

The Identification — Essentially by Staining Techniques — of White and Near - White Mineral Grains in Composite Samples

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Abstract

It is pointed out that if all the grains of a given mineral species can be readily recognised then the amount of that species in a composite sample can be rapidly determined. Recognition can often be facilitated by employing staining — and allied — techniques and the application of these to the identification of many economically important white minerals is described.

If all the fragments of any given mineral species in a composite sample of grains can be readily identified by inspection alone it follows that "close" mill-control is greatly facilitated and the evaluation of cluvial/alluvial material becomes a comparatively simple matter.

Grains of many mineral species can be identified at a glance provided they are not exceedingly small, but those of others — the black and white varieties in particular — often cannot be so identified. However, by employing staining — and allied — techniques many diagnostic difficulties can be easily overcome and it is the application of these to the recognition of grains of certain white — or near-white — minerals of direct or indirect economic importance that this paper is devoted.

Practical Details of the Methods

Many of the staining methods noted below are not generally known because they are widely scattered throughout the literature, whilst others have been developed by the writer but have not hitherto been published.

For reasons of economy of space the fundamental chemistry of the methods has usually been omitted.

1. Cassiterite.

The tinning test.

Place a little of the sample in a zinc tray and cover the grains with 5N. HCl. After about five minutes decant and wash. Cassiterite grains — regardless of their initial colour — are usually coated with dull-grey elemental-tin by this treatment.

Other notes :—a. A number of variations of the above method are known, and by using zinc dust and dilute HCl the test may be conducted in any acid-resistant container, but in this case enough acid must be added to dissolve all the zinc.

b. Certain samples need to be boiled with HCl or aqua-regia before conducting the tinning test in order to remove protective coatings of limonite, etc.

c. On rare occasions "natural" cassiterite is encountered which does not react to the test, and that which has been heated to about $1,000^{\circ}\text{C}$. for thirty minutes, or longer, may not tin, or may be only very slowly reduced.

2. Barium minerals.

Barite.

The chromate method. (Gaudin, A. M., 1935, p.555.)

Barite grains may be stained yellow as follows: Boil the sample for a few minutes with a very strong solution of sodium carbonate, then decant and wash well. Finally warm the treated grains with N. potassium chromate.

Other notes:—a. In the absence of barium-containing carbonates and certain secondary lead minerals this test is specific for barite.

b. Witherite grains can often be conveniently identified by boiling the sample directly with potassium chromate. (Hosking, K. F. G., unpublished studies.)

Witherite.

In addition to the above, witherite grains may also be stained by the following methods:—

A. The permanganate/ H_2SO_4 method.

Cover the sample with a saturated solution of potassium permanganate very slightly acidified with H_2SO_4 . Warm at a temperature near the boiling-point for five minutes then decant and warm the solids with oxalic acid until the solution is decoloured. Only witherite grains and those of other barium-containing carbonates will be stained pink. (Hosking, K. F. G., unpublished studies.)

B. The sodium rhodizonate method.

(Hosking, K. F. G., unpublished studies.)

Rotate the sample for about thirty seconds in a 0.2 per cent. freshly-prepared solution of sodium rhodizonate, then add the minimum quantity of 1:20 HCl necessary to decolourise the solution and quickly flood the sample with water. Witherite grains — in common with many secondary lead minerals and baryto-calcite — are stained pink to red by this treatment.

3. Secondary lead minerals.

A. The sodium rhodizonate method.

The sodium rhodizonate method which is described immediately above and which is based on observations by Feigl (1947, p.429) enables all the white — and some of the other — secondary lead minerals to be stained a distinctive red.

B. The potassium iodide method.

(Hosking, K. F. G., unpublished studies.)

Grains of all white minerals — and some of the coloured secondary species — are stained a brilliant yellow if they are first immersed in a strong, freshly-prepared solution of potassium iodide and then 1 : 7 HNO_3 is added until the volume of the solution is increased by about a half. Little or no agitation is necessary and the staining is effected almost immediately and is specific for lead minerals.

Other notes : This method has been applied directly to concentrates on a vanning shovel in order to reveal cerussite.

C. Raffinot's method of staining cerussite (1953, p.3).

Raffinot notes that grains of cerussite, and anglesite, may be stained black by treating them with a solution of sodium sulphide, but remarks that this is not always a satisfactory aid to identification as it is not always easy to distinguish between such stained grains and grains of galena. He recommends staining cerussite by warming the sample for five minutes at 70°C . with a 1 per cent. ammonia solution containing 0.1 per cent. of dithizone and 2 per cent. of sodium cyanide. This treatment causes cerussite grains to be stained red. Anglesite is not stained effectively by this method as it is too soluble. The addition of the sodium cyanide prevents any secondary zinc minerals which may be present from being stained.

D. Head and Crawford's staining methods for distinguishing cerussite and anglesite in ores, concentrates and tailings.

(See U.S. Bureau of Mines, R.I. 2932, May, 1929.)

Head and Crawford recommend the following methods of staining cerussite and/or anglesite grains in order to distinguish them easily in crushed samples :—

a. To produce a bright yellow coating of lead chromate of equal intensity on both cerussite and anglesite grains, treat the sample with a cold saturated solution of potassium dichromate for fifteen minutes.

b. To stain anglesite yellow, but not cerussite, treat the sample for one minute with a cold aqueous solution containing 2 per cent. potassium dichromate and 0.5 per cent. sodium hydroxide.

c. To stain cerussite yellow, but not anglesite, immerse the sample in a cold 1 per cent. solution of CrO_3 for one minute. (Galena, however, will be tarnished orange.)

Other notes :—The originators of these tests suggest that staining is best carried out on a watch-glass and that the grains should be tumbled during the whole period in which they are immersed in the solution.

4. White zinc minerals.

Sphalerite.

Raffinot (1953) has developed the two following techniques in order to differentiate between grains of pale-coloured sphalerite and those of certain other minerals with which the species is commonly associated.

A. The dithizone method.

Boil the sample for ten minutes in a solution of sodium hypochlorite (18° Baumé) containing 10 per cent. sodium carbonate. Then wash the sample repeatedly with water and place it in a 0.1 per cent. solution of dithizone in 1.0 per cent. ammonia and warm for five minutes at 50° C. This treatment stains the sphalerite grains red, but grains of certain secondary lead and zinc species react similarly.

B. The diethylaniline method.

Subject the sample to the preliminary hypochlorite/carbonate treatment noted in the above test then wash the grains and place them in cold ferricyanide oxalic acid diethylaniline solution. After a few minutes decant and wash the sample with water. By this treatment, sphalerite grains — together with those of certain secondary zinc species which are noted below — are stained orange to vermilion.

Reagent :—Just before use mix equal volumes of 3 per cent. potassium ferricyanide and 3 per cent. oxalic acid containing 0.5 per cent. diethylaniline.

Secondary zinc minerals.

Methods A and B below have been developed by Raffinot (1953), whilst C, D and E have been devised by the writer who has also amplified B. (Hosking, K. F. G., unpublished studies.)

A. The dithizone method.

This method enables grains of smithsonite, hydrozincite and hemimorphite — and probably other zinc minerals — to be stained red, whilst the preliminary sodium sulphide treatment converts the superficial portions of secondary lead minerals to black lead sulphide and thus prevents them from reacting similarly.

Procedure :—Immerse the sample in 10 per cent. sodium sulphide for five minutes, then decant and wash the grains well with water. Warm the sample for five minutes at 50° C. with a 1 : 1 mixture of 0.2 per cent. dithizone in CCl_4 and 2.0 per cent. ammonium hydroxide. Finally, decant and wash well.

B. The ferricyanide/oxalic acid/diethylaniline method.

By the treatment noted below Raffinot successfully stained smithsonite, hydrozincite and hemimorphite grains reddish-orange, while the present writer has established that descloizite, hopeite,

parahopeite, tarbuttite and willemite can also be coloured distinctly by the treatment. The following species, which sometimes occur in zinc deposits, do not react :—barite, celestite, witherite, strontianite, fluorite, quartz, cerussite and anglesite. However, minerals with appreciable quantities of readily available cations which form coloured insoluble ferrocyanides may also be stained.

Procedure :—Place the sample in the cold ferricyanide/oxalic acid/diethylaniline reagent (which is prepared as noted earlier). After three minutes decant the solution and wash the grains well with water.

C. The ammonium mercuric thiocyanate/copper sulphate method.

Grains of smithsonite, hydrozincite and hemimorphite — and probably grains of other secondary zinc minerals — are stained purple by the following treatment.

Procedure :—Place a little of the sample in a small beaker and add c. 1 ml. of 0.1 per cent. copper sulphate, 6 ml. of ammonium mercuric thiocyanate and three or four drops of 5N. HCl. Heat the solution to 65° C. and after five minutes remove the beaker from the source of heat. Tumble the grains gently in the warm solution for a further thirty seconds, then decant and wash the sample lightly with water.

Reagent :—Ammonium mercuric thiocyanate. Dissolve 9 g. ammonium thiocyanate and 8 g. mercuric chloride in 100 ml. of water.

D. The acridine hydrochloride method.

Grains of smithsonite, hydrozincite and hemimorphite are stained greenish-yellow by the following treatment, but it is to be noted that iron gives a red and cobalt a green product under the same conditions.

Procedure :—Add about 5 ml. of 10 per cent. potassium thiocyanate, 4 ml. of a 1 per cent. solution of acridine hydrochloride in alcohol and 2 ml. of 2 per cent. HCl. to a few grams of the sample in a small beaker. Heat to about 70° C. and maintain this temperature for four minutes, then decant and wash the grains with water.

E. The 8-hydroxyquinoline method.

Grains of smithsonite, hydrozincite and hemimorphite — and doubtless other secondary zinc minerals — fluoresce brilliant yellow under either long- or short-wave ultra-violet light when treated as follows :—

Warm the sample for five minutes, at about 65° C., with a mixture consisting of equal volumes of a 0.5 per cent. solution of

8-hydroxyquinoline in 60 per cent. ethanol, and 5N. ammonia. Then decant and wash the grains well.

Other notes :—In addition to zinc oxinate, the oxinates of the following metals also fluoresce when treated with ammonia and examined under ultra-violet light :—Ba, Sr, Mg, Ca, Al, Sn (ii), Sn (iv) and Cd. (See Pollard, F. H. and McOmie, J. F. W., 1953, pp.53-54.) However, minerals containing these elements which are likely to be associated with zinc deposits will not, in the vast majority of cases, form oxinates by the above treatment.

5. White tungsten-containing minerals.

Scheelite — the most important white tungsten-containing mineral — is often conveniently recognised by the fact that it fluoresces characteristically under short-wave ultra-violet light. However, for convenience of recognition under the microscope it is better to stain the mineral by one or other of the following methods.

A. The stannous chloride/HCl method.

Cover a little of the sample in a small beaker with stannous chloride/HCl solution and warm — at about 60° C. — for five minutes, then decant, wash, and examine wet. This treatment causes scheelite — and all other tungsten-containing species except those of the ferberite-wolframite-hübnerite series — to be stained blue.

(Hosking, K. F. G., unpublished studies.)

Reagent :—Stannous chloride/HCl. Boil a pea-size portion of mossy tin with c. 10 ml. conc. HCl for five minutes. (It is to be noted that not all of the tin will dissolve and the solution should be prepared immediately before use.)

B. The aqua-regia method.

Boil a few grams of the sample for c. 30 minutes with slightly diluted aqua-regia, then decant and wash. Scheelite — and the commonly-associated wolframite — are stained canary-yellow by this treatment. However, if the yellow grains are removed and washed with ammonia the yellow coat is dissolved and then the relative amounts of black wolframite and "white" scheelite can be determined.

6. Silver halides.

White — and other — silver halides may be selectively stained red by gently agitating the sample for a minute in a cold mixture of potassium nickel cyanide, ammonia and dimethylglyoxime. (Hosking, K. F. G., unpublished studies.) The staining is somewhat patchy but is, nevertheless, of diagnostic value.

Reagent :— Prepare immediately before use, by mixing K₂[Ni(CN)₄] solution with a little 0.880 ammonia and a saturated alcoholic solution of dimethylglyoxime. (See Feigl, F., 1954.

7. Asbestos.

Morton and Baker (1941, pp.515-523) devised the following test for differentiating between small fragments of chrysotile and other varieties of asbestos in order to assist the Canadian industry.

Procedure :—Place a few drops of a 1 per cent. solution of iodine in glycerin on a microscope slide and disperse a little of the sample to be tested in the liquid. Within a short space of time chrysotile — but not other varieties of asbestos — is stained brown. However, brucite and serpentine are also similarly stained.

8. Brucite and hydromagnesite.

Grains of these minerals may be easily detected when admixed with grains of calcite by subjecting the sample to a short roast and then immersing the cooled grains in a solution of silver nitrate. Grains of the magnesium species are coated brown to black, whilst calcite grains are unaffected. (Holmes, A., 1930, p.273.)

9. Staining methods for differentiating between grains of calcite and quartz.

Gaudin (1935, p.554) points out that calcite can be stained in a variety of ways to suit the requirements of almost any problem and notes that when it is boiled with ferric chloride it becomes yellow to brown ; with nickel nitrate, green ; with silver nitrate, brown to black. Quartz is unaffected by these reagents.

The present writer has found that calcite grains in a quartz/calcite mixture can be strongly stained by using the following method :—Boil the sample with 10 per cent. copper sulphate for five minutes then decant and wash thoroughly. Finally, tumble the grains in a 1.0 per cent. alcoholic solution of rubeanic acid then decant and wash lightly with water. The calcite grains are thus stained dark green to black, whilst the quartz grains are unaffected. (Hosking, K. F. G., unpublished studies.)

10. Methods of differentiating between grains of calcite and dolomite.

Holmes (1930, pp.265-267) recommends the following methods for differentiating between grains of calcite and dolomite :—

A. The Lemberg method.

Immerse the sample in cold Lemberg's solution. This treatment causes grains of calcite to be stained violet within five to ten minutes, whereas dolomite grains show no colour change for at least twenty minutes, after which they are faintly speckled with blue.

Reagent :—Lemberg's solution is prepared by boiling together sixty parts of water, four of Al_2Cl_6 , and six of logwood chips for twenty-five minutes. During the period of boiling the solution is constantly stirred and water is added periodically to replace that lost by evaporation.

B. The silver chromate method.

Immerse the sample for three or four minutes in 10 per cent. silver nitrate solution heated to about 65°C. , then decant and wash well to remove all free silver salts. Finally, cover the grains with potassium chromate and after a minute decant and wash the residue. Calcite grains thus treated are reddish-brown, whilst dolomite and quartz grains are unaffected. Aragonite is stained less deeply than calcite.

C. The copper nitrate method.

Boil the sample for a few minutes with very dilute copper nitrate. This treatment causes calcite grains to be stained green, whilst dolomite and quartz grains are unaffected.

11. Magnesite and dolomite.**A. The Titan Yellow method.**

The following method — which was developed by the writer (Hosking, K. F. G., unpublished studies) and is based upon Kolthoff's magnesium test (1927, p.254) — enables differentiation to be made between grains of magnesite and dolomite and facilitates the recognition of magnesite grains in a mixture which also contains such minerals as quartz, calcite, fluorite, dolomite and the sulphates and other carbonates of the alkaline earths. Furthermore, in the absence of other "reactive" magnesium species grains of dolomite may be distinctively stained by the method provided the sample is first calcined.

Procedure :—Place a few grams of the sample in a beaker and add 0.1 per cent. Titan Yellow until the grains are covered with a layer of solution about 2 cm. deep. Heat until the solution just boils, then decant and wash repeatedly until the wash-water is colourless. Add 5N. sodium hydroxide and tumble the grains gently for about thirty seconds, then decant and wash gently with water. This treatment causes grains of magnesite and calcined dolomite to be stained pink to vermillion. The treated sample should be examined whilst wet.

B. The diephenylcarbazide method.

In order to differentiate between grains of magnesite and dolomite, Feigl (1947, pp.442-443) recommends the method detailed below :—

Procedure :—Cover a little of the test-material with a hot alcoholic alkaline solution of diephenylcarbazide. After five minutes decant, and wash the grains repeatedly with water until no more colouring-matter goes into solution. This treatment causes the magnesite grains to become red-violet, whereas the dolomite grains are unaffected.

Dolomite grains may also be stained by the above procedure provided they are first ignited.

12. Gypsum and anhydrite.

In the absence of other "soluble" sulphates grains of gypsum and anhydrite can be distinctively coloured by the following means.

Procedure :—Cover the sample with a saturated solution of potassium permanganate in 0.5N. barium chloride. Bring the solution just to the boil and after two minutes decant and add oxalic acid solution. Warm until the solution is pale brown to colourless. This treatment causes grains of gypsum and anhydrite to be stained pink to red. (Hosking, K. F. G., Unpublished studies.)

13. Fluorite, fluor-apatite and cryolite.

Whilst grains of fluorite, fluor-apatite and cryolite cannot be stained, some idea of the amount of any one of them which is present in a sample, can — in the absence of the other two and readily soluble phosphates and sulphates — be obtained by using the method described below which was developed by the writer (Hosking, K. F. G., Unpublished studies) and based on a test described by Feigl (1947, pp.202-204).

Procedure :—Impregnate a piece of spot-reaction paper with pink zirconium/alizarin reagent and whilst the paper is still wet sprinkle a portion of the sample over it. Place the paper on the top of a beaker containing gently-boiling water and after a few minutes remove the former and tap it to remove the grains. Where a grain of any of the three species under discussion has rested the paper will be pale yellow to colourless.

Reagent. Zirconium/alizarin solution. Dissolve 0.05 g. zirconium nitrate in 50 ml. water and 10 ml. HCl, and mix this with a solution of 0.05 g. sodium alizarin sulphonate in 50 ml. water.

14. A method of differentiating between grains of felspar and quartz.

Grains of felspar — but not accompanying grains of quartz — may be stained by the following method which was developed by Engel (1938, pp.69-70) in order that the grades of products produced during experimental work on the separation of felspar from quartz by flotation could be rapidly estimated by visual means.

Procedure :—Cover a few grams of the sample in a beaker with equal volumes of HCl and warm distilled water. Digest for five minutes then wash until free from acid and dry on a sand-bath. Cover the dried material with Safranin O and warm gently for at least fifteen minutes. When the staining appears to be complete — that is, when certain components are obviously stained yellow or pink — decant and wash the grains thoroughly with distilled water.

(The grains must be tumbled during the washing process in order to remove any traces of the stains on grains other than felspar.) Decant, then dry the sample on a sand-bath. Felspar grains will either be distinctly yellow or pink.

Reagent. Safranin O solution. Dissolve 2.0 g. Safranin O in 30 ml. ethyl alcohol and add 70 ml. water.

Other notes :—Engel found the above method satisfactory for the problem in hand, but suggested that it might not be applicable to all felspars. The present writer has applied it to several Cornish "orthoclases" and has found it completely satisfactory.

15. Amblygonite.

Grains of amblygonite can be readily recognised in the presence of those of all other similar pegmatite minerals after staining them in the manner described below. (Hosking, K. F. G., unpublished studies.)

Procedure —Place a few grams of the sample in a small beaker and cover to a depth of about half-an-inch with a solution prepared by dissolving 5.0 g. ammonium molybdate in 100 ml. cold water and pouring it into 35 ml. conc. HNO_3 . Bring the solution nearly to the boil and continue heating at this temperature for about five minutes, occasionally agitating the grains. Finally decant, and wash the sample several times with water. This treatment causes amblygonite grains to be stained yellow.

Other notes :—If apatite grains are subjected to the above treatment a yellow precipitate develops in the solution but the grains are not stained. It is possible, however, that the lithium-bearing phosphates triphylite and lithiophyllite might react like amblygonite but they have not yet been examined.

16. Bauxite.

Grains of bauxite may be stained in the three following ways :—

A. The Alizarin S method.

This method was developed by the writer (Hosking, K. F. G., unpublished studies) in order to make rapid comparisons between various products of mill-tests which were conducted in order to examine the possibility of improving the grade of certain bauxitic material.

The samples contained grains of bauxite, kaolinite, felspar, quartz and ilmenite, and a large percentage of the components were filmed with limonite.

Procedure :—Boil 10 g. of the sample for a few minutes in HCl in order to remove the limonite. Cool ; dilute well with water ; swirl ; allow the solids to settle and decant. Repeat the washing until all the soluble iron salt is removed. Cover the residue with N. NaOH

and after two minutes add 0.1 per cent. alizarin S until an intense violet colour develops. Tumble the grains in the solution for one minute, and after a further four minutes add 5N. acetic acid until the violet colour is discharged. Decant and wash the grains well with water. The bauxite fragments are stained purplish-pink.

Other notes :—The method is based on Attack's test for aluminium (1915, p.936).

B. The Malachite Green method.

Gaudin (1935, pp.554-555) recommends the use of Malachite Green for staining hydrous oxides, and notes that "the action seems to be specific for minerals with hydroxyl radicals." If the mineral is colourless, Malachite Green stains it blue, but if it is coloured the dye causes it to assume a colour which is intermediate between blue and its natural colour. In particular, Gaudin notes that the dye will stain grains of bauxite and limonite, and states that similar reactions take place when other organic dyes are employed.

Before using this method to stain bauxite it is clear that a preliminary acid treatment would often be required to remove limonite, and it is distinctly possible that minerals of the clay group might also be stained.

C. The 8-hydroxyquinoline method.

The writer has shown (Hosking, K. F. G., unpublished studies) that grains of bauxite may often be conveniently identified by warming the sample for a few minutes with equal volumes of a 0.5 per cent. solution of 8-hydroxyquinoline in 60 per cent. ethanol and 5N. acetic acid and then examining the lightly-washed grains under either long- or short-wave ultra-violet light. The bauxite fragments are immediately recognisable because they fluoresce yellow-green.

Conclusion.

In conclusion it is hoped that this paper will be of use to mineral-dressers — and others — and that it will demonstrate the immense value, and the possibilities, of staining techniques. In due course it is hoped to write another paper on the staining of coloured mineral grains.

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What We Want To Know

Does a stone wall a prison make ?
 Who is being inspected ?
 Who went to London for a rest ?
 Has anyone caught a glimpse of the obvious ?
 Is the cure for female hysteria truly efficacious ?
 Does Monk run because there is no room in the car ?
 Who is below 138 ?
 Has everyone seen the writing on the wall ?
 Which surveyor sang so much that he couldn't get his
 Weisbach ?
 Why doesn't Herr Kartoffel go into production ?
 Where do we switch on ?
 Does the Panda Inn have any geological significance ?
 Can copper be deposited from blue ink ?
 Who had the most petrol cans ?
 Do beards hinder one's love life ?
 Where does all the tracing paper go ?
 Who swore at the referee ?
 Was it tears that splashed or was it rain ?
 If you want to get ahead, do you have to get a hat ?
 How far east is the Rand ?