Flame and Allied Tests for Minerals in Review

An appraisal
designed to
fill a gap
in the literature

K. F. G. Hosking, Ph.D., A.M.I.M.M.

Abstract

In the accompanying review—which is written to fill an obvious gap in the literature—the following tests are described and their merits appraised: Classical flame tests; flame tests for tin, gold, and bismuth; tests depending on the luminescence of the hydrogen flame; electric-arc tests and micro-chemical flame analysis.

Flame tests are of great value to the mineralogist, yet no textbook—as far as the writer is aware—deals comprehensively with them. This fact in his view justifies the present article.

Classical Flame Tests

The expression " classical flame tests " is used here to denote those tests which appear in practically all accounts of blowpipe analysis. Essentially the method consists of picking up a little of the powdered sample on the end of a platinum or iron wire or magnesia flame stick, previously damped with concentrated HCl, and holding it in a flame—preferably a non-luminous one. Volatile compounds of certain elements are thus liberated which impart a characteristic colour to the flame.

Alternatively, a good flame coloration may often be obtained by dipping a fragment of the mineral in question, held in forceps, in concentrated HCl and then holding it in a suitable flame. Furthermore, dust generated by scratching a mineral vigorously with a penknife in the near vicinity of a flame is often capable of imparting a diagnostic colour to the latter.

By placing the sample-charged wire or rod first in a cool and then in a hot part of the flame colorations due to more than one element may be detected. Thus, as potassium chloride is more volatile than the chlorides of the alkaline earths, it is possible to detect first potassium and then an alkaline earth when they are both present.

Examination of flame colours through coloured glass and celluloid filters often assists diagnosis. A cobalt or, better, didymium glass filter is generally used to detect the potassium flame in the presence of the masking sodium flame. The Merwin screen, another device, is composed of two strips of celluloid—one blue and the other violet—which partly overlap so that three filters are available. This screen is of considerable assistance when examining flames, chiefly because it enables the potassium flame to be identified in the presence of the sodium and permits certain differentiation to be made between the calcium and strontium flames. It does not, however, facilitate differentiation between the similar lithium and strontium flames, but, with experience, it is possible to distinguish between them by employing a green glass filter (Winchell, 1942, p. 200). Winchell (1942, p. 200),[1] having decided that a given red flame is either due to strontium or lithium, differentiates between the two by testing the ignited residue on the wire for alkalinity. The strontium residue—unlike that of lithium—is alkaline. Smith (1953, pp. 62–4) differentiates between the two flames in question by adding barium chloride to the test substance. The lithium flame appears *before*, and the strontium flame *after*, that due to barium.

Vogel (1947, p. 108) is of the opinion that " the only trustworthy way to employ flame tests in analysis is to resolve the light into its component tints and to identify the cations present by their characteristic set of tints." For routine tests he suggests that this is best accomplished by means of a direct-vision spectroscope, but he limits the general use of this piece of apparatus to the detection of sodium, potassium, lithium, and thallium. It is, in his opinion, of less value for the detection of the alkaline earths as their spectra are comparatively complex. The present writer, in common with most mineralogists, is of the opinion that trustworthy results can usually be obtained from flame tests without employing a spectroscope, although it is most useful for analysing " mixed " flames. In Dana's *Manual of*

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

Mineralogy, 15th edition, p. 107, a "home-made" diffraction spectroscope is described which is suitable for simple qualitative work.

Flame Tests Employing Different Reagents and/or Techniques

It is necessary to use techniques and/or reagents differing from those described above in order to obtain satisfactory flame colorations when testing certain refractory minerals. Furthermore, certain elements whose chlorides do not impart a characteristic colour to the flame may be detected by flame tests in which compounds other than chlorides are used. The majority of these special flame tests are briefly described below in order to indicate the range of methods used.

Tests for Lithium, Sodium, and Potassium in Silicates

Usually silicates containing lithium, sodium, or potassium do not give characteristic flame colorations when heated alone or in the presence of hydrochloric acid in the flame of a bunsen burner or an alcohol lamp. In such cases Dana (1932, p. 364) recommends carrying out the test on a 1 : 1 mixture of powdered sample and gypsum which is introduced into the flame on a damped platinum wire. Beringer (1931, p. 217) uses Turner's Flux (a mixture of 4·5 parts of potassium bisulphate and 1 part of fluorite) instead of gypsum when testing for lithium or sodium. For obvious reasons it cannot be employed when testing for potassium. Recently MacKay and Brown (1955, p. 186) have suggested that lithium can be most effectively identified in minerals in the field by subjecting them to the intense heat of a "Prestolite" (acetylene) torch and examining the flame either through didymium glass or by means of a hand spectroscope.

Tests for Borates and Phosphates

If the more soluble borates and most phosphates are damped with sulphuric acid and introduced into a flame the latter is coloured a characteristic green. The more refractory boron-containing minerals—for example, tourmaline—do not so react. However, the characteristic flame coloration may be obtained from all borates and phosphates by employing Turner's Flux in the manner noted above.

Low, Weinig, and Schoder (1945, p. 10) test all refractory minerals suspected of containing appreciable amounts of boron as follows: A little of the powdered sample is fused with sodium hydroxide in a silver loop. The product is crushed and warmed with a little methanol and HCl and the vapours thus produced are introduced into a colourless flame. In the presence of boron the flame is coloured green.

Tests for the Chloride Ion

To test for the chloride ion McGrigor (1915, p. 63) prepares a bead of microcosmic salt on a platinum wire and fuses a little cupric oxide into it until the flame of copper ceases to appear. A little of the sample is taken up on the bead which is then introduced into a colourless flame. In the presence of chloride ion the flame becomes azure blue.

Bromides similarly treated colour the flame bright blue with green streaks and iodides colour the flame green (McGrigor, 1915, pp. 62 and 67).

Flame Tests Applicable to the Naturally Occurring Sulphates of the Alkaline Earths

These minerals do not readily give good flame colorations when subjected to the normal test. However, an adequate coloration is usually obtained if the mineral under examination is first partially converted to sulphide by heating it before the reducing flame of the blowpipe and the product subjected to the usual flame test.

Alternatively, good flame colorations may be obtained by mixing any of the minerals under discussion with a little silver chloride paste, taking up the mixture on an iron wire, and introducing it into the flame. The reagent is a good one to use in flame tests generally (excepting when testing for phosphates, chlorides, or borates) as it prolongs the duration of the flame colour.

Flame Tests for Tin, Gold, and Bismuth

Hydrogen, which is generated from the reaction between zinc and hydrochloric acid in the presence of any soluble and most insoluble tin compounds, imparts a blue colour to the non-luminous flame of a Bunsen burner. This constitutes a selective test for tin and the reaction only fails when arsenic is present in amounts equal to or greater than that of the tin. To show the presence of tin in cassiterite by this method it is necessary to fuse the mineral with fusion mixture and carry out the test on the resultant product.

Usually the test substance and reagents are placed in a porcelain dish and stirred with a test-tube half filled with cold water, after which the bottom of the tube is introduced

into the flame. The presence of tin is indicated by the appearance of a blue mantle around the glass.

A similar test for tin in which coal-gas is used instead of hydrogen is conducted as follows : A drop of the test solution is placed on a magnesia stick and evaporated to dryness by holding it near to a flame. The area occupied by the test substance is damped with a drop of concentrated HCl and placed in the reducing zone of the flame from a microburner. The development of a blue flame mantle indicates tin.

The above tests, which have been developed and investigated by Feigl and others (see Feigl, F., 1947, p. 88), are based on the earlier researches of Meissner (1930, p. 247), and the test-tube method noted has been employed by the Russians to obtain semi-quantitative data concerning the distribution of cassiterite in alluvial deposits (Sokoloff and Hawkes, 1950, pp. 65–6).

Mehrotra (1948, p. 321) reports that when a solution of a gold salt is subjected to the above tests a brilliant green mantle forms. He also states that copper interferes and, in the presence of tin, the green mantle is masked by the blue tin mantle.

In the absence of tin, arsenic, copper, and gold, bismuth ions cause a transient greenish-blue mantle to develop which is most evident when the magnesia stick method of testing is employed.

Tests Depending on the Luminescence of the Hydrogen Flame

Extremely small quantities of bismuth, antimony, and manganese may be detected by mixing the sample with calcium carbonate and placing the mixture in a hydrogen flame. Colours of diagnostic value are imparted to the flame at the moment when the mixture, containing any of the three elements noted above, is introduced. Bismuth imparts a transient cornflower blue, antimony a blue-green, and manganese a yellow colour. (See Feigl, 1947, pp. 62 and 86, and Donau, 1913, p. 949.)

An almost identical method has been described by Neunhoeffer (1951, pp. 91–4) for detecting certain of the rare earths. The rare earth is precipitated together with a large excess of calcium carbonate and is eventually ignited. When the ignited mixture is placed at the edge of a hydrogen flame the rare earths activate the calcium oxide to luminescence and the colours produced by various members of the group are as follows :

Table 1

Colours Imparted to an Electric Arc

(*After Peterson, Kauffman, and Jaffe, 1947, p. 332.*)

Element	*Colour on positioning screen or other characteristics*
Al	Greenish-blue.
Sb	White fumes.
As	Garlic odour.
Ba	Green.
Be	Greenish-blue.
B	Green.
Ca	Orange.
CaF_2	Canary-yellow.
Cb	Blue with red fringe. Pitted lower electrode and white oxide coating.
Cr	Green.
Cs	Bluish-white.
Cu	Green.
Fe	Blue with yellowish-white fringe. Sparks and popping bead.
Li	Red.
Mg	Green.
Mo	Blue metallic coating on lower electrode.
Nd	Light orange-red.
K	Bluish-white.
Pr	Greenish-gray.
Sc	Light orange.
Sm	Red.
Ag	Green.
Na	Yellow.
Sr	Red.
Ta	Blue with a red fringe. Pitting on lower electrode and white oxide coating.
Tl	Green (very intense).
Ti	White.
U	Bluish-white.
W	Blue when current is reduced. Pitting of lower electrode and yellow oxide coating.
Y	Red.
Zr	White flashes.

Ytterbium, pale blue-violet ; lanthanum, brick-red ; cerium, yellowish-green ; praseodymium, red ; neodymium, orange-red ; samarium, yellowish-green ; dysprosium, pale green ; thulium, yellowish-green.

As most rare-earth minerals usually contain several rare earths this test is not likely to be of great value to the mineralogist excepting when conducting prolonged specialist studies.

Electric Arc Tests

Peterson, Kauffman, and Jaffe (1947, pp. 322–335), describing the rapid identification of many elements occurring in minerals by utilizing a Bunsen-type spectroscope to examine the spectra produced when samples are arced between graphite electrodes, state that (p. 331) " many elements when present in major amounts can be quickly identified *without* a spectroscope through recognition of

the colours they impart to the arc. They will be imaged on the test screen in the form of a halo surrounding the centre portion of the arc." The colours due to various elements are noted in Table 1. Although many of the elements produce either red or green tints the authors state that with practice the halo due to any given element noted in Table 1 can be distinguished from all others! An earlier detailed study of the use of arc images in chemical analysis has been conducted by Mott (1920).

It would appear that this aid to mineral identification would be well worthwhile using in a laboratory even if the entire assembly for spectroscopic analysis were not available and in this connexion it is relevant to state that the nature of the fusion products on the electrodes are often additional aids to mineral identification.

Micro-Chemical Flame Analysis

Geilman and Isermeyer (1950, pp. 249–262) have made the classical flame reactions the basis of a scheme for the detection of traces of a number of volatile elements. Oxide, metal, and halide sublimates are deposited on the base of a silica test-tube filled with cold water. The colour of the sublimate is noted, if the latter is sufficiently strongly developed, after which the film is dissolved in a suitable reagent and the resultant solution is examined for the presence of " likely " elements by micro-chemical means.

The flame in which the sublimations are conducted is obtained by using a mouth blowpipe as a burner and the gas is so adjusted that the flame is from 20 mm. to 25 mm. high. The hole from which the gas emerges should be such that the flame is slim and sharp and has a slightly luminous tip. During the actual test period the blowpipe is adjusted so that the luminous tip *just* touches the base of the water-filled tube. If this adjustment is made correctly the sublimate will occupy a circle of from 2 mm. to 3 mm. diameter.

Production of Oxide and Metal Sublimates

In order to obtain oxide or metal sublimates a piece of high-grade asbestos string 2 mm. to 3 mm. long and from 0·3 mm. to 0·5 mm. thick is damped and tapered by twisting between the fingers. Holding the taper in tweezers, the extreme tip is cut off. Three to five mg. of the test substance is taken up on the end of the damp taper and the sample area is dried by holding it near the flame. When the sample is dry the water-filled tube is placed in position and the taper is held in the fusion zone of the flame. Adequate sublimates of the more volatile elements—*e.g.*, tellurium, zinc, cadmium, and antimony—are obtained after 15 seconds' heating, but elements such as lead, bismuth, thallium, and tin require 30 seconds for a reasonable quantity of sublimate to accumulate.

Throughout every test the colour of the flame is noted.

Modifications of the Normal Technique

If it is suspected that the element sought occurs in very small quantity in the test material several portions of the sample are heated, but all the sublimates are collected on one tube.

By altering the flame position during a given test so that two or more spots of sublimate are obtained, a partial separation of the very volatile from the less volatile elements may be effected. Such a separation is, however, very imperfect because the flame is so hot that the temperature of the small sample rises very rapidly.

If the substance sought is not extremely volatile and is associated with a large quantity of very volatile material—such as, arsenious oxide or mercuric sulphide—it is wise to remove the latter by placing 0·05 g. to 0·1 g. of the sample in an ignition tube and heating it at the lowest temperature necessary to sublime the more volatile fraction. The residue is then tested in the normal way, but if it is small it is advisable for ease of handling to mix it first with an indifferent substance such as aluminium oxide.

Should it be necessary to test for a very small quantity of readily volatile material in a large excess of much less volatile substance—*e.g.*, traces of mercuric sulphide in zinc sulphide—it is best to place 0·05 g. to 0·1 g. of the sample in an ignition tube over which is then placed another ignition tube and to drive the easily volatile material into the covering tube by the application of the minimum amount of heat. This sublimate is then examined by the appropriate micro-chemical methods.

Production of Halide Sublimates

Tests depending on the production of halide sublimates are not as sensitive as those in which metals and oxides are sublimed. They are, however, especially useful for identifying copper, silver, and nickel in samples after the more readily volatile components have been removed.

To produce a halide sublimate a portion

Table 2
Characteristics on Sublimates
(Based on descriptions by Geilman and Isermeyer, 1950.)

Element	*Type of Sublimate*				
	Metal	*Oxide*	*Chloride*	*Bromide*	*Iodide*
Sb	Brownish	White	—	—	Yellow
As	Brown-black	White	—	—	Yellow
Pb	Brown	Yellow	—	—	Yellow
Cd	Black (+ brown oxide edge)	Brown	White	White	White
Ge	—	Black-brown or white	—	—	—
In	Black (+ brown edge)	Yellow	White	Yellowish	Brown-yellow
Mo	—	Yellow + blue	—	—	—
Ni	—	—	←——— Greenish-white ———→		
Hg	Black-grey	—	←——— Grey-white ———→		Yellow (± red)
	Sulphides and selenides of mercury give direct red sublimates				
Re	—	Yellow (+ blue edge)	—	—	—
Ag	—	—	White	←——— Yellowish ———→	
Se	Black (+ red edge)	White	—	—	—
Te	Black (+ brown edge)	White to yellowish	—	—	—
Th	Black-brown	White-yellow	White	Yellowish	Red-yellow
Bi	Black (+ brown edge)	Yellow-white	White	Yellowish	Brown-red
Zn	Black (+ brown edge)	White	←——— Colourless and hygroscopic ———→		
Sn	Black (+ brown edge)	White	—	—	—

of the test substance is fused with borax on a piece of platinum wire of 0·1 mm. to 0·2 mm. diameter so that a bead of from 2 mm. to 3 mm. diameter is produced. A small crystal of alkali metal halide (Cl^-, Br^-, or I^-) is added to the molten bead which is then placed in the oxidizing zone of the flame. The sublimate is collected on a water-filled tube.

Examination of Sublimates

Having prepared the sublimate of metal, oxide, or halide, it is examined visually and then brought into solution on a microscope slide in order that the elements present may be determined by micro-chemical means. Sometimes the sublimate is so slight as to be invisible, but it will give positive results when subjected to suitable micro-chemical tests.

The solvents employed for attacking a given sublimate depend on its composition. The attacking agents recommended by the originators of the method are (p. 256) :—

(1) 20% HNO_3 for Pb, Bi, Se, Te, Hg, and Tl.

(2) 20% HCl for Zn and Cd.

(3) 1 volume of 20% HCl + 1 volume of 30% H_2O_2 for Sn, Sb, Te, and Se.

(4) 1 volume of NH_4OH + 1 volume of 20% H_2O_2 for As, As_2O_3, MoO_3, Re_2O_7, and GeO.

(5) Water + a little HCl or HNO_3 for all iodide sublimates.

(6) Concentrated HCl or NH_4OH for AgCl.

The appearance of the sublimates is summarized in Table 2. For information concerning the micro-chemical tests advocated by the authors the original paper should be consulted, but the present writer has found that the more accessible tests of Short (1940) are generally quite adequate for the purpose under discussion.

Practical Applications of the Method

The method is of value in that it permits of the rapid identification of minor constituents of small samples of minerals without resorting either to complex chemical methods or to physical methods entailing the use of costly apparatus.

By using the above techniques the originators have, for example, demonstrated the presence of small amounts—0·05% and less—of arsenic, lead, and zinc in pyrite and of 0·05% of copper in limonite.

It is possible to identify elements when they occur in much smaller amounts than those noted above by first concentrating them.

Concentration is achieved by bringing a comparatively large quantity of the sample—one gram. or more—into solution and co-precipitating the elements sought with a "trace-catcher." The resulting precipitate is collected by centrifuging, washed with water then with acetone, and dried. Finally it is treated in the manner noted earlier in order to obtain a sublimate which is examined by micro-chemical means. Thus, the presence of cadmium and lead in a zinc salt containing 0·001% and 0·008% of these elements respectively was shown by co-precipitating their sulphides and cupric sulphide and examining the product in the manner described above.

As the method is both interesting and useful, and as no account in English has hitherto appeared, the writer feels justified in having discussed it at some length.

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South African Mining in 1957

L. A. Waspe

The industry begins to benefit from the various programmes designed to improve labour efficiency

Introduction

Provisional returns of the labour complement of the South African mining industry are not yet available, but in gold-uranium operations the European labour shortage persisted and appeared to be greater on the Free State mines, especially in the artisan staff. However, 1957 saw a reduced overall demand on the country's man-power to an extent rendering possible the suspension of recruiting artisans overseas, while recruiting of trainees for the mining schools has more recently been confined largely to Holland and Italy and to a less extent to Western Germany. Domestic recruiting has been intensified generally, although enrolment at the schools has remained below their capacity. The seasonal increase in the native labour complement over the early months of 1957 reflected slight advances on the corresponding 1956 figures, but the subsequent seasonal trend showed declines from the 1956 levels. To date the seasonal improvement in 1958 has been below the corresponding 1957 returns. According to the lastest available reports 62% of the gold-uranium native labour complement of the major mines have been recruited beyond