROCHEMICAL EXAMINATION OF SECONDARY ORE-MINERALS OF THE ZONE OF OXIDATION AND CERTAIN OTHER SOFT, NON-OPAGUE SPECIES OCCURRING IN ORE-DEPOSITS

Step 1. Examine the mineral under short-wave ultraviolet light. A wide variety of species may or may not fluoresce, but those below invariably do so. Therefore, if the species under examination displays any of the fluorescence colours noted below, this, in conjunction with other obvious characteristics of the mineral, such as colour and shape, together with the composition of any minerals with which it is associated, may indicate its identity.

(i) Scheelite and the related species powellite and cuproscheelite.
Colours under short-wave ultraviolet light: — Blue, white and straw-yellow.

Test for Ca, Cu, WO_4, MoO_4.

(ii) Hydrozincite.

Colour under short-wave ultraviolet light: — Blue.

Test for Zn, CO_3.

(iii) Certain secondary uranium minerals.
Colours under short-wave ultraviolet light:— Very bright yellow, yellow-green and green.

If the fluorescence of the sample indicates uranium, test for Cu, Pb, Fe, AsO_4 PO_4^{--}, SiO_4^{--}, CO_3^- and SO_4^-. (Other radicals, such as Ca, Mg, Ba, etc., may be present, but may not be identifiable by means of simple micorchemical tests.)

Step 2: Warm a little of the powdered mineral on a slide with a drop of water. Examine under the microscope.

If the powder dissolves the sample is probably lead chloride or a sulphate.

Acicular colourless crystals deposited from the cooling colourless solution = $PbCl_2$.

A blue solution = $CuSo_4$. A deep green solution = $NiSO_4$. A pale green solution = $FeSO_4$. A pink solution = $Co\ SO_4$. A colourless solution = $ZnSO_4$.

Apply the appropriate confirmatory tests.

Step 3. If the sample is insoluble in water, evaporate to dryness, add a drop of 1:1 HNO_3 to the residue and warm. If the powder is not decomposed continue the attack with further drops of acid.

If a colourless gas (CO_2) is evolved the species is a carbonate. Confirm this by testing another portion of the sample with 1:1 HCl when CO_2 should again be evolved readily (and usually without the application of heat).

If the species is not decomposed, refer to Step 3A below.

Step 4. If the mineral is decomposed by 1:1 HNO_3, evaporate just to dryness and examine the residue.

Apart from the well-known colour indications of the presence of such elements as Cu, Ni, and Co, look for the following:—

(a) The lead nitrate lattice.
(b) The reddish-brown, gelatinous precipitate of V_2O_5.

(c) Yellow WO_3.

If Pb, V or W are indicated at this stage apply the appropriate confirmatory tests.

Step 5. Leach the residue with a drop of 1 per cent. HNO_3 then transfer some of the filtrate to another part of the slide and apply the ammonium molybdate/ HNO_3 test to it.

Small yellow isometric crystals indicate the presence of arsenate and/or phosphate.

Step 6. Filter off a little of the molybdate-containing solution and transfer it to another part of the slide. Merge a drop of ammonium mercuric thiocyanate with it.

A red solution = Fe. Colourless prisms (usually with an hour-glass appearance) = Cd. Indigo-blue prisms = Co. Yellow-green mass, prisms and crosses = Cu. Brown spherulites = Ni. White feathery crosses =Zn. Purple feathery crosses, etc. = Zn + Cu. Blue feathery crosses, etc. = Zn + Co.

Step 7. If the molybdate/HNO_3 test (see Step 5) is positive, test for the presence of phosphate by decomposing a fresh portion of sample with 1:1 HNO_3 leaching the residue with 1 per cent. HNO_3 and applying the ammonium molybdate/tartaric acid test to the filtrate.

Small, yellow, isometric crystals = phosphate.

Step 8. Decompose a fresh sample of the mineral with 1:1 HNO_3, evaporate to dryness and leach the residue with a drop of 1:5 HCl.

If the sample is white, or near white, test for the alkaline earths by subjecting a little of the solution to a flame test.

Crimson flame = Sr. Brick-red flame = Ca. Olive-green flame = Ba.

Transfer some of the filtrate to another part of the slide and add a small fragment of KI to it.

Amorphous orange to yellow powder = As (or AsO_4^-). Amorphous white, gray, or yellow powder = Cu. Solution turns yellow near the fragment = Sb or Bi. Amorphous chocolate-brown precipitate = Se or Te.

Step 9. Add a fragment of caesium chloride to the solution containing the KI fragment. Orange amorphous powder at the edge of the drop = As (or AsO_4^-). Orange hexagons = Sb. Red hexagons = Bi.

Step 10. Having arrived at this point it may be necessary to conduct confirmatory tests for some of the radicals provisionally shown to be present by the above tests and to carry out further tests for one or more of the following:— aluminium, molybdenum, molybdate, tungsten, tungstate, vanadium, vanadate, chromate, magnesium, sulphate, chloride, silicate. The choice of tests to be carried out must be governed by the results of the previously-conducted physical tests and the above microchemical tests.

Step 3A. If the mineral is not decomposed on warming with one or several successive drops of 1:1 HNO_3, it is probably either one of the rock-forming silicates (which are not within the scope of this paper, but which are usually fairly hard and/or of characteristic appearance), or one of the species listed below, and for which appropriate tests have already been described in this section. The tests which must be carried out to establish the identity of these species must be dictated by the physical characteristics of the sample.

41

Minerals insoluble in 1:1 HNO_3	Observations
A. Often or always white	
Bauxite	Soft. Also often reddish (Fe).
Barite	Orthorhombic.
Celestite	Orthorhombic.
Gypsum	Very soft.
Anhydrite	Very soft.
Chlorarygyrite	Horn-like. May have a purple coating.
Cotunnite	Rare. Soluble in hot water.
Calomel	Rare. Turns black in ammonia.
Oxides of As and Sb	Soluble in HCl.
B. Often or always coloured	
Fluorite	Octahedral cleavage. Green, purple, etc.
Oxides of manganese	Brown or balck. Soft or hard.
Limonite	Yellow to brown.
Hematite	Red in powder form.
Kermesite	Red. Yellow with 40% KOH.
Silver halides other than	
Chlorargyrite	Various shades of yellow.
Sulphur	Various shades of yellow. Soluble in CS_2
Tungstite	Yellow powder.

Conclusion

Unlike the identification of the primary ore-minerals, that of the secondary minerals depends a great deal on establishing the nature of the anions. As no truly satisfactory scheme for anion identification has yet been developed by the chemists, it has not been possible to prepare an all-embracing scheme for the identification of the secondary minerals. That such a scheme has not been devised is not of great consequence as those physical properties of the secondary minerals which, from a diagnostic point of view, are of major importance, can usually be relatively easily determined. Thus, as stated earlier, microchemical reactions are largely used to confirm the results of physical tests.

The microchemical tests described in this paper are the simplest, most rapid and most reliable which the writer has been able to obtain from the literature or to devise. Often, when a test for a given radical is conclusive, confirmatory tests have been omitted. This may be a subject of criticism. but it must be remembered that the establishment of a mineral's identity rarely, if ever, rests on chemical tests alone. Furthermore, the quantity of material available for testing will often preclude the use of confirmatory tests.

Finally, because the simplest, most rapid, and most reliable tests have been sought, tests depending on the development of characteristic crystalline precipitates have often been discarded, even though such tests exist for practically every radical discussed in this paper.

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