VI.—*Improvements in the Methods of Determining the Composition of Minerals by Blowpipe Analysis.* By ALEXANDER JOHNSTONE, F.G.S. (Edinburgh, London, and Paris).

(Read 2nd May 1889.)

IT is now beginning to be clearly recognised that mineralogy is not a mere *branch* of chemistry or physics, but is more or less an independent science which requires to be pursued with as much singleness of purpose as any other department of knowledge. As the science of naturally occurring elements and compounds, mineralogy is essentially practical. One of its chief objects is of course the identification of its raw materials or minerals, whether occurring in veins, lodes, or rock masses. When mineralogy was regarded as a department of physics, its minerals were frequently successfully identified by physical methods, some rapid, many slow, but most of them taken alone, decidedly uncertain in their results. Considered as a branch of chemistry, the minerals were generally accurately enough determined by the processes of modern chemical analysis, which however have the great disadvantage, if correct, of being extremely slow. The methods of identification of the modern mineralogist must, I consider, be both rapid and easy. He has no time or inclination to spend over the slow determinations of the multitudinous materials which fall before his hammer. He must either determine all quickly, or one and two slowly, and leave the others unknown, or send them on to a chemical friend to be identified, which is also a highly unsatisfactory proceeding. I hold what I consider the reasonable and proper view that the mineralogist should be able to identify all his own materials without the slightest assistance from either the specialist in chemistry or physics. He should, of course, be acquainted with fundamental chemical and physical methods, but should arrange, modify, and work these in an altogether independent fashion to suit his own special mineralogical requirements. His methods of determination also must be simple, easy and sure; a difficult method is little better than none, as it is almost always certain to be unsafe, no matter how skilfully and carefully it be conducted.

The science and art of blowpipe analysis is the department which gives by far the greatest assistance to the mineralogist. It has been unjustly neglected in the past, at least since Plattner's time, but its position is now improving, and new researches by mineralogists are continually simplifying its methods, and creating new, or changing for the better the mode of applying old time-honoured tests. The day is not far distant, I hope,

when we shall have rapid and trustworthy tests for every known element, under all possible known natural conditions. When that day does arrive we shall undoubtedly have the analytical chemists coming over to us, and learning from us, and the science of inorganic chemistry itself may then in its turn be considered by the authorities of the world at the time, to be but a handmaiden of its former supposed subordinate mineralogy. The operations of blowpipe analysis are at the present time about ten in number, viz. :—

- A. *Heating in the Closed Tube.*
- B. *Heating in the Open Tube.*
- C. *Heating on Charcoal, alone.*
- D. *Heating on Charcoal, with flux.*
- E. *Heating on Platinum Wire.*
- F. *Heating in the Borax Bead.*
- G. *Heating in the Microcosmic Salt Bead.*
- H. *Heating to produce a Film on Porcelain.*
- I. *Heating on Platinum Foil with flux and nitre.*
- J. *Heating on Platinum Forceps to determine fusibility.*

I have affixed at the end of this paper tables which show all the fairly decisive, correct, and workable tests known at present, that come in under each of the above operations. I have vigorously eliminated all tests and methods which in my practice I have found to be unsatisfactory.

In connection with operation A. I have been fortunate enough to discover an extremely simple, easy, rapid, and very correct method for the detection of mercury. All substances containing mercury, it is well known, yield when heated in a piece of glass tubing closed at one end, a sublimate which is either metallic or non-metallic in character. Most compounds of mercury are decomposed by heat alone, and so furnish, when subjected to a certain temperature, the former sublimate; but mercurous chloride (calomel) and bromide, and mercuric chloride (corrosive sublimate) and iodide, and to a certain extent the sulphide also (cinnabar), are volatile without decomposition, and accordingly produce sublimates of non-metallic lustre. All compounds of mercury, however, when dry and intimately mixed with three or four times their bulk of fusion mixture (dry anhydrous carbonates of soda and potash) yield, under the influence of heat, metallic mercury, which condenses on the cooler portions of the tube above the assay. When this metallic sublimate is small in amount, or mixed with other matters, it may easily be mistaken for arsenic, and sometimes, though rarely, for antimony. The method which I have introduced decides the question at once. Pour a single

drop of moderately concentrated nitric acid into the tube coated with the metallic sublimate, and immediately afterwards a *drop* of a fairly strong fresh or undecomposed solution of potassium iodide in water, and warm the bottom of the tube *slightly*. The potassium iodide is at once split up by the nitric acid, and the newly liberated iodine acts with energy on any mercury in the sublimate or assay, producing the unique scarlet iodide of mercury on the sides of the tube.¹ The formation of this scarlet iodide is a very good indication of the presence of mercury. In operation B. I have also introduced a new test, which has, I think, likewise the merit of simplicity and accuracy. Antimony and *most* of its compounds give when heated *alone* in the *open tube*, and *all* its compounds when heated with flux, a distinct white sublimate. But native arsenic, arsenical compounds, sulphide of lead, ammonium chloride, &c., also give good white sublimates in the open tube. Whether or not the sublimate is antimony oxide, or contains that body, can be easily ascertained by pouring down the sides of the tubes upon it a drop of ammonium sulphide. If antimony is present, the highly characteristic orange-coloured sulphide of antimony will immediately form. This test can also be applied in operation A. if a black metallic sublimate forms near the assay after heating with flux; but it can in all cases be best used, especially if the quantity of antimony is very small, in the next operations (C. and D.) on charcoal.² If any white incrustation or coating forms on charcoal in either of these operations, simply touch it with ammonium sulphide, and the orange sulphide will distinctly form if any antimony is present, especially if the test be applied while the charcoal (which should have a smooth surface) is still in a fairly warm condition.

In operation D. I have been able to confirm the presence of tin, which is usually considered by the ordinary worker to be one of the most difficult of ore metals to detect satisfactorily, and, at the same time, easily and quickly. The beads or scales of white malleable metal supposed to be tin, obtained by heating the powdered mineral with flux,³ and afterwards grinding and lixiviating the fused residue, are heated on porcelain for a very short time with *two or three* drops of moderately strong hydrochloric acid. After the process of heating, one drop of the acid must be left on the porcelain undried up. A drop of gold chloride solution is then added, and soon, if the metal treated in this way was tin, or an alloy containing tin, the very characteristic "purple of Cassius" distinctly appears.

¹ See *Chemical News*, May 10th, 1889.

² Or aluminium plate can be used in place of the charcoal.

³ Obstinate stanniferous minerals, such as tin pyrites, require to be treated also with cyanide of potassium, and with borax.

It is well known that by the usual method of performing operation E. only the fusible minerals give the characteristic flame colourations or spectrums. I have been able to obtain these, however, from the most infusible silicate by heating, and so partially decomposing the refractory substance for about five or six minutes with solid ammonium fluoride before applying the test.¹ I thoroughly and repeatedly moisten the platinum wire first with hydrochloric acid, and get what results I can with this residue in the Bunsen flame; and, second, with silver chloride, using it in the same manner; and, finally, I moisten my clean wire with strong sulphuric acid, and heat the substance with it in the flame, and watch for any indication of boric acid.

I have found that the presence of iron in operation I. can be instantly and accurately ascertained by moistening the residue fused on the platinum foil with fusion mixture and potassium nitrate, or by the nitrate alone, with strong, pure, nitric acid, and then adding a drop or two of potassium or ammonium sulphocyanide solution. The bright red colouration which results from this test if iron is present is an exceedingly delicate, characteristic, and infallible indication.

I have gone very carefully through Bunsen's elaborate system of film tests, but have only been able to find the metallic films of mercury (which, when treated by my method detailed above, show the scarlet iodide very well) and selenium, and the oxide films of cadmium, and lead and bismuth of much value in blowpipe analysis.

Professor Szabo's method of detecting calcium, barium, lithium, potassium, &c., in infusible or difficultly fusible silicates, I have, after many trials, found to be tedious and extremely uncertain in results. Mr Grenville Cole, who has paid considerable attention to this plan, particularly in connection with the determination of felspars, has devised a very simple and effective stand for holding the fragment of mineral to be tested, steadily, in any region of the flame, but no amount of invention, in my opinion, will much improve Szabo's method.

I have very slightly modified Von Kobell's Scale of Fusibility (see table of operation J. at the end of the paper).

Rapid and trustworthy tests are still required for the following metals:—Aluminium, beryllium, caesium, cerium, iridium, lanthanum, lithium, magnesium, nickel, potassium, rubidium,

¹ See paper by the author, "On the Macroscopic Determination of Igneous Rocks," in "Trans. Edin. Geol. Soc., vol. v., page 488; and also article by the same, "On the Rapid Decomposition of Insoluble, Natural, and Artificial Silicates for the purpose of Qualitative Analysis," in *Chemical News*, vol. lviii. No. 1518.

DETERMINATION OF THE COMPOSITION OF MINERALS. 47

thorium, tantalum, thallium, titanium, tungsten, uranium, vanadium, yttrium, and zirconium; and for the following non-metallic elements:—Boron, fluorine, and silicon. Of course *new* rapid satisfactory tests for any of the other elements are also always acceptable.

THE OPERATIONS OF QUALITATIVE BLOWPIPE ANALYSIS.

A. Heating in the Closed Tube.

Result.	Inference.
1. The substance changes colour, - - -	One of the "heavy" metals present (<i>e.g.</i> , Sn, Sb, Pb, Cu, Bi, Hg, Cd, Cr, Fe, Zn, Ti, Nb).
2. The substance glows or phosphoresces, - - (Often seen better by heating powder on platinum foil.)	Fluorite, Willemite, Gadolinite, ZnO, &c.
3. The substance evolves water, - - - -	Hydrate.
The substance evolves water which has alkaline reaction, - - - -	Am. salts.
The substance evolves water which has acid reaction, - - - -	Volatile acid (HCl, HF, H ₂ SO ₄ , HNO ₃ , &c.) present.
4. The glass of tube above the assay is etched, and the vapour arising from the heated substance turns Brazil wood paper yellow, -	Presence of fluorine.
5. The substance fuses, - - - -	The degree of fusibility of the substance is most probably 1, and certainly not more than 2 (Von Kobell's scale).
6. The substance carbonizes, - - - -	Organic compound.
Test any water given off; (1) if alkaline, -	Nitrogenous body.
(2) If acid, - - - -	Non-nitrogenous.
7. A sublimate is formed on the cooler part of the tube, - - - -	Sulphur (yellow to reddish), selenium, tellurium (condenses in small drops with metalloidal lustre), osmium (sublimate of whitish drops with disagreeable odour), iodine (violet fumes, more especially if heated with KHSO ₄ or H ₂ SO ₄), Hg, As, Sb.
Heat another portion of the powdered substance mixed with about three times its bulk of fusion mixture.	Presence of Am.
a. Odour of hartshorn evolved, - - -	Presence of As.
b. Odour of garlic evolved, - - -	
c. Metallic sublimate which is—	
(a) Close on assay, - - - -	Sb.
(b) Well above assay, - - - -	Hg, As.
Pour into the tube one drop of conc. HNO ₃ , then one drop of KI; warm slightly.	
A scarlet substance formed on sides of tube, - - - -	Hg.
8. The residue is magnetic, - - - -	Fe, Ni, Co.
9. Heat strongly a little more of the powdered original substance with magnesium wire. Put in a drop of water, and smell.	
Odour of PH ₃ (phosphine), - - -	Presence of phosphorus.

A. Heating in the Closed Tube—continued.

Result.	Inference.
10. Heat <i>strongly</i> a little of original powdered substance with soda flux (Na_2CO_3) and charcoal dust, then pour into tube a <i>little</i> hot water. The water assumes a purplish colour, - - - - -	Tellurium.
11. Heat <i>gently</i> original substance with a little strong H_2SO_4 .	
a. Substance effervesces (or does so with HCl or slightly warmed HNO_3), - - -	CO_2 . (Carefully distinguish between effervescence, and boiling of the liquid.)
b. Brownish vapours evolved with nitric odour, - - - - -	Nitrata.
c. Brownish vapours evolved, which turn starch paper yellow, - - - - -	Bromide.
d. Violet vapours evolved, which turn starch paper blue, - - - - -	Iodide.
e. White pungent acid fumes, which etch the glass above the assay, - - - - -	Fluoride.
f. White pungent acid fumes, which do not etch glass, - - - - -	Chloride.
Confirm by heating a little more of original substance with H_2SO_4 and MnO_2 . Chlorine gas evolved recognised by its odour and bleaching properties, - - - - -	Chloride.

B. Heating in the Open Tube.

Result.	Inference.
1. Odour of SO_2 (burning sulphur) evolved - - -	S. (The fumes redden moist litmus paper.)
Odour of garlic, - - - - -	As.
Odour of decaying horse-radish, - - - - -	Se.
2. Substance changes colour, - - - - -	See previous table (A. 1).
3. Sublimate formed, - - - - -	As, Sb, S, Se, Te, Bi, Pb, Hg. Mo.
a. When R. flame of blowpipe is directed on sublimate it becomes blue or copper-red, - - - - -	Molybdenum.
b. The sublimate is dark brown when hot, yellow when cold, - - - - -	Bi.
c. Sublimate is grayish. It fuses to clear drops, which solidify on cooling, - - - - -	Te.
d. Steel gray sublimate, - - - - -	Se.
e. Distinct white sublimate. Touch it with Am_2S , it becomes orange, - - - - -	Sb.

C. Heating on Charcoal.

Result.	Inference.
1. Characteristic odours evolved, - - - These should be at once observed after a short exposure to the heat— <i>first</i> of the R.F., and <i>second</i> of the O.F.,	As, Se, S (see B. 1)
2. The substance deflagrates, - - -	Nitrates and certain other bodies very rich in oxygen.
3. The substance fuses readily, - - -	Fusibility not more higher than 2.
4. The substance swells up, - - - and forms a glass on cooling - - -	Borax, Sassolite, Alum, &c. Borax, Sassolite, &c.
5. After strong heating an infusible residue is left, which is a. Coloured, - - - or b. White or gray, - - - which— Is alkaline to test paper, - - - Moisten (b) with $\text{Co}(\text{NO}_3)_2$, and heat again. The mass assumes a Blue colour, - - - Violet colour, - - - Pinkish colour on cooling, - - - Green colour, - - -	Cu, Co, Ni, Mn, Fe, Cr, Ti, &c. Ca, Sr, Mg, Zr, Al, Zn, and Sn (glow brightly), Ba, SiO_2 , &c. Ca, Ba, Sr, Mg. Al, SiO_2 (faint). Zr (dirty violet), P_2O_5 (rarely). Mg, Ta (after long ignition). Zn and Ti (yellowish green), Nb (dirty green), Sn (bluish green).
6. One or more sublimates or coatings are produced, which may be— a. Yellow on cooling, - - - Heat a little more of the substance with Cu I + S in the R.F. A red sublimate is formed, - - - b. Yellowish-white on cooling, - - - c. Brown-red on cooling, - - - d. Red-brown to red (usually very slight), - - - e. Steel-gray, - - - f. White, while hot and cold, - - -	Bi, Pb. Bi. In. Cd. Ag. Se. Sb, As, Tl, Te, Sulphides and Halogen Salts of the Alkalies, and Hg.
Touch the sublimate with a drop of Am_2S , and warm very slightly. The sublimate assumes an orange colour, g. Yellowish while hot, white on cooling, - - -	Sb. Zn, Sn (slight coat near assay), Mo.
7. A bead or beads or scales of metal produced, -	See Operation D.
8. The residue is magnetic, - - -	Fe, Ni, Co.
9. The substance is completely volatilised, - - -	Stibnite, Bismuth, Tetradymite, Orpiment, Realgar, Arsenolite, Arsenic, Antimony, Bismuth, Valentinite, Cinabar, Calomel, Iodic Mercury (and other rare Hg minerals), Salmiak, Tellurium, Allemnite, Organic bodies, &c.
10. The substance burns with a flame, - - -	Sulphur, Orpiment, Realgar, certain Organic bodies, &c.

D. Heating on Charcoal with Fusion Mixture in the R.F.

Note.—If only a white infusible residue without incrustation was obtained in C., it is not necessary to do this operation.

Result.	Inference.
1. The substance is reduced to the metallic state. (The residue, after proper fusion, should always be pounded in a mortar and lixiviated.)	
a. The metal is yellow and malleable, - -	Gold.
b. The metal is white and malleable, - -	Ag (not easily oxidisable). Sn (easily oxidisable).
Heat the white metal for a moment with a very little strong HCl, and then add a drop of AuCl ₃ . The purple of Cassius is formed, - -	Sn (Tin).
c. The metal is bluish gray and malleable, -	Pb (marks paper).
d. The metal is red and malleable, -	Cu.
e. The metal is yellowish-white, and somewhat brittle, - -	Bi (confirm by 6 a, Operation C.).
f. The metal is bluish white and brittle, -	Sb (easily volatile).
2. Sublimates or coatings formed, - -	See Operation C.
3. The residue is magnetic, - -	Fe, Co, Ni.
4. Place the residue fused with fusion mixture on a bright silver coin, and moisten with a little dilute HCl. A dark stain produced on the coin, - -	S. (This test can only be used in the absence of Se.)

E. Heating on Platinum Wire.¹

Dip the Pt. first in HCl or AgCl (it is advisable to try both separately), then hold in inner flame.

Result.	Inference.
1. The non-luminous Bunsen, lamp, or blowpipe flame is coloured—	
a. Golden yellow, - - - - -	Na.
b. Pinkish violet, - - - - -	K.
c. Yellow-red to brick-red, - - - - -	Ca.
d. Purple-red to crimson, - - - - -	Li.
e. Crimson, - - - - -	Sr.
f. Yellowish green, - - - - -	Ba, Mo.
g. Intense green, blue near assay, - - - - -	Cu.
h. Green, - - - - -	Te, Tl.
i. Blue, - - - - -	CuCl ₂ , Se, Pb.
j. Greenish blue, - - - - -	Sb, CuBr ₂ .
k. Light or grayish blue, - - - - -	As.
2. Moisten substance with H ₂ SO ₄ , and heat in flame.	
a. Yellowish green colouration produced, -	Boric acid.
b. Bluish green colouration produced, -	P ₂ O ₅ .

¹ Infusible or difficultly. Silicates should first be fused with ammonium fluoride, then heated on platinum wire as above, and the flame observed by means of the spectroscope. (See paper, "On the Macroscopic Determination of Igneous Rocks," in the "Transactions" of this Society, vol. v. page 488.)

DETERMINATION OF THE COMPOSITION OF MINERALS. 51

F. Heating on the Borax Bead.

This need not be done if the residue in operation C. was white.

Result.	Inference.
1. The bead is coloured—	
a. Blue in both flames when cold, - - -	Co.
b. Green in both flames when cold, - - -	Cr.
c. Bluish green in O.F., red in R.F. when cold,	Cu.
d. Yellow in O.F., green in R.F. when cold, -	V.
e. Yellow in O.F., bottle-green in R.F. when cold,	Fe, U (yellow green).
f. Yellow in O.F., brown in R.F. when cold,	W.
g. Rose colour in both flames when cold, -	D.
h. Reddish brown in O.F., grey or colourless in R.F., - - -	Ni.
i. Violet (amethyst) in O.F., grey or colourless in R.F., - - -	Mn.

G. Heating in the Microcosmic Salt Bead.

Result.	Inference.
1. The whole or portion of the substance is insoluble in the bead (observe when hot), -	SiO ₂ .
2. The substance is completely dissolved in the bead, and colours it—	
a. Violet in R.F. on cooling, - - -	Ti, Nb (sometimes bluish).
b. Blue in R.F. on cooling, - - -	W (brown while hot), Co.
c. Fine green in R.F. on cooling, - - -	U.
5. Other colours as with Borax (see F.).	

H. Heating on Asbestos Thread in the Bunsen Flame to produce a Metallic or Oxide Film on Porcelain (Bunsen's Film Tests).

Result.	Inference.
1. a. The metallic film produced by heating in the upper reducing flame is red, - - -	Se.
b. The metallic film is gray. When touched with strong HNO ₃ and KI solution it becomes scarlet and yellow, - - -	Hg.
2. a. The oxide film produced by heating in the upper oxidising flame is yellow, - - -	Pb, Bi.
b. The oxide film is brown, - - -	Cd.

I. Heating on Platinum Foil with Fusion Mixture and Potassium Nitrate (KNO₃).

Result.	Inference.
1. A bluish green colour appears after the mass is fused, - - - - -	Mn.
2. A yellow colour appears after the mass is fused, - - - - -	Cr.
3. When the fused mass is touched with pure HNO ₃ and potassium sulphocyanide, a bright red colouration is formed, - - -	Fe,

J. Heating on Platinum Forceps to determine the Fusibility of a Fragment of the Substance, by Von Kobell's Scale.

Result.	Inference.
1. Easily fusible in candle flame, - - - - -	Fus. 1 or less.
2. Difficultly fusible in candle flame, - - - - -	Fus. from 1 to 2.
3. Infusible in candle flame, but easily before a good blowpipe flame, - - - - -	Fus. from 2 to 3.
4. Difficultly fusible before the blowpipe - - -	Fus. from 3 to 4.
5. Only fusible before the blowpipe in the very finest splinters, - - - - -	Fus. from 4 to 5.
6. Infusible before the blowpipe, - - - - -	Fus. 6.

Note.—Any good chemical text-book may be consulted for the meanings of the symbols employed in the above tables.