The Identification — Largely by Staining Techniques — of Coloured Mineral Grains in Composite Samples

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IT is pointed out that the ease with which grains of a coloured mineral can be identified in a composite sample is a function of their size and of the colours of the other components. Staining, and allied methods, which can facilitate the identification of such grains are obviously of considerable value in the field, mill and laboratory and, therefore, the writer has described most of those known to him. Some of these have been collected from the literature and others he has developed himself but has not previously published.

This paper is essentially a sequel to an earlier one (Hosking, 1957) in which the staining of grains of a number of white or near-white, minerals was discussed. Some of the staining methods described in this earlier paper apply equally well to certain strongly coloured minerals. In particular, most cassiterites — irrespective of their colour — react positively to the Tinning Test. Practically all supergene lead minerals may be stained yellow by the Potassium Iodide Technique and most zinc minerals of the oxidation zone acquire an orange to vermilion coating when subjected to the Diethylaniline Test. Furthermore, all tungstates — excepting those of the ferberite/wolframite/hübnerite series — and tungstic ochre, are stained blue by treatment with stannous chloride and HCl.

It is obvious that the degree of ease with which grains of any given coloured mineral can be identified in a composite sample is a function of the grain size and the colours of the associated minerals. Thus, grains of garnet can be readily recognised in the presence of quartz grains, but it is often very difficult to differentiate between grains of garnet and, say, danalite, by inspection alone. It is also easy to distinguish between large grains of pyrite and chalcopyrite by visual examination, but it is not easy to do so when the grains are small. It follows, therefore, that staining, and allied methods which facilitate the identification of mineral grains should be of considerable value in the laboratory, field and mill.

Practical Details of the Methods

Some of the methods noted below are fairly well known, but others, because they are scattered throughout the literature, or because they have been developed by the writer, will be new to many.

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

1. Fluorescence tests.

Certain varieties of many of the minerals with a non-metallic lustre fluoresce when irradiated with long- and or short-wave ultraviolet light, but the colour of the emitted light often varies from sample to sample. Only a few species exhibit a reasonably constant response to ultraviolet radiation. **Scheelite** invariably fluoresces under short-wave ultraviolet light and the colour of the irradiated mineral varies with increasing powellite ($CaMoO_4$) content from blue through white to straw-yellow, and this constitutes a means of estimating the composition of scheelite. It must be noted, however, that **cupro-scheelite** invariably fluoresces yellow under short-wave light.

Transparent zircons fluoresce golden-brown under short-wave light but certain opaque white Nigerian varieties fluoresce golden-yellow while the brown opaque varieties (malacon) of Nigeria are non-fluorescent.

Monazite may be detected by irradiating the sample by a short-wave lamp from which the filter has been removed. Grains of this mineral then appear brilliant greenish-yellow. (When conducting this test it is advisable to safeguard the eyes by observing the sample through a piece of plate-glass.)

Finally it should be mentioned that **certain uranium minerals** of the oxidised zone fluoresce brilliant yellow or green under either long- or short-wave ultraviolet light.

2. Heating tests.

The colours of certain minerals change characteristically when they are heated. Thus all **brown cassiterites,** when heated for c. 15 minutes at approximately 1,000° C., become orange to vermilion on cooling. [Milk-white cassiterite which contains minute red partings (hematite ?) become pink when similarly treated.]

Brownish-pink transparent zircons become colourless after heating for a few minutes at a comparatively low temperature, and this is made use of by Chinese miners in Malaya to differentiate between samples of fine cassiterite and zircon.

It is possible to distinguish between **rhodonite** and **rhodochrosite** by calcining the sample, as this treatment causes grains of the latter mineral to become black.

Finally, provided the sample has not been previously heated, some idea of the amount of **fluorite** in a sample can be obtained by heating it to c. 150° C. on an iron plate in a dark-room : each fluorite grain will then display a transient luminiscence. The colour of the emitted light varies with the variety of fluorite and may be emerald-green, purple, blue or reddish. Grains that have been thus examined will not react positively if the test is repeated.

3. Test employing refractive index liquids.

It is worth remembering that differentiation between grains of similar transparent species under the microscope may sometimes be facilitated by immersing the sample in a liquid of refractive index approximately equal to the mean R.I. of one of the species so that its grains almost disappear. Thus, it is easy to differentiate between grains of topaz and quartz if they are immersed in ethylene dibromide as the quartz then becomes ghost-like whilst the topaz appears dark-edged.

4. Lead minerals with a metallic lustre.

(Hosking, unpublished studies.)

Grains of galena, bournonite and jamesonite can be stained red by the following procedure and it is likely that all lead species with a metallic lustre would behave similarly :—Roast the sample on an iron crucible lid until the grains just become dull, then transfer it to a watch-glass and cover it with a fresh 0.2 per cent. aqueous solution of sodium rhodizonate. Gently agitate the grains and after a few seconds add sufficient buffer solution (1.0 g. tartaric acid and 1.9 g. sodium bitartrate in 100 ml. water) to discharge the colour of the solution.

Other notes :—This test also serves as a simple means of differentiating rapidly between grains of pairs of such similar species as bournonite and tetrahedrite, and jamesonite and stibnite.

5. The silver nitrate method of identifying grains of certain minerals with a metallic lustre.

This method is based on certain observations by Gaudin (1935, p.561) and has been developed independently by Raffinot (1953, pp.5-6) and the writer (Hosking, unpublished studies). Raffinot's investigations were, however, somewhat more limited than those of the writer.

Briefly, when grains of certain minerals are agitated for c. 1 minute in cold 0.1 N silver nitrate they become coated with silver, whilst those of other species develop characteristically coloured coatings if they are boiled in the solution for a minute. The reactions of certain minerals to these tests are noted in Table I and a perusal of this will show that silver nitrate can often be of considerable value for routine evaluations in the mill.

TABLE I.

The reactions between grains of certain minerals and 0.1 N silver nitrate.

Mineral	Nature of coating, etc.	Method of conducting test
Arsenopyrite	Grains cohere	Boil for 1 minute
Bornite	Gray coating of silver	Agitate grains in cold solution
Bournonite	No apparent change	Boil for 1 minute
Chalcocite	Gray coating of silver	Agitate grains in cold solution
Chalcopyrite	Blue or purple film	Boil for 1 minute
Cuprite	Gray coating of silver	" " " "
Galena	Grains somewhat dull	" " " "
Niccolite	Gray coating of silver	Agitate grains in cold solution
Pentlandite	Slight orange-yellow film. Pa chy	Boil for 1 minute
Pyrite	No apparent change	" " " "
Pyrrhotite	Purplish-brown film	" " " "
Sphalerite	No apparent change	" " " "
Stannite	" " "	" " " "
Tetrahedrite	" " "	" " " "

Notes :— (i) The silver coating tends to develop somewhat quicker on chalcocite than on bornite.

(ii) When the above staining method is employed as an aid to the estimation of chalcopyrite in a sample which also contains pyrrhotite, the stain on the latter may be removed (to avoid confusion) by washing the sample in 1.0 per cent. sodium nitrite. (Raffinot, 1953, p.6.)

6 Minerals containing the sulphide ion.

Grains of minerals that contain the sulphide ion can be identified most conveniently by employing the sodium azide/iodine test. (See Feigl, 1928, p.369 and 1947, pp.227-229 and p.301). This test depends on the fact that sulphides catalyse the otherwise extremely slow reaction between sodium azide and iodine ($2NaN_3 + I_2 = 2NaI + 3N_2$) so that there is an immediate and often vigorous evolution of bubbles of nitrogen. Thiosulphates and thiocyanates likewise catalyse this reaction but they do not occur as minerals.

Feigl does not specifically suggest that this test would be of great value when mill and similar products have to be examined but the writer has found this to be the case.

To examine a sample of grains for sulphides place it on a glass slide and cover it with the reagent (3 g. NaN_3 in 100 ml. 0.1 N iodine) then examine it under the microscope. A train — or at least a coating — of nitrogen bubbles is initiated by every grain of untarnished sulphide.

Other notes :—(i) Under standard conditions the rate of evolution of the gas is to some extent governed by the amount of sulphide sulphur in the mineral. Thus, differentiation can readily be made between arsenopyrite and loellingite (which often contains a little sulphide sulphur). Furthermore, members of the danalite, helvite genthelvite group only contain a small percentage of sulphide sulphur and so, when they are immersed in sodium azide/iodine, the evolution of nitrogen bubbles is slow. (Nevertheless, the test enables differentiation to be made between grains of these minerals and those of garnets which they resemble.)

(ii) Certain sulphides tarnish quickly and may then not react to the test. (Possibly this is the reason for the generally feeble reaction of pyrite, even when the grains are quite bright.) It is, therefore, wise to subject all but freshly broken sulphide grains to a short treatment in boiling HCl, followed by a wash in recently boiled water, before they are immersed in the azide/iodine.

(iii) It is also to be noted that certain flotation reagents contain sulphide sulphur which may become adsorbed on non-sulphide grains which would then react positively to the test.

7. The danalite/helvite/genthelvite group.

Members of this beryllium group of minerals occur with garnets and closely resemble them. However, the following tests, that were devised by Gruner (see Glass, Jahns and Stevens, 1944), enable differentiation to be made easily.

Procedure A.

Place a little of the powdered or crushed rock in a 50 ml. beaker and add enough sulphuric acid to cover it. Add a pinch of arsenious oxide and boil for one or two minutes. Decant and wash the sample twice with water. Examine the contents in the beaker — still covered by a little water — under the microscope. Grains of any of the beryllium species noted above will appear brilliant canary-yellow.

Procedure B.

Even when the gangue is essentially yellow garnet the stained fragments are easily distinguished. However, to simplify recognition under such conditions a little metallic antimony should be substituted for As_2O_3 in the above test : this would cause grains of the beryllium minerals to be stained a brilliant red.

Other notes :—The fact that the sodium azide/iodine test can be used to identify danalite and related species has been noted earlier.

8. Raffinot's method of staining arsenopyrite.

Raffinot (1953, p.6) overcomes the difficulty of differentiating between small grains of pyrite and arsenopyrite in mill products by employing the following method :—

Place a few grams of the sample in a small beaker and cover them with a 3 per cent. solution of potassium ferrocyanide in 5 per cent. HCl. Bring the solution just to the boil, then decant and wash the grains with water. Arsenopyrite grains are stained a vivid blue by this treatment, whereas pyrite grains are unaffected.

Other notes :—The writer has shown that chalcopyrite and stannite grains are also unaffected by the above treatment, whereas loellingite grains are stained blue and, therefore, cannot be distinguished from arsenopyrite grains.

9. Chalcocite.

Grains of chalcocite — unlike those of similar minerals — are readily stained blue if they are immersed for two minutes in a cold 20 per cent. solution of ferric chloride. A slight amount of warming tends to increase the intensity of the colour. (Hosking, unpublished studies.)

10. A means of differentiating between grains of malachite and atacamite.

Procedure :—Immerse the sample in a warm solution composed of equal volumes of 1 per cent. silver nitrate and 1 : 7 HNO_3. Then decant and wash with distilled water. Atacamite grains are coated white with silver chloride which becomes purple on exposure to sunlight, whilst malachite grains are unchanged.

(Hosking, unpublished studies.)

11. Methods of differentiating between grains of chrysocolla and malachite.

Provided the grains are monomineralic the two minerals under discussion can be separated by shaking with bromoform. The chrysocolla floats and the malachite sinks. However, this method does not apply when the grains are composite, and then differentiation can be best effected by employing differential staining techniques. The following method is often satisfactory :— Immerse a little of the sample in warm 5N. acetic acid and after 30 seconds add sufficient warm 10 per cent. sodium xanthate to treble the volume. Tumble the grains for a minute, then decant and wash the residue with water. Malachite grains are stained yellow by this treatment, whilst grains of chrysocolla are **usually** unaffected. However the reactivity of different varieties of chrysocolla is very variable, and therefore it is wise to conduct appropriate preliminary tests on the chrysocolla of a given mine before the above method is applied to the routine examination of its mill-products.

(Hosking, unpublished studies.)

12. Stibnite and kermesite.

Grains of both stibnite and kermesite are stained yellow if they are immersed in 40 per cent. potassium hydroxide for five minutes. As neither jamesonite nor red minerals similar to kermesite react to this test useful differentiations can be readily made by its employment. (Hosking, unpublished studies.)

Other notes: It has been noted earlier that the sodium rhodizonate test may also be used to distinguish readily between grains of stibnite and jamesonite.

13. Calaverite.

Grains of gold and gold/silver tellurides are not readily identified when they are associated with the common sulphides. The following method of staining grains of calaverite — which could probably be used for staining other tellurides — is of considerable assistance: —

Immerse a little of the sample in 1 : 1 HNO_3. Bring the acid **just** to the boiling point, then decant and wash the grains with water. (This treatment causes calaverite to assume a pinch beck-brown tarnish, whilst pyrrhotite and chalcopyrite become iridescent. Gold is unaltered, and pyrite shows little or no tarnish.) Cover the grains with stannous chloride/HCl and warm gently for c. 3 minutes, then decant and wash the sample lightly. This causes calaverite grains to become dull black and tends to remove the tarnish from the sulphides. (Hosking, unpublished studies.)

Reagent. The $SnCl_2$/HCl reagent should be prepared immediately before use by boiling 4 or 5 g. of tin with 15 ml. of concentrated HCl for c. 5 minutes.

14. Wolframite and manganese-rich minerals generally.

Heat a few pellets of NaOH on a square of asbestos paper (of side $1\frac{1}{2}$ ins.) in such a way that as the hydroxide melts it runs over the paper, forming first a thin veneer and then sinking into it. At the moment when that portion of the paper over which the melt has spread assumes a matt appearance, sprinkle the sample over it and continue heating for c. 30 seconds. As a result of this process wolframite, and other manganese-rich grains, are surrounded by bluish-green haloes. (Hosking, unpublished studies.)

Other notes:—Unless the grains are fine the test is unsatisfactory because of partial loss of sample by decrepitation.

15. Nigerian thorite.

In Nigeria, thorite often closely resembles the associated zircon. Mackay (1950-51) identifies thorite in Nigerian products by the fusion test described in the following section, whilst Jones (see

Macleod and Jones, 1955) subjects the sample to prolonged treatment with hot HCl which leaches the iron and thorium from the thorite, leaving a characteristic white silica shell, and bleaches the zircon. Hosking and Patterson (1956) have developed several quick staining tests to differentiate between the species in question and of these the following is the most satisfactory :—

Transfer c. 2 g. of the sample to a 100-ml. beaker and cover with the minimum of concentrated HCl. Cover with a watch-glass and boil rapidly for four minutes. Decant, and wash the residue five or six times with water, but leave the solids just covered with water after the last wash. Add c. 5 g. of **finely-ground** ammonium molybdate and swirl to effect solution. Add 10 ml. of concentrated HNO_3 and boil rapidly for three minutes. Decant, wash eight times with water, dry, and examine.

This treatment causes thorite grains, unlike those of other species normally occurring in Nigerian gravity concentrates, to assume a matt, intense lemon-yellow appearance, whilst zircon grains become leached and glassy. Any dark minerals are coated, to varying degrees, with a whitish veneer.

16. Nigerian columbite and thorite and chemically simple uranium minerals.

Mackay (1950-51) developed the following test, primarily in order to identify columbite rapidly in Nigerian products. However, it also facilitates the identification of thorite in these products, and the writer employs it in order to identify grains of pitchblende and other chemically simple non-fluorescent uranium species in mill products, and, in particular, in concentrates from the Cornish tin mines.

In essence the test is conducted as follows :—A quantity of flux (the composition of which is noted below) is so melted in a nickel tray that the bottom is covered with a **thin** veneer of melt. After cooling, a representative fraction of the sample is scattered over the tray and the whole is heated until the flux melts, and then for a further 30 seconds. Finally, the cooled product is examined under short-wave ultraviolet light. Under these circumstances columbite grains are surrounded by pale yellow fluorescent haloes, whilst grains of thorite, and of chemically simple uranium minerals, are associated with intense yellow haloes. Grains of monazite and of zircon are sometimes characterised by the presence of very pale yellow fluorescent haloes.

Reagent. The flux has the following composition :—

Sodium bisulphate	...	2 per cent. by weight.
Sodium fluoride	...	5 per cent. by weight.
Sodium carbonate } **Potassium carbonate**		Balance in equal parts.

17. Ilmenite.

Flinter (1955) states that he finds the best chemical aid to the identification of grains of ilmenite in Malayan products is to boil the sample for c. 20 minutes in concentrated HCl. This " will cause the ilmenite to take on a dull greyish or brownish coating similar in appearance to leucoxene ".

Bartnik (1955-56) employs the following method in order to differentiate between ilmenite and columbite in black sand dumps :- Boil the sample for one hour in HCl and then wash the sample once with distilled water in order to remove slimes. Then ignite the sample for 15 minutes in a muffle furnace at 700° C. This treatment causes the ilmenite to become corroded and coated with yellowish-brown oxides whilst the columbite remains black and lustrous.

18. The evaluation of certain tin/tungsten/tantalum-niobium concentrates by a method depending on staining techniques.

In the Belgian Congo the amounts of cassiterite, wolframite, scheelite and columbite/tantalite in concentrates of grains is greater than 0.5 mm. diameter have been determined in the following manner (Vanden Herrewegen, 1954) :—

From 2 to 5 g. of concentrate are boiled for c. 20 minutes in a solution consisting of 25 ml. HCl, 15 ml. HNO_3 and 60 ml. water. This causes wolframite and scheelite grains to become yellow. The yellow grains are picked out and their yellow coat is removed by treatment with ammonia. The white grains are removed and weighed as scheelite and the dark grains as wolframite. The remaining grains are placed in a zinc dish and covered with dilute HCl. After 12 minutes the tinned cassiterite grains are removed and weighed. All grains that are not black are then removed from the residue and the black fraction is placed in a crucible together with a few pellets of KOH and two drops of water. The contents of the crucible are warmed and after the grains have been bathed for a short while in the strong hydroxide solution the latter is decanted and a little HCl, which has been diluted with a third of its volume of water, is added. This dissolves any remaining KOH and causes the columbite/tantalite grains to become white. The residue is then washed well and the white grains are picked out from under a layer of water and dried and weighed.

REFERENCES

BARTNIK, J. A. Trans. Instn. Min. Metall., Lond., **65**, 1955-56, 512.

FEIGL, F. Z. anal. Chem., **74**, 1928.
Qualitative analysis by spot tests. (London ; Elsevier Publishing Co., Ltd., 1947.)

FLINTER, B. F. A brief guide to the identification of the dark opaque and semi-opaque minerals known to occur in Malayan alluvial concentrate. Geological Survey of Malaya, note No. 8, 1955.

GAUDIN, A. M. Staining minerals for easier identification in quantitative mineragraphic problems. Econ. Geol., **30**, 1935, 552-562.

GLASS, J. J., JAHNS, R. R. and STEVENS, R. E. Amer. Min., **29**, 1944, 163-191.

HOSKING, K. F. G. The identification — essentially by staining techniques — of white and near-white mineral grains in composite samples. Camborne School of Mines Magazine, **57**, 1957, 5-16.

HOSKING, K. F. G. and PATTERSON, J. H. Thorite in Nigerian products. Mining Magazine, **94**, 1956, 73-75.

MACKAY, R. A. Trans. Instn. Min. Metall., Lond., **60**, 1950-51, 129-131.

MACLEOD, W. N., and JONES, M. P. The effects of heat and hydrochloric on the properties of some Nigerian minerals. Colon. Geol. miner. Resour., **5**, 1955, 166-173.

RAFFINOT, P. Identification des minéraux en grains par coloration de leur surface. Congrès des laveries des mines métalliques françaises. Paris, 1953. (6 pages.)

VANDEN HERREWEGEN, F. Détermination rapide des proportions de wolframite, colombo-tantalite et cassiterite d'un concentré. Bull. Inst. colon. belge, **15**, 1954, 476.

What We Want To Know

Who " missed " the boat ?
Why did Carn Brea ?
Did George meet Phillip ?
Who is dreaming of a rosy future ?
What did Carrick Du ?
Where do you put the " third wire " ?
Is prospecting really necessary ?
How do you crush a piece of rock " in situ " ?
Means of ventilation in Room 12 on Fridays.
Where was the Secretary at the last colloquia meeting ?
Who " stole " the Westor Mine Plan ?
Temperature of the Fountain on Saturdays.
Who felt faint in the First Aid lecture ?
Who saw the uranium at Ponsanooth ?
Are metal-planes and paper-darts related ?
If a certain lecturer always sets Entrance Examinations ?
Why is the " pit " being dug on the north-side of the K.E.M. garage ? Has the grass died on the south-side ?
That's as may be . . . !