On a rapid method for the accurate recognition of sulphides, arsenides, antimonides, and double compounds of these bodies with metals.

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THE process to be described has been applied to the minerals mentioned below, but I have no doubt that all similarly constituted minerals will also be easily recognised by the method.

I am quite sure that all mineralogists have experienced much annoyance and difficulty in obtaining really satisfactory results with the ordinary blow-pipe reactions in regard to some of the compounds of arsenic, antimony, and sulphur with metals, particularly in the separation of the metal or metals from the above-mentioned elements. In order to obtain the metal the assay requires a most careful and tedious roasting on charcoal in the *oxidising flame* of the blow-pipe, in order to volatilise away the sulphur, arsenic, or antimony. When this roasting is complete the residue (oxide) is mixed with either sodium carbonate, or that salt and cyanide of potassium, and fused for a considerable time on charcoal in the reducing flame in order to obtain a bead of the metal. Sometimes borax is used to eliminate a metal from a mixed oxide residue, dissolving one oxide and leaving the other. If the oxides left after the oxidising process above-mentioned are not soluble in borax, then the bead which is obtained in the subsequent reducing process is an alloy, and practically useless as a means of recognition of the metals entering into its composition. Having often been disappointed with the results obtained by the above-mentioned blow-pipe processes, I determined to find, if possible, a more rapid and certain method of analysis of minerals.

The apparatus required is that which all mineralogists have been in the habit of using for a long period, viz.

1st. Small porcelain crucibles.

2nd. Test-tubes.

3rd. A small platinum basin and a platinum crucible.

4th. A platinum spoon made rather deep, something like a platinum crucible with a handle.

5th. Hard-glass tubing, closed at one end and about 4in. long; a cork is placed in the open end, with a hole bored through it, and a hard-glass tube of small bore passed just through the cork. The straight piece out-side the cork is bent either *twice* at right angles (if required to pass vapours into water or solution), or *once* at right angles, and drawn out to a fine nozzle if required to test for arseniuretted or antimoniuretted hydrogen.

6th. A Bunsen burner of the ordinary type, or a spirit-lamp.

7th. Funnels, beakers, porcelain evaporating basins, stir-rods, &c. &c., and small pieces of clean sheet-iron and sheet-copper.

<div align="center">Reagents.</div>

Ammonium nitrate	(solid)
Sodium nitrate	,,
Potassium bi-sulphate	,,
Metallic zinc	,,
Hydrochloric acid	(solution)
Potassium ferrocyanide	,,
Potassium ferricyanide	,,
Ammonia-liquor	,,
Caustic soda	,,
Silver nitrate	,,
Stannous chloride	,,
Bi-chromate of potassium	,,

All the above reagents can be carried about in the *dry solid* condition for travelling, except the hydrochloric acid and the ammonia. With regard to the latter it can be carried in the form of solid ammonium carbonate or ammonium sulphate; and the ammonia liberated from the respective salts in the usual manner, and passed either into the solution to be tested or else into water. I cannot at present give as easy a way of producing hydrochloric acid when it is wanted from dry materials, but think that it could be prepared in sufficient quantity by heating to-gether in a glass tube (with delivery tube attached as described above) a mixture of potassium or sodium bi-sulphate and sodium chloride. Hydro-chloric acid gas would then be liberated. Nitric acid is not required in this method at all.

Having thus briefly touched upon the present method of the treatment by the blowpipe of the minerals containing volatile elements, I will at once proceed to describe the method proposed by myself to attain the

same object.   The oxidising reagent I use is pure *crystallised ammonium nitrate*.   This salt, on being heated to about 250° C., decomposes, intumesces, and the products of its decomposition are nitrous oxide (N_2O) and water.   *Thus the products are both gases, and nothing remains behind, which is certainly a very great consideration.*   The *nitrous oxide*, at the high temperature used, rapidly gives up its *oxygen* to any element having an affinity for that gas, and *oxidises* it, so that finally the principal decomposition products of the original ammonium nitrate which are evolved as gases are nitrogen and vapour of water.   The *modus operandi* is exceedingly simple.   The mineral to be tested is crushed up and powdered into an exceedingly fine powder, a platinum or porcelain crucible is taken and filled to about one-fourth of its bulk with coarsely crushed ammonium nitrate crystals, then upon this about 0·5 gram of the finely powdered mineral is placed, and the crucible and contents held with a pair of tongs over the Bunsen lamp, just in the flame.   A violent reaction is at once set up, and care must be taken to withdraw the crucible from time to time from the lamp in order to avoid loss by boiling over the sides.   Sometimes it is necessary to add some more ammonium nitrate crystals to the partially cooled " melt " in the crucible and heat again in order to complete the reaction.   *An excess of ammonium nitrate cannot possibly do any harm, and it ensures success.*

The crucible having been allowed to cool, the contents are extracted with water and the solution separated from the insoluble matter.   During the fusion of the mineral in the crucible, characteristic colours of various metallic salts are most distinctly observed, occasionally, therefore, the operator must watch this fusion closely.   The fusion and lixiviation of the melt only occupy a minute or two when one has attained some experience, but the whole analysis need not exceed fifteen minutes even in complicated compounds.   When melting the mineral in a glass tube with the ammonium nitrate and passing the products of combustion into water, care must be taken to carefully dry the ammonium nitrate in a water oven previous to use, as it rapidly absorbs moisture from the air, and the water thus evolved in the fusion tube would cause the hot glass to crack.   The thoroughly dried ammonium nitrate is conveniently kept in a *well stoppered* bottle.

Sulphides of Arsenic.

Orpiment (As_2S_3).

Realgar (AsS).

Fused in glass fusion tube with tube bent twice at right angles, the open end of the delivery tube dipping into water.   Sulphuric acid was found in

the water in distinct quantity by the usual barium chloride test ; therefore the mineral was a *sulphide*. In the fusion tube was a slightly coloured solid residue which could be eventually completely dissolved in boiling water ; it gave the reaction for *arsenic acid* (with nitrate of silver) and all the other reactions for arsenic ; mirror on being treated with metallic zinc and acid potassium sulphate, and the arseniuretted hydrogen, decomposed into metallic arsenic by heating the hard-glass delivery tube to redness. *The mineral was therefore arsenic sulphide.*

Antimony Sulphide.

Stibnite (Sb_2S_3).

Fused in the same kind of apparatus as that used for the sulphides of arsenic, yielded sulphuric acid in the water and a mixture of Sb_2O_3 and Sb_2O_5. A little sulphuric acid was also detected in the water which had been used to boil the residue in the fusion tube. On adding a solution of potassium bisulphate to the residue in the fusion tube, and a piece of pure metallic zinc, antimoniuretted hydrogen was at once evolved, and a mirror of metallic antimony obtained on heating the delivery tube to redness. Other tests applied proved this mirror to be really antimony. The mineral did not give reactions for any other element likely to be present, hence it was *sulphide of antimony*.

If it is suspected that both arsenic and antimony are present in a mineral in large amount, they can be easily separated from each other by substituting *sodium nitrate* for ammonium nitrate, when a compound of antimony and sodium, insoluble in cold water, is obtained (antimonate of sodium), whilst the arsenic forms arsenite and arsenate of sodium, both of which are soluble in cold water after standing some time.

Löllingite.

Fe As₂.

Fused with ammonium nitrate in a platinum crucible or porcelain crucible. Melt red-coloured. Dissolved in hot water gave the reactions for arsenious and arsenic acid with silver nitrate and the usual arsenic reactions. The insoluble residue gave the reactions for iron. The mineral was therefore an *arsenide of iron*.

Proustite.

Ag₃ASs₃.

Fused in the same manner as the last-mentioned mineral, yielded a *black* residue containing arsenic oxide (this residue will be the subject of special examination, as it is peculiar). The melt was treated to separate

the black residue.   A solution of silver sulphate was obtained, which gave the characteristic reactions for silver and sulphuric acid.   The black residue was treated with the acid-potassium-sulphate solution and metallic zinc, and arsenic was detected in the usual manner.   The solution in water also gave the characteristic reaction for arsenic acid with silver nitrate.   All the silver of the proustite was converted into sulphate, on account of the high percentage of sulphur in this mineral.   The mineral was therefore a *sulph-arsenite of silver.*

Pyrargyrite.

$Ag_3 \underline{Sb} S_3$.
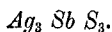
Treated in the same way as the preceding mineral, sulphate of silver was obtained in solution in water, and insoluble antimonious [and antimonic oxide (Sb_2O_3 and Sb_2O_5) remained as a residue.   The antimony reactions were obtained, and only silver and sulphuric acid detected, consequently the mineral was a *silver sulph-antimonite.*

Argentite.

$Ag_2 S$.

On treating this mineral in the same manner as pyrargyrite, sulphate of silver was produced in small amount, owing to the small percentage of sulphur present in argentite.   On adding a small quantity of "flowers of sulphur" to the powdered mineral, and then fusing the mixture with the ammonium nitrate, a larger quantity of silver sulphate was obtained.   The solution gave the reactions for silver and sulphuric acid only, consequently the mineral was a *sulphide of silver.*

Iron-Pyrites.

Marcasite.   Pyrites. FeS_2.
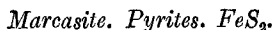
Fused as above gave a reddish brown residue of ferric oxide (Fe_2O_3) and a brown solution in water, which gave the characteristic reaction for *ferric*-salts with potassium ferrocyanide solution, and also the reaction for sulphuric acid.   The mineral was therefore *sulphide of iron.*

Galena.

PbS.

Gave a *white* residue (insoluble in water) of *lead sulphate*, and nothing in solution.   The residue was dissolved in hot hydrochloric acid, when a portion of the solution gave a white precipitate (of barium sulphate) on the addition of a solution of barium nitrate, and another portion of the hydrochloric acid solution, on being neutralised with sodium carbonate

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and boiled with a solution of potassium bichromate, gave the charac-
teristic yellow lead chromate reaction.   The white lead sulphate
residue mentioned above, on being treated *directly* with the solution of
potassium bichromate, also gave the lead chromate reaction.   The mineral
was therefore a *sulphide of lead*.

Copper-glance   (Redruthite).

$Cu_2S.$

Gave a *blue* melt *whilst hot*, which became brown on cooling.   The melt
dissolved completely in water into a blue solution, which gave the usual
reactions for copper and sulphuric acid.   The mineral was therefore a
sulphide of copper.

Bismuth-glance.

$Bi_2S_3.$

The melt was brown when cold.   A solution of *sulphate of bismuth*
was obtained, which gave the reactions for bismuth and sulphuric acid.
An excellent and delicate reaction for bismuth is that which was shown to
me by Professor Bunsen at Heidelberg 21 years ago, which I have never
yet seen described in any work on qualitative analysis.   In applying it to
the solution of the melt first add a slight excess of caustic soda solu-
tion to it, when a *white* precipitate of hydrated bismuthic oxide
(Bi_2O_3 H_2O) is obtained.   In another vessel add an excess of caustic soda
solution to a solution of stannous chloride, when a white precipitate of
hydrated stannous oxide (SnO H_2O) falls out, but immediately re-dis-
solves in the excess of caustic soda.   The bismuth precipitate obtained
as above is washed into a white basin and a portion of the caustic
stannous solution poured upon it and well stirred with it, when very soon
a dense *black* precipitate is seen in the white basin, this precipitate being
an oxide of bismuth Bi_2O_2, formed by the reduction of the Bi_2O_3 through
the SnO.

Millerite.

$Ni\ S$ (with Co and Fe).
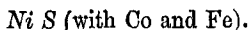
Gave a *green* solution of sulphate of nickel, which gave the characteristic
reactions for nickel and sulphuric acid, and also those for cobalt and iron.
There was an insoluble brown residue of ferric oxide from the melt.

The mineral, therefore, was a *sulphide of nickel*.
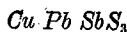
Copper Pyrites.

$CuFeS_2.$

Gave the same reactions as those obtained in the case of chalcocite, *with
the addition* of a copious reddish brown insoluble residue from the melt of

ferric oxide. The solution of the melt in water was *blue.* The melt in the crucible was reddish-brown.

The mineral was therefore a *sulphide of copper and iron.*

Bournonite.

Cu Pb SbS₃

$Cu\ Pb\ SbS_3$

Melt after fusion *yellowish-green.* Treated with water gave a solution of *copper sulphate,* in which both copper and sulphuric acid were detected as in chalcocite, &c. The insoluble residue (after dissolving out all the copper sulphate) was found to be sulphate of lead and antimonious and antimonic oxides. A portion of this insoluble residue was treated with acid sulphate of potassium (as in stibnite), when all the antimony was eliminated as *antimoniuretted hydrogen,* and the residue of lead sulphate treated as the sulphate of lead obtained from galena, and the presence of lead demonstrated.

The mineral therefore was a *copper-lead sulph-antimonite.*

### Tetrahedrite, or Fahl-ore.

$Cu_8\ Sb_2\ S_7.$
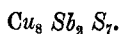
The melt was *green whilst fusing,* but *brown* when cold. Treated with water gave a *blue* solution of copper sulphate, ferric sulphate, and traces of zinc sulphate and arsenious acid. The usual tests were applied to this solution, and copper, iron, and sulphuric acid detected.

The residue insoluble in water was found to be antimonic oxide (Sb_2O_5) and ferric oxide. On boiling the residue with *caustic potash* the Sb_2O_5 was dissolved and the ferric oxide remained. On adding hydrochloric acid in excess to the antimonate of potassium and a piece of metallic zinc antimoniuretted hydrogen was detected in the way described above.

The mineral therefore was a *copper-iron,—&c. sulph-antimonite.*

Smaltite.

$(Co,\ Fe,\ Ni)\ As_2.$
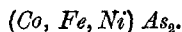
The melt was *pink* whilst fusing. Treated with water and boiled, an insoluble residue of cobalt, iron and nickel oxides remained, whilst *arsenious acid* passed into solution, and the arsenic was detected in the usual manner. The oxides of the metals thus obtained were dissolved in hydrochloric acid and tested chemically for cobalt and nickel, also iron, and these metals were detected.

Where arsenic and antimony combine with metals forming antimonides and arsenides, *and no sulphur is present,* oxides of the metals are obtained together with oxides of antimony and arsenic. By adding sulphur to

these compounds, *the metals are converted into sulphates and become soluble.*

I have still to discover a good method for the separation and detection of cobalt and nickel, suitable for mineralogical analysis.

In conclusion I must acknowledge the great assistance I have received from my assistant, Mr. Gilbert Rigg, in this investigation.

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NOTE.—Since writing the above I have made some further experiments, and have succeeded in separating cobalt from nickel in the most complete manner. If the mineral is an arsenide or antimonide of cobalt and nickel it is fused as described in the treatment of smaltite, and when all the metals are converted into oxides a lump of ammonium nitrate is added to the melted mass from time to time, and the whole is kept gently simmering for three or four minutes. The melted mass assumes a pink colour due to the formation of nitrate of cobalt. After cooling the melt is boiled out with water; NiO remains behind absolutely free from CoO. The cobalt nitrate solution is evaporated to dryness in a porcelain basin and ignited at about 250°C, when all the ammonium nitrate present is volatilised and pure pink cobalt nitrate remains in the basin. If the mineral is a sulphide of nickel and cobalt fuse it with 10 per cent. of its weight of powdered carbon (previously added to the powdered mineral), and about four times its weight, or more, of caustic soda in a silver crucible. Sodium sulphide is produced, and dissolved out by water from the cooled melt, and the oxides of cobalt and nickel remain behind; they are then treated with ammonium nitrate as described above.   C. A. B.