

comes the removal of silver. This is based on two facts—first, silver combines more readily with zinc than with lead and, secondly, zinc-silver alloys are insoluble in lead. Thus, by the addition of zinc, silver may be made to leave the lead bullion and combine with zinc. The latter metal is added in sufficient quantity to saturate the lead at the temperature of operation (400° C.) and provide an excess to combine with the silver. Crusts rich in silver are formed and are removed for recovery of the precious metal. The residual lead contains 0.4% to 0.6% zinc and its elimination is secured by a process known as vacuum de-zincing. The de-silverized lead is heated to just above its melting point and a large steel bell-shaped apparatus attached to a vacuum pump is

submerged in the molten lead. The temperature is raised and zinc distills from the lead and condenses on the interior surface of the bell. After a suitable interval of time the vacuum is shut off and the bell removed, leaving the lead in a zinc-free condition. The zinc in the steel bell is collected and re-used in the de-silverization process.

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Mineral Identification Using Solid Reagents

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Tests using a
technique
developed
in the U.S.S.R.
are described

Synopsis

Often the identification of a given mineral may be facilitated by grinding a little of the specimen directly—or after it has been decomposed by simple chemical means—with a small quantity of a solid reagent with which it reacts to form a characteristically-coloured substance. Tests of this type—which have been developed almost exclusively by the Russians, and which are not generally known in English-speaking countries—are described.

Introduction

From time to time details appear in *Analytical Abstracts* of a test for one or another of the elements in minerals which depends, essentially, on grinding a small portion of the specimen directly—or after the powder has been decomposed by a simple and rapid chemical method—with a solid reagent with which the element in question forms a characteristically-coloured substance. Almost invariably these tests have been developed by Russians and although they are powerful aids to mineral identification, and a French translation of Isakov's (1955) text on the subject is available (see Pietresson de Saint-Aubin and Jedwab, 1956), they are

not generally familiar to mineralogists in English-speaking countries.¹

In the present paper the writer outlines the fundamentals of this analytical technique and gives details of a number of the tests which he has found particularly useful. Needless to say, much of the material contained herein has been culled from Isakov's work (*op. cit.*).

Fundamentals of the Technique

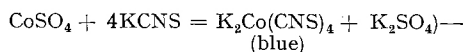
Many minerals react with surprising rapidity with solid reagents when the two are ground together. This is probably due not only to the development of fresh highly-reactive edges and corners, and the partial disruption of the crystal lattices,² but also to the heat of friction and the transient

¹ A list of references is given at the end of the article.

² KOVALEV, G. A. (*Mem. All-Union Min. Soc. Russia*, 1957, **86**, 401-403) has demonstrated that dry grinding of minerals leads to partial or complete disappearance of lines on the X-ray powder photographs.

but high pressure to which the system is subjected during comminution. Absorbed water is also, doubtless, important.

Although most grinding tests depend for their success on double decomposition—as, for example, when cobalt is detected in, say, bieberite by the intense blue which appears when the mineral is ground with potassium thiocyanate :—



reactions of combination and decomposition are also occasionally used. Thus, the identification of powdered silver is facilitated by grinding it with sulphur, as the two elements combine to form black silver sulphide. On the other hand, when green copper carbonate is ground in air it decomposes in a characteristic way to black cupric oxide and carbon dioxide.

Many minerals, however, have to be subjected to a preliminary chemical attack before grinding tests can be employed successfully. Usually this preliminary treatment either involves grinding with potassium bisulphate, or fusion with either an ammonium salt or a mixture of ammonium salts, but on occasion decomposition is effected by grinding with iodine. Generally the most effective reagent with which to fuse the sample to decompose it is “solid aqua-regia.”¹

In practice one or two small fragments—each not above 0.1 mm. long—of the mineral under test (which may on occasion be best selected under the binocular microscope or with the aid of a hand lens) are ground with about the same volume of the “colour-generating” reagent in a depression in a porcelain spot plate (or on a porcelain crucible lid) by means of a glass pestle 6 cm. long and about 0.6 cm. in diameter. *Unless very small quantities of the test substance and the reagent are used the all-important colour of the reaction product may be obscured.* Often the final colour may be enhanced, either by breathing on the ground mixture or by adding one or two small drops of water to it.

¹ Solid aqua-regia is prepared as follows :—

One part (by weight) of ammonium chloride is well mixed with 2.5 parts of ammonium nitrate. The mixture is gently heated in a porcelain crucible until fusion is complete; then it is allowed to cool and is stored in a glass container. This “cake” is very convenient for field work as it is non-hygroscopic and relatively stable.

Normally preliminary fusions are carried out in small test tubes or porcelain micro-crucibles, but, when working in the field and whenever the quantity of mineral available for examination is severely limited, fusion is usually best effected in a thin-walled, right-angled capillary tube of internal diameter about 1–1.5 mm., which has one arm 10 cm. long and the other only approximately 1 mm. The shorter arm is charged by plunging it first into the powdered flux and then on to the fragment to be examined so that the latter becomes embedded in the flux. The mixture is heated for about 30 sec. in the flame of an alcohol lamp, or even by the flame from a match. Sometimes fusion may be achieved simply by focusing the sun’s rays on to the charge by means of a lens. After fusion the cooled charge is extracted by the aid of a needle or a thin glass rod and ground on a plate with the appropriate reagent.

As in most analytical procedures the influence of interfering elements is overcome by complexing them or by converting them to a valency state in which they will not participate in the particular reaction. Thus, if a mixture of ferrous and cobaltous sulphates is ground with ammonium thiocyanate, a reddish colour appears which is due to the development of ferric thiocyanate. If then the ferric ions are reduced by grinding a little sodium thiosulphate into the mixture the red colour is destroyed and the intense blue of the cobalt-containing complex anion $[\text{Co}(\text{CNS})_4]$, is seen.

Frequently, however, some or all of the elements which cause serious interference when a given test is carried out in solution may be ignored when virtually the same test is effected by grinding the solid components together. For example, as both nickel and ferrous ions form red complexes with dimethylglyoxime in ammoniacal solution the ferrous ions must be removed before testing for nickel. However, of the two elements in question, only nickel forms a red complex when a solid is ground with dimethylglyoxime.

According to Isakov (*op. cit.*) those elements such as osmium, selenium, and ruthenium, which form volatile compounds are best detected, not by grinding with reagents, but by allowing the volatile compounds to react directly with specific colour-forming reagents, for by so doing difficulties due to interfering elements are virtually eliminated. Thus, to detect selenium in a

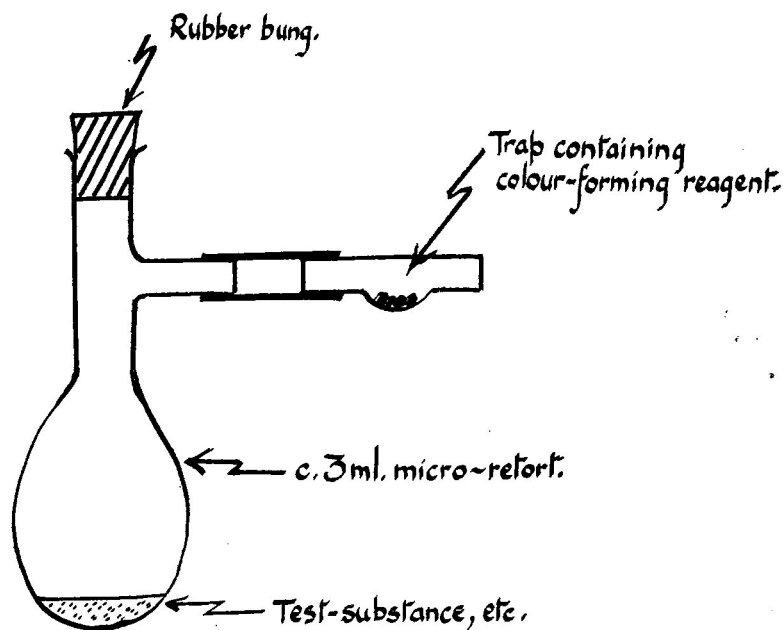


Fig. 1.—
Detection
Apparatus.

mineral, a little of the powdered sample, together with four to five times its volume of solid aqua-regia, are placed in a 3 ml. micro-retort. The retort is stoppered with a rubber bung and a glass trap containing a few small crystals of stannous chloride is attached to the side arm by means of a short length of rubber tubing (Fig. 1). The retort is then warmed for 3 or 4 min., when the presence of selenium is indicated by a red tint appearing in the trap.

In addition to certain obvious advantages the grinding technique offers another in that certain specific reactions can be employed which would be quite useless were they attempted in aqueous solution. The following test for tin in cassiterite is an example of the type which will only "work" when solids are ground together:—

A little of the powdered mineral is mixed with some zinc powder and a drop of 1 : 4 HCl is added. The mixture is then evaporated to dryness and a small quantity of dimethylglyoxime is ground vigorously with it. The presence of tin is indicated by the development of a rose-red complex which, unlike that due to nickel, is stable in very dilute HCl. Further tests, which are only successful when the grinding technique is used, are described later.

Practical Details of Certain Tests

It must be emphasized that the following is but a selection of the tests described by Isakov and others (see references at the end of the paper). It contains, however, those

tests which are particularly good and which, if carried out, will enable the potential of the technique to be determined. For reasons of economy of space a discussion of the chemistry of the various reactions has been omitted.

Finally, it must be stressed again that unless very small quantities of test substances and reagents are used the tests will usually be inconclusive.

Antimony

Test 1.—The potassium hydroxide test for stibnite (Sb_2S_3).

*Procedure:—*Grind a very small fragment of the mineral with an equally small piece of potassium hydroxide. The presence of stibnite is indicated by the development of a pale-yellow colour which, within a few minutes, changes to orange-red.

Test 2.—The Sudan III test for trivalent antimony.

*Procedure:—*Add one or two drops of concentrated H_2SO_4 to a little of the finely-ground mineral and then evaporate to dryness. Cool, and grind the residue with an extremely small fragment of Sudan III. The immediate appearance of an intense blue indicates the presence of trivalent antimony.

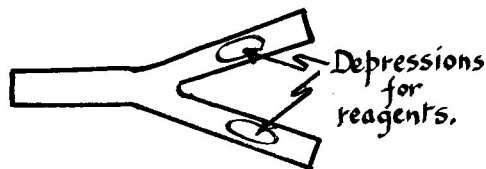


Fig. 2.—Y-Shaped Trap for Simultaneous
Detection of Osmium and Ruthenium.

Other notes :—(i) The test will fail if too much reagent is used as the product will be black.

(ii) Under the conditions of the test the reaction is specific.

(iii) If one breathes on the mixture the blue disappears: this shows that the reaction cannot be carried out in aqueous solution.

Arsenic

Test 1.—The detection of arsenic in arsenates.

Procedure :—Grind a small fragment of the mineral with a little KHSO_4 . Breathe on the mixture, then grind a little silver nitrate with it and add a small drop of water. The presence of the arsenate ion is indicated by the development of a reddish-brown colour.

Test 2.—The detection of arsenic in arsenides and sulpharsenides.

Procedure :—Place a little of the finely-ground mineral in a micro-retort and add to it 4–5 volumes of solid aqua-regia which has not been previously melted. Mix well. Attach a glass trap containing a little ammonium molybdate damped with nitric acid and, after "corking" the retort, warm it for a few minutes. The appearance of a yellow colour in the trap proves the presence of arsenic.

Barium

To detect barium in witherite (BaCO_3) or barytocalcite [$\text{CaBa}(\text{CO}_3)_2$].

Procedure :—Fuse a little of the powdered mineral with about four times its volume of solid aqua-regia which has not been previously melted. Grind a small portion of the cooled melt with a few fragments of potassium chromate. The appearance of a yellow colour indicates the presence of barium.

Bismuth

The following tests may be used to detect bismuth in any mineral in which it is a major component.

In order to detect bismuth in minerals with a metallic lustre—for example, bismuthinite (Bi_2S_3)—a little of the test-substance must first be decomposed by warming it with four to five times its volume of ammonium nitrate, then a portion of the product is ground with the appropriate test-reagent. On the other hand, if the element is to be sought for in such minerals as bismite (Bi_2O_3), or bismutite ($\text{Bi}_2\text{CO}_3 \cdot \text{H}_2\text{O}$?), preliminary decomposition is effected by grinding with KHSO_4 .

Test 1.—The ammonium chromium thiocyanate test.

Procedure :—Having breathed on a small portion of the bisulphate—or nitrate-decomposed sample—add a fragment of ammonium chromium thiocyanate to it and grind the mixture. Bismuth is indicated by the appearance of an orange-red colour on breathing on the ground material.

Other notes :—Unless a very small amount of reagent is used, the final colour is not orange-red, but yellow.

Preparation of the reagent :—Grind together, in a porcelain crucible, one part (by weight) of either chromic nitrate or chloride and three parts of ammonium thiocyanate. The product, which is green and damp, must be carefully dried in an oven before use. When dehydrated the reagent is of a lilac colour and it must be stored in a tightly-stoppered glass bottle.

Test 2.—The pyrogallol test.

Procedure :—A little of the appropriately decomposed sample is damped by breathing on it and then a little pyrogallol is ground into it. The presence of bismuth is indicated by the appearance of a yellowish-green colour.

Other notes :—The test is specific for bismuth and cannot be executed in aqueous solution.

Boron

To detect boron in evaporite minerals.

Procedure :—Grind a fragment of the mineral with a few grains of quinalizarin and then add a small drop of concentrated H_2SO_4 . In the presence of boron the reddish-violet colour of the original mixture instantly changes to blue.

Other notes :—Most of the elements which interfere when the test is carried out in aqueous solution do not do so under the above conditions.

Cerium

The detection of cerium in monazite (essentially a phosphate of the rare earths) and other cerium-rich species such as loparite [$(\text{Na}, \text{Ce}, \text{Ca})(\text{Nb}, \text{Ti})\text{O}_3$], and rinkite [$(\text{Ca}, \text{Na})_2(\text{La}, \text{Ce})_2\text{Ti}(\text{SiO}_4)_4(\text{F}, \text{OH})$].

Procedure :—Place a little of the ground mineral in a crucible and add one or two drops of concentrated H_2SO_4 . Warm until the acid has evaporated and then cool. Transfer a little of the residue to a porcelain plate and grind it with a few grains of potassium carbonate, then add one or two drops of hydrogen peroxide. The presence of cerium is indicated by the development of a yellow colour which is intensified on warming.

Chromium

The detection of chromium in chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$).

Procedure :—Fuse a fragment of the mineral with a little sodium peroxide in a right-angled capillary tube. The development of yellow sodium chromate indicates the presence of chromium and this may be confirmed by grinding some of the fusion product with a little silver nitrate when a reddish-brown colour will appear.

Other notes :—The presence of chromium in crocoite (PbCrO_4), tarapacaite (K_2CrO_4), and vauquelinite ($\text{Pb}_2\text{Cu}(\text{CrO}_4)_2$), may be confirmed simply by grinding directly with silver nitrate.

Cobalt

The ammonium thiocyanate-sodium thiosulphate test, described earlier, is suitable for detecting cobalt in minerals in which it occurs in considerable quantity. However, in most cases the test will fail unless the mineral is first ground with KHSO_4 .

The final blue colour will fade rapidly if the mixture becomes damp but it may be restored by warming.

Copper

Most copper minerals must be decomposed before they are subjected to the two tests described below. Cuprite, tenorite, chalcocite, chalcophyrite, and other minerals with a metallic lustre, must first be warmed with four to five times their volume of solid aqua-regia, whilst most of the minerals developed in the zone of oxidation—e.g., the carbonates, phosphates, and arsenates—must first be ground with KHSO_4 .

Test 1.—The ammonia test.

Procedure.—Add one or two drops of 0.880 ammonia to a little of the appropriately decomposed mineral. The development of a blue compound, within 1 or 2 minutes, indicates copper.

Test 2.—The potassium ferrocyanide test.

Grind a little of the decomposed mineral with a few fragments of potassium ferrocyanide. On breathing on the mixture the presence of copper is indicated by the appearance of a brown colour.

Gold*The detection of native gold and of gold in tellurides.*

Procedure.—Warm a little of the finely-divided mineral with five or six times its volume of solid aqua-regia until the mixture is yellow. Quickly transfer a little of the product to a porcelain plate and add a few small crystals of stannous chloride to it, followed by a small drop of concentrated HCl. The presence of gold is indicated by the immediate appearance of a brownish-black colour.

Lead*The detection of lead in minerals developed in the zone of oxidation.*

Procedure.—Grind a little of the mineral with a small quantity of KHSO₄. Add a few fragments of potassium iodide and continue grinding. The presence of lead is indicated by the development of a yellow colour which becomes more intense on the addition of a drop of water.

Other notes.—(i) Certain supergene lead minerals—notably, anglesite (PbSO₄)—will react positively when ground directly with potassium iodide.

(ii) The identity of galena may be confirmed by the fact that it is one of the few minerals which, when ground with KHSO₄, results in the liberation of H₂S. (Pyrrhotite is another.)

The detection of lead in minerals with a metallic lustre—e.g., galena, jamesonite, etc.

Procedure.—Fuse a little of the powdered mineral with about four times its volume of either solid aqua-regia or ammonium nitrate, then grind a little of the cooled melt with KI as in the above test.

Manganese

As a preliminary to the detection of manganese in most minerals the powdered sample must first be warmed with about five times its volume of solid aqua-regia. Rhodochrosite (MnCO₃), and manganocalcite [(Ca, Mn)CO₃], however, need only be ground with KHSO₄.

Test 1.—The silver nitrate-ammonia test.

Grind a little of the decomposed mineral with a crystal of silver nitrate and then add a drop of 1:1 NH₄OH. Manganese is indicated by the mixture becoming black, either immediately, or after slight warming.

Test 2.—The sodium bismuthate test.

Procedure.—Grind the product of decomposition with a little sodium bismuthate, then add a drop of 1:1 HNO₃. The presence of manganese is confirmed by the development of the reddish-purple permanganate ion.

Molybdenum

The detection of molybdenum in ferrimolybdate [Fe₂(MoO₄)₂], and other molybdenum-bearing species of the zone of oxidation.

Procedure.—Grind a little of the substance with a fragment of ammonium thiocyanate, then add a small crystal of stannous chloride and continue

grinding. The development of a cerise colour proves molybdenum.

The detection of molybdenum in molybdenite (MoS₂).

Procedure.—Fuse a little of the mineral with about six times its volume of ammonium nitrate and subject a portion of the product to the ammonium thiocyanate-stannous chloride test described above.

Nickel*The general detection of nickel.*

Procedure.—Grind a small quantity of the mineral with a little KHSO₄, then add a few grains of dimethylglyoxime and continue grinding. The presence of an appreciable amount of nickel is indicated by the development of a rose-red colour.

Other notes.—(i) Garnierite [Ni₃(Si₄O₁₀)(OH)₄·4H₂O], and other nickel silicates react positively when ground directly with dimethylglyoxime.

(ii) As noted elsewhere, ferrous iron does not interfere as it only forms a red complex if NH₄OH is added to the final product.

Osmium and Ruthenium

Osmium and ruthenium often occur together and both elements form volatile oxides. The two elements may be detected simultaneously as follows:—Place a little of the mineral in a micro-retort together with four to five times its volume of solid aqua-regia. Stopper the retort and connect a Y-shaped trap (Fig. 2) to the side-arm. One arm of the trap should contain a little solid sodium hydroxide and the other a little rubenic acid. After warming the retort for a few minutes a yellow or brown colour will appear in the arm containing NaOH if osmium is present, whilst the development of a blue tint in the rubenic acid arm will prove the presence of ruthenium.

Palladium

Procedure.—Fuse a little of the mineral with four to five times its volume of solid aqua-regia and grind some of the product with a few fragments of potassium iodide. Palladium is indicated by the mixture turning black and confirmation may be obtained because when palladium is present the mixture will become brownish if after grinding a little more potassium iodide with it a drop of water is added.

Platinum

Procedure.—Fuse a little of the mineral with four to five times its volume of solid aqua-regia. The development of a yellow melt indicates platinum and the presence of the element may be confirmed by grinding a little of the cooled product with a grain of potassium iodide and then adding a drop or so of water. In the presence of platinum a red colour appears.

Other notes.—Quite clearly palladium will interfere, but it must be remembered that this paper contains but a sample of the tests developed by the Russians. In Isakov's work (*op. cit.*) a number of tests are described for each element so that it is possible to identify each one with a high degree of certainty.

Silver

Procedure.—Decompose the mineral by warming it with four to five times its volume of flux which is composed of a mixture of two parts (by weight) of ammonium chloride and one part of ammonium

nitrate. Whilst the mixture is still warm, grind a few fragments of sodium thiosulphate into it. The immediate development of a red product, which quickly changes to brown and eventually becomes black, proves the presence of silver.

Other notes.—Under the conditions of the test bismuth causes the development of a pale yellow colour which slowly changes to red.

Sulphur

The detection of elemental sulphur.

Procedure.—Grind a little of the mineral with a few grains of thallos sulphide. The presence of elemental sulphur is indicated by the development of reddish-brown bands.

Preparation of the reagent.—Grind together thallos carbonate and sodium sulphide.

Tellurium

The detection of elemental tellurium and the telluride ion.

Procedure.—Place a little of the powdered mineral in a crucible and add one or two drops of H_2SO_4 . The appearance of a purplish-red colour on warming proves tellurium.

Thallium

Test 1.—The cobaltinitrite test.

Procedure.—Warm, in a crucible, a little of the powdered specimen with a drop or so of concentrated H_2SO_4 and continue until the charge is dry. Grind a small quantity of the residue with a fragment of sodium cobaltinitrite and then add a small drop of water. The presence of thallium is indicated by the development of a rose-red colour.

Test 2.—The potassium iodide test.

Procedure.—Grind a little of the H_2SO_4 decomposed material with a small crystal of potassium iodide and then add a few fragments of sodium thiosulphate and continue grinding. Thallium is indicated by the presence of a yellow colour.

Other notes.—Sodium thiosulphate is introduced to prevent interference by lead or silver.

Titanium

Procedure.—Fuse a little of the powdered mineral with a little KHSO_4 then grind a portion of the cooled melt with a few grains of tannin. In the presence of titanium a reddish-brown or yellow colour develops on the addition of a drop of water.

Tungsten

The detection of tungsten in members of the ferberite-hübnerite ($\text{FeWO}_4\text{--MnWO}_4$) series.

Procedure.—Warm a small quantity of the powdered mineral with a little solid KOH until the charge is yellow. Grind the melt with a small crystal of stannous chloride and then add a drop of HCl and warm gently. The presence of tungsten is indicated by the development of a strong blue colour.

The detection of tungsten in minerals other than those of the above series.

Procedure.—Grind a little of the mineral with a few small crystals of stannous chloride and then add a drop of HCl . The presence of tungsten is indicated by the rapid development of a blue colour.

Other notes.—Stannous chloride may be replaced by either powdered aluminium or zinc, but then the

mixture must be gently warmed after the addition of the acid.

Vanadium

Procedure.—Warm with a few drops of concentrated H_2SO_4 then evaporate to dryness and cool. Grind a little of the residue with a fragment of ferric sulphate and breathe on the product. The development of a reddish colour indicates vanadium.

Other notes.—Confirmation may be obtained by adding a drop of concentrated HCl to another portion of the H_2SO_4 -decomposed mineral. If vanadium is present the mixture reddens.

Zinc

The detection of zinc in minerals developed in the zone of oxidation.

Procedure.—Grind a little of the mineral with an equal volume of ammonium sulphate and breathe on the product. Grind some of the mixture with a small quantity of copper mercuric thiocyanate and add a drop of 1 : 1 H_2SO_4 . Zinc is indicated by the appearance of a lilac colour.

The detection of zinc in dark minerals, especially sphalerite (ZnS).

Decompose a little of the mineral by warming it with three to four times its volume of solid aquaregia and then carry out the above test on a portion of the product.

Preparation of the reagent.—When the reagent (which is green) is needed, prepare it by grinding a small amount of mercuric acetate with an equally small amount of ammonium thiocyanate and then grinding a very small fragment of copper sulphate into the mixture.

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