

*Colour reactions in the micro-chemical determination
of minerals.*

(With Plate IV.)

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THE rapid determination of the chemical elements present in a mineral has been a desideratum ever since minerals became of economic use. Various methods have been employed, starting with blowpipe work, which in the early days proved of great value, especially in experienced hands. With the development of chemistry and the discovery of new elements, this process was largely abandoned in favour of the standard 'wet method' of chemical analysis. Later on, micro-chemical reactions came into limited employment. Here the appearance of easily crystallizable salts under the microscope was used for diagnostic purposes. This method has been extensively examined of late years and became so overloaded with precautions that its chief asset, that of rapidity and ease of employment, has been largely lost. Quite recently colorimetric reactions have been applied to qualitative analysis. These appeared so promising that the present author was encouraged to endeavour to apply them to the examination of minerals.

A scheme for the qualitative determination of the commoner elements was published by G. Gutzeit¹ in 1929, which at first sight looked very attractive. Some of the reactions, however, were not reliable, and on that account did not appeal to the author, who was seeking a method that could be put into comparatively inexperienced hands. In 1931 a book was published by Dr. F. Feigl² in which is a comprehensive study of the whole subject of colour or 'spot' reactions. This book was taken as a basis on which to work. The likeliest reaction for each element was selected and tested in presence of all other elements which gave any reaction. This involved a considerable expenditure of time, but in the end a number

¹ G. Gutzeit, *Helv. Chim. Acta*, 1929, vol. 12, p. 829.

² F. Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*. Leipzig, 1931.

of reagents was found which gave specific reactions under simple and easily attained conditions. Some few elements did not give any characteristic reaction and have been omitted. Again, in one or two cases it was found that certain reactions were indeterminate in presence of one other element. These have been included, as more characteristic reactions are not available at the moment.

The method of carrying on the tests can be very briefly described. The solution to be tested is contained in a small test-tube, and one drop is placed by means of a small pipette either in a cavity of a spotting-plate or on a filter paper. A drop of the reagent is then added and the colour observed. When it is necessary to treat the test solution prior to the actual testing this treatment is carried out in a watch-glass, the solution being filtered if necessary. In the main the development of a colour on adding the reagent is sufficient to indicate whether an element is present. Some few of the reactions here described gave stains with more than one element, and it is necessary to treat the stain further to see whether either or both are present, or the original solution may be specially treated and re-tested.

It should be noted that when a test is being carried out on filter paper it is advisable to allow the two solutions to mix by spotting the second solution just beyond the edge of the first. By this means any change in colour in the reagent is more easily detected, as the original colour is always present as a comparison.

The apparatus required is of the simplest description. For holding the solution to be tested small test-tubes 3 inches by $\frac{1}{2}$ inch are most suitable. Small wooden stands for these should be provided or a small rack to hold six tubes. The reactions are carried out either on a spotting-plate provided with shallow cavities or on filter paper. The filter paper should be a good ashless paper and should not give any reaction with the reagents that are to be used on it. Where heat has to be employed small porcelain dishes are required. As it is difficult to obtain any of a reasonably small size the lid of a crucible from which the ring has been removed has proved very satisfactory. For carrying out precipitations prior to the actual testing watch-glasses are eminently suitable. A number of pipettes must be prepared by drawing out pieces of thin glass tubing to a fine point. As some of the reactions are best seen against a black background it is a good plan to cover the working part of the bench with a sheet of plate glass underneath which for one half of its area is a

piece of black paper and under the other half white paper. By this means the required background may be readily obtained. The reagents should be kept in tightly closed bottles. If the work is to be carried out in a permanent laboratory the most satisfactory is a one-ounce ether bottle having a cap ground on to the outside of the neck. Using such a bottle without an inside stopper a small pipette can be kept permanently in the bottle and any danger of contamination obviated.

It is frequently necessary to filter a small quantity of liquid and there are three methods whereby this can be achieved. In the first case a filtering tube is prepared by drawing out a piece of fine glass tubing so as to form a fine capillary tube about one inch long. This capillary is left attached to the long end of the original tube while at the other end it is cut off just where it widens out. By this means a tube is obtained consisting of three parts: (1) a wide part the diameter of the original tube, (2) a capillary part one inch long, having at its end (3) a slight expansion in diameter. A very small fragment of filter paper is rolled up and inserted in the widened part of the capillary. By placing this filter paper in the drop of liquid to be filtered and applying suction at the end of the wide tube, clear liquid may be drawn up into the capillary. The filter paper can then be removed and the clear liquid blown out either on to filter paper or a spotting-plate.

If the final reaction is to be carried out on a filter paper, a second method may be adopted. A pointed strip of filter paper is dipped into the liquid to be filtered, when the clear liquid will pass up on to the filter paper where it may be tested. Finally, the third method consists of taking the liquid and precipitate up in a small pipette and pressing the point of this pipette firmly on to a filter paper, when the liquid will pass on to the paper leaving the precipitate in the centre of the spot.

One or two special pieces of apparatus are required for certain tests, but these will be described in their appropriate place. A small percussion mortar and a small agate mortar are required in order to powder the material under test. In this connexion it should be remembered that the smallest sizes of these obtainable will be sufficient for any of this work.

Method of preparing the solution for testing.—When dealing with substances that are soluble in water or in *dilute* hydrochloric acid it is quite sufficient to prepare a weak solution in either of these

liquids. In no case is it necessary to have a solution stronger than 0.5 %. Strong hydrochloric acid may be employed if it gives a clear solution of the substance, but the excess of acid must be removed before the tests are applied, since in many cases a strong acid interferes with the reactions. Most minerals, however, will not give with either of these methods a solution that can be relied upon to contain all the elements originally present. The most satisfactory way to treat an unknown mineral is to fuse a small quantity of the finely powdered material with sodium carbonate in a loop of platinum wire. Complete decomposition is obtained by adding to the fused bead a small quantity of sodium peroxide. When metals which alloy with platinum are suspected the mineral powder should be mixed with the sodium carbonate before preparing the bead. The fused bead so obtained is treated with distilled water in a watch-glass and the liquid decanted or filtered from any insoluble material. The insoluble residue is then treated with strong hydrochloric acid. By this means a separation is obtained which greatly assists the ensuing testing. In the aqueous solution will be found all acidic elements which form soluble sodium salts; the remaining elements will be found in the hydrochloric solution, except the two which form insoluble chlorides and can easily be distinguished.

By the use of sodium peroxide the elements are obtained in their highest state of oxidation. Thus chromium will appear in the alkaline solution as sodium chromate. Although titanium forms a sodium titanate, it appears in the acid solution, since the sodium titanate formed is insoluble in water. The great advantage of the method is that it ensures that silica will not appear in the hydrochloric acid solution. This removes the uncertainty caused by the insolubility of silica if solution is attempted by the use of either hydrochloric acid or aqua regia. Again, baryte is broken up in this process; the sulphate radicle is removed as sodium sulphate in the aqueous solution and the barium appears as barium chloride from the action of hydrochloric acid on the barium carbonate.

By the treatment outlined here the aqueous alkaline solution may contain the major quantity of the following elements: Na, K, B, Al, Si, Sn, P, V, As, Sb, S, Cr, Mo, W, Cl, F; while the acid solution may contain similarly: Cu, Ag, Au, Mg, Ca, Ba, Sr, Cd, Hg, Ti, Pb, U, Mn, Fe, Co, Ni. Certain elements may appear in both solutions, among these are Sb, As, &c.

The complete reactions of all the elements so far examined will be

found in table I (plate IV). There are a number of omissions in this list. It is hoped later on to fill these gaps, but up to the present it has not been possible to obtain results which are comparable in reliability with those that are here given. The most notable omissions are lithium, beryllium, and platinum, all of which fail to show any really characteristic reactions. Quinalizarine is a reagent frequently advocated for beryllium, but so far it has not been found possible to determine the conditions which will render this a reliable test without considerable experience and probably special apparatus. It was therefore considered advisable to omit it from the present discussion. With regard to the rare-earths, cerium, thorium, lanthanum, &c., a considerable amount of work remains to be done before they can be fitted into the scheme.

The following descriptions of the reactions should be read in conjunction with table II (p. 27). They give the detailed information necessary to make the determination of the various elements as simple and conclusive as the method permits. The elements are arranged according to the periodic classification.

Sodium—Zinc uranyl acetate is the only satisfactory reagent for sodium. All interfering elements may be removed by precipitation with Am_2S and Am_2CO_3 and filtering. Owing to the prevalence of this element a positive reaction will be common.

Potassium.—Sodium cobaltinitrite in the presence of acetic acid gives a yellow precipitate. Similar precipitates are given by Pb, Ba, Zr, but these are all soluble on heating. Thallium gives a precipitate which is indistinguishable from potassium, and in presence of this the test is inconclusive. The test should be carried out in a watch-glass on a black background.

Copper.—The reaction with ammonium mercury thiocyanate and zinc sulphate in presence of ammonium phosphate in a faintly acid solution is specific and sensitive as the phosphate prevents any interference by iron.

Silver.—The well-known reaction with potassium chromate is specific in presence of acetic acid.

Gold.—Stannous chloride reduces solutions of gold giving a purple stain. Mercury and molybdenum give similar stains. In the case of molybdenum the stain will disappear on the addition of KCNS and subsequent boiling in water. The mercury stain does not yield to any treatment, so in presence of this metal the test for gold is indeterminate.

Magnesium.—Titan yellow in alkaline solution gives coloured lakes with a number of the elements, but these can all be removed by precipitation with ammonium sulphide. If zinc, cadmium, cobalt, nickel, or iron only be present, the addition of potassium cyanide will enable the reaction to be carried out without the necessity of filtering. Aluminium although it gives no reaction itself inhibits the reaction with magnesium and must therefore be removed.

Calcium is a difficult element to deal with and the best results are obtained with the sodium salt of dihydroxy tartaric osazone. Other reacting elements must be removed by precipitation with ammonium sulphide and subsequent filtration. After adding the reagent at least fifteen minutes must be allowed to elapse before concluding that calcium is absent. Magnesium except in very strong solutions gives no precipitate.

Strontium and Barium.—Both these are detected by sodium rhodizonate and both give brown stains. The only other reacting element is lead, and all three behave differently when their stain is treated with dilute hydrochloric acid. The strontium stain disappears at once. The lead stain turns purplish and fades slowly, while the barium is unaffected in colour and fades very slowly. Thus barium may be detected in presence of either of the other elements. To detect strontium, add a little potassium chromate to the solution, filter on to a filter paper by means of a pipette according to the third method described above, and test the edge of the drop with the reagent. Both barium and lead chromate are retained as precipitates. The reagent does not keep in solution and should be made up fresh as required.

Zinc.—The reaction described under copper is specific if copper sulphate be substituted for zinc sulphate and the same procedure adopted.

Cadmium.—Diphenyl carbazide and potassium thiocyanate give colour reactions with several elements, but the effect of ammonia on these enables cadmium to be detected in their presence. A blank test should be made for comparison as the reagent is decidedly coloured. Care should be taken that the dilution of both tests is the same. Cobalt reacts similarly to cadmium and if there is any quantity present the test is inconclusive. The reagent does not keep well in solution.

Mercury as well as silver, gold, and copper gives a violet coloration with dimethyl-amino-benzal rhodanine. By treating the solution with HCl and then sodium phosphate it is easy to eliminate silver

TABLE II. Method of applying tests.

Element.	Reagent.	Apparatus.	Method of applying test.	Colour.
Na	Zinc uranyl acetate	Watch-glass	1 drop solution, 1 drop Am ₂ S, 1 drop Am ₂ CO ₃ , filter, neutralize, 5-6 drops reagent, stir.	Yellow
K	Sodium cobaltinitrite	"	1 d. soln., 1 d. acetic acid, few grains solid reagent, warm.	Yellow ppt.
Cu	Am ₂ Hg(CNS) ₄ + ZnSO ₄	Porc. dish	1 d. soln., 1 d. Am ₂ HPO ₄ , acidify conc. H ₂ SO ₄ , 1 d. ZnSO ₄ , 1 d. reagent, warm.	Violet red
Ag	K ₂ CrO ₄	Spot plate	1 d. soln., 1 d. reagent, 1 d. acetic acid.	Red
Au	SnCl ₂ + HCl	F. paper	1 d. soln., 1 d. Am ₂ S, warm, filter, 1 d. KCN, boil in water.	Purple
Mg	Titan yellow	Spot plate	1 d. soln., 1 d. Am ₂ S, warm, filter, 1 d. reagent, 1 d. NaOH.	Pink
Ca	Dihydroxy tartaric osazone	Watch-glass	1 d. soln., 1 d. Am ₂ S, warm, filter, few grains reagent.	White ppt.
Sr	Sodium rhodizonate	F. paper	1 d. soln., 1 d. K ₂ CrO ₄ , 1 d. reagent on edge of spot.	Brown
Ba	"	"	1 d. soln., 1 d. reagent, 1 d. dil. HCl.	Brown
Zn	Am ₂ Hg(CNS) ₄ + CuSO ₄	Porc. dish	1 d. soln., 1 d. Am ₂ HPO ₄ , acidify H ₂ SO ₄ , 1 d. CuSO ₄ , 1 d. reagent, warm.	Violet
Cd	Diphenyl carbazide thiocyanate	Spot plate	1 d. reagent, 1 d. soln., 1 d. AmOH.	Violet
Hg	Dimethyl-amino-benzal rhodamine	F. paper	1 d. soln., 1 d. HCl, 5 d. Na ₂ HPO ₄ , filter on paper, 1 d. reagent on edge.	Pink
B	Turnuric	Porc. dish	1 d. reagent, 1 d. soln., 1 d. HCl, evapor. to dryness, 1 d. NaOH.	Green
Al	Alizarine S	Spot plate	1 d. soln., 1 d. NaOH, boil, filter, 1 d. reagent, 2 d. acetic acid.	Pink
Tl	Potassium iodide	"	1 d. soln., 1 d. reagent, 1 d. Na ₂ S ₂ O ₃ .	Yellow
Si	Am ₂ MoO ₄ + benzidine	Porc. dish	2 d. reagent, 1 d. soln., warm, 2 d. oxalic acid when cold, 1 d. benzidine, 2 d. Na acetate.	Blue
Zr	Hydrogen peroxide	Spot plate	1 d. soln., 1 d. H ₂ PO ₄ , 1 d. reagent.	Yellow
Sr	Phosphomolybdic acid	F. paper	1 d. soln., 1 d. HCl, 1 d. reagent.	Violet
Pb	Dithion	Spot plate	1 d. soln., 1 d. HCl, few grains Mg powder, transfer to filter paper, 1 d. reagent.	Blue
P	Am ₂ MoO ₄ + benzidine	Porc. dish	1 d. soln., 3 d. KCN, 1 d. AmCl, 1 d. reagent. (Run blank.)	Pink
V	Aniline	F. paper	2 d. reagent, 1 d. soln., 1 d. benzidine, 2 d. Na acetate.	Blue
As	Gutzzeit reaction	Sp. appar.	1 d. reagent, 1 d. soln. containing HNO ₃ .	Green
Sb	Phosphomolybdic acid	F. paper	1 d. reagent, 1 d. soln., warm.	Black
Bi	Thiourea	Spot plate	1 d. soln., 1 d. reagent, 1 d. HNO ₃ .	Blue
Cr	Diphenyl carbazide	"	1 d. soln., 1 d. H ₂ O ₂ , 1 d. AmOH, warm on watch-glass, acidify H ₂ SO ₄ , transfer, 1 d. reagent.	Yellow
Mo	KCNS + SnCl ₂	F. paper	1 d. conc. HCl, 1 d. soln. in centre, 1 d. reagent, 1 d. SnCl ₂ . (Colour on edge.)	Red
W	KCNS + SnCl ₂	"	" " " " " " (Colour in centre.)	Blue
SO ₄	K ₄ Fe(CN) ₆	"	1 d. soln. in watch-glass, 4 d. Na ₂ S ₂ O ₃ , transfer to filter paper, 1 d. reagent on edge.	Brown
Mn	Mercuric nitrate	Porc. dish	1 d. soln., 1 d. reagent, evapor. nearly to dryness, 2 d. water.	Yellow
F	Am ₂ S ₂ O ₃ + AgNO ₃ + H ₃ PO ₄	"	1 d. soln., 1 d. AgNO ₃ , 1 d. H ₃ PO ₄ , few grains solid Am ₂ S ₂ O ₃ , warm.	Purple
Cl	SiO ₂ + H ₂ SO ₄ &c.	Sp. appar.	" " " " " " " " " " " "	Blue
I	K ₂ Cr ₂ O ₇ + H ₂ SO ₄	"	" " " " " " " " " " " "	... Violet
Fe	Starch paste	Spot plate	1 d. soln., 1 d. reagent, 1 d. KNO ₂ .	Blue
Co	Potassium thiocyanate	"	1 d. soln., 1 d. reagent, 1 d. HCl.	Red
	β-nitroso-α-naphthol	"	1 d. soln., 1 d. AmCl, 2 d. AmOH, boil, 2 d. water, filter, 2 d. H ₃ PO ₄ , 1 d. KI, 2 d. Na ₂ S ₂ O ₃ , filter, 1 d. reagent.	Brown
Ni	Dimethylglyoxime	F. paper	1 d. soln., 1 d. H ₂ O ₂ , heat spot on paper, 1 d. reagent on edge.	Pink

and copper. Gold, however, is not affected by the treatment and renders the reaction inconclusive. It is advisable to run a blank test owing to the colour of the reagent.

Boron.—The well-known reaction with turmeric is specific.

Aluminium.—The best reagent is alizarine S. In acetic acid solution this gives a pink coloration. Many other elements give a similar coloration, but most of these are removed by boiling with caustic soda and filtering. A number which give soluble salts with NaOH, such as molybdenum, chromium, vanadium, may be eliminated by precipitating with barium chloride and boiling. The excess of barium is removed by precipitation with NaOH and filtering. It is advisable in this last precipitation to evaporate to dryness.

Thallium reacts with potassium iodide to give a yellow precipitate which being insoluble in sodium thiosulphate is readily distinguished from other coloured iodides.

Silicon and Phosphorus.—Soluble silicates and phosphates react with ammonium molybdate in nitric acid solution to form yellow complex molybdates. These complex molybdates bring about the oxidation of benzidine in alkaline solution with the formation of a blue quinoid compound and molybdenum blue. On this is based the method for detecting these two acids. Phosphates react with ammonium molybdate in the cold, while a gentle heat is necessary to bring about the combination with silicates. To detect silicates in presence of phosphates the reaction should be carried out in a porcelain dish and warmed. The liquid is removed from the precipitated phosphomolybdate and treated with two drops of oxalic acid when perfectly cold. To this is added a drop of benzidine and then several drops of sodium acetate. A blue colour shows the presence of a silicate as the oxalic acid prevents the reaction with phosphates. To detect phosphates in presence of silicates the original solution is evaporated to dryness twice with nitric acid whereby the silica is rendered insoluble. Water is added to the residue and the clear liquid tested as above when a blue coloration indicates the presence of a phosphate.

Titanium is detected by the yellow colour given to its solutions by hydrogen peroxide. Interference may be caused by the presence of iron, molybdenum, chromium, and vanadium when these occur in the acidic form. If the original solution be acidified with phosphoric acid, iron will cause no trouble. The three other elements may be removed by precipitation with barium chloride.

Zirconium gives a specific reaction with alizarine in presence of hydrochloric acid.

Tin and Antimony both react with phosphomolybdic acid to give a blue coloration. Both metals must be in the lower state of oxidation. This permits a distinction between the two, and if both are present they should be precipitated as sulphides by ammonium sulphide in presence of a very little hydrochloric acid. The precipitate is then boiled with concentrated hydrochloric acid, which gives the antimony as SbCl_3 and the tin as SnCl_4 . Under these conditions antimony reacts with phosphomolybdic acid, while tin does not. If another drop of the same solution be reduced by magnesium powder and tested on filter paper with ammonium molybdate solution a blue coloration will be obtained if tin be present. The antimony reaction with phosphomolybdic acid takes place rather slowly and the colour may take some time to develop.

Lead.—Dithizon (diphenyl thiocarbazon) gives colour reactions with a number of metals, but the addition of potassium cyanide and ammonium chloride will prevent any other element but lead from reacting. The reaction is best carried out on a spotting-plate and a blank should be run, since the potassium cyanide imparts a definite colour to the reagent. Dithizon does not keep well in solution and should not be used unless it is of a clear deep green colour. In the literature carbon disulphide is recommended as a solvent for dithizon, but carbon tetrachloride has been found to be in every way more suitable.

Vanadium in the presence of nitric acid gradually develops a deep green colour with a solution of aniline in hydrochloric acid. Chromates behave similarly, but by boiling with strong hydrochloric acid they are reduced to chromium chloride which shows no reaction.

Arsenic.—The most reliable and sensitive reaction for arsenic is that developed by Gutzeit, and consists in noting the effect of AsH_3 on mercuric chloride. The reaction is carried out in a small bottle provided with a rubber stopper through which passes a narrow glass tube, the bottom end of which is sealed and has a small hole blown in one side. On the top of this tube is placed a piece of filter paper impregnated with mercuric chloride solution, while a roll of paper impregnated with lead acetate is inserted inside the tube. The solution to be tested is poured into the bottle which contains zinc free from arsenic and pure dilute hydrochloric acid. A little stannous

chloride should be added to reduce the arsenic solution if necessary. By this means any arsenic is converted into AsH_3 , which passes through the side hole of the tube, is freed from any H_2S by the lead acetate paper, and then attacks the mercuric chloride paper giving a yellow to black stain, the depth of which is a measure of quantity of arsenic present. The reaction is specific.

Bismuth reacts with thiourea in presence of nitric acid to give a yellow coloration. Vanadium and chromium under similar conditions give bluish colorations, but these are not sufficiently strong to interfere with the bismuth reaction even when only small quantities of the latter are present.

Chromium.—The test for chromium depends on the oxidizing action of chromates on diphenyl carbazide in presence of sulphuric acid with the development of a violet coloration. The oxidation to chromate is best carried out by means of alkaline hydrogen peroxide, and should be continued until the addition of a little H_2SO_4 gives no blue colour. Mercury, molybdenum, and vanadium interfere with the test, but the mercury can be inhibited by HCl , and Mo and V by oxalic acid.

Molybdenum and Tungsten both react with potassium thiocyanate in presence of stannous chloride and hydrochloric acid. Molybdenum gives a red coloration which is soluble in hydrochloric acid to a red solution, while tungsten gives a blue insoluble colour. The coloration given on filter paper by the solution is treated with a drop of concentrated hydrochloric acid when a red ring developing on the periphery indicates the presence of molybdenum and a blue spot in the centre that of tungsten.

Uranium forms a brown precipitate with potassium ferrocyanide. Coloured precipitates are also formed with iron, copper, and titanium. These may be eliminated by sodium thiosulphate which reduces the iron and copper and precipitates the titanium as TiO_2 . Filtration is carried out with a pipette on filter paper according to the third method above, and the edge of the spot is tested with the reagent.

Sulphur, according to the method of obtaining a solution of the material described above, appears as sulphate, and may be tested for by means of mercuric nitrate, which, on heating to dryness and treating with water, forms a yellow basic mercuric sulphate. The same reaction is given with insoluble sulphates such as lead sulphate and barium sulphate, and thus forms a ready means of determining these in the natural state.

Manganese is unique in giving a highly coloured permanganate when treated with ammonium persulphate in presence of a trace of silver nitrate and concentrated phosphoric acid. The presence of hydrochloric acid is not detrimental if sufficient silver nitrate be added to precipitate all the chloride. Gentle heat is necessary to complete the reaction which is specific.

Fluorine is easily recognized by the reaction between fluorides, silica, and concentrated sulphuric acid when silicon fluoride is given off. The test is carried out in a small glass tube. The material to be tested is mixed with powdered silica and two drops of concentrated H_2SO_4 . On warming the gas is evolved. This is caught and decomposed in a drop of water on a glass rod held over the mouth of the tube. After one minute heating the liquid on the rod is tested for silica by means of Am_2MoO_4 and benzidine in the usual manner given under silicon. A blue coloration indicates the presence of fluorine. The test is specific.

Chlorine. The test for this element depends on the formation of chromyl chloride by the reaction of potassium bichromate and sulphuric acid on a chloride, and the subsequent conversion by the action of water of this chromyl chloride into chromic acid and its detection by means of diphenyl carbazide, with which it forms a violet colour. The solid substance to be tested is mixed with finely powdered potassium bichromate and a few grains of the mixture placed in a small ignition tube about $1\frac{1}{2}$ inches long, resting on the top of this tube is another slightly larger in diameter and having one end drawn out to a capillary. In this capillary is a drop of a solution of diphenyl carbazide, and this projects a very short way into the ignition tube. A drop of concentrated sulphuric acid is added to the mixture in the ignition tube and the capillary is placed in position. The ignition tube is warmed, and if chlorine be present in the substance tested, the reagent in the capillary will become violet. If bromine or iodine are suspected, a little phenol added to the mixture will prevent their interference.

Iodine.—The standard test with starch paste using potassium nitrite as a reducing agent is quite satisfactory.

Iron gives a red colour with potassium thiocyanate in presence of hydrochloric acid. It is discharged by stannous chloride, and may thus be distinguished from the colour given by molybdenum.

Cobalt.—The most sensitive reagent for this metal is β -nitroso- α -naphthol. Similar brown stains are given with other elements, but

these may all be removed by precipitation with ammonia in presence of ammonium chloride and the addition, after filtration, of potassium iodide and sodium thiosulphate to the filtrate. If there be no copper present the treatment with potassium iodide and sodium thiosulphate can be omitted. Nickel gives a similar colour to cobalt, but it is destroyed by dilute hydrochloric acid.

Nickel.—Dimethylglyoxime gives a pink coloration with nickel and coloured precipitates with iron, manganese, and cobalt. These last may be eliminated by oxidizing the solution with hydrogen peroxide in presence of ammonium carbonate and filtering on to filter paper by the pipette method. The edge of the spot should then be tested with the reagent.

In carrying out a qualitative analysis by the tests given above no special scheme is necessary. The time required for each test is so short that the whole range may be gone through in about half an hour, at the end of which all the constituents, as far as they are contained in the tables given here, will be known. Comparatively little experience is necessary, and that little will be gained by going through the tests on pure material as a preliminary. The technique is largely one of obtaining a reliable and complete solution of the mineral being examined and becoming accustomed to dealing with very small quantities. In this last lies the main advantage and main difficulty of the method. Any one who is accustomed to ordinary analytical methods will find some difficulty at first in accommodating his ideas to the apparently microscopic quantities employed. But once this new attitude has been acquired the procedure will be very simple.

Knowledge of mineralogy will of course indicate what tests may safely be omitted, but if that knowledge is not available, then all the elements should be tested for and table II gone through in its entirety, after which the composition of the mineral should not be in any doubt.

In conclusion I wish to record my thanks to the authorities of Edinburgh University for their courtesy and kindness in allowing me the facility for carrying out this work. Also to the staff of the Geological Department of that University for much helpful criticism.

Reagents required.

Alizarine: saturated solution in alcohol, add HCl till yellow, dilute with equal volume alcohol, and filter.

Alizarine S: 0.1 % solution in water.

Ammonium mercury thiocyanate: 9 gm. $(\text{NH}_4)\text{CNS}$, 8 gm. HgCl_2 . 100 c.c. water.

Ammonium molybdate: 5 gm. $(\text{NH}_4)_2\text{MoO}_4$, 100 c.c. water (dissolved cold), then add 35 c.c. HNO_3 (density 1.2).

Ammonium persulphate: solid.

Aniline: aniline hydrochloride dissolved in concentrated HCl.

Benidine: 0.05 gm. benidine dissolved in 10 c.c. glacial acetic acid, dilute to 100 c.c. with water.

Dihydroxy tartaric osazone: solid.

Dimethyl-amino-benzal rhodanine: 0.03 % solution in acetone.

Dimethylglyoxime: 1 % in alcohol.

*Diphenyl carbazide: 1 % in alcohol.

* do. do. thiocyanate: saturated solution in cold alcohol. Saturate with KCNS and add crystal of KI .

Diphenyl thiocarbazon (dithizon): 0.002 % in carbon tetrachloride.

Hydrogen peroxide: 20 vols.

Mercuric nitrate: 10 % $\text{Hg}(\text{NO}_3)_2$ in 1 % HNO_3 .

β -Nitroso- α -naphthol: 2 gm. dissolved in 100 c.c. glacial acetic acid and diluted with 100 c.c. water.

Potassium bichromate: solid.

do. chromate: 1 % in *N* acetic acid.

do. ferrocyanide: 2*N* solution.

do. iodide: *N* solution.

do. thiocyanate: 2*N* solution.

Phosphomolybdic acid: 5 % solution.

Sodium cobaltinitrite: solid.

* do. rhodizonate: 5 % solution.

Thiourea: 10 % solution.

Titan yellow: 0.1 % solution.

Turmeric: 20 gm. turmeric extracted with 50 c.c. alcohol, filtered, and diluted with 50 c.c. water.

Zinc uranyl acetate: 10 gm. uranium acetate dissolved in 6 c.c. of 30 % acetic acid by heating. Dilute to 50 c.c. with water. 30 gm. zinc acetate dissolved in 3 c.c. of 30 % acetic acid. Dilute to 50 c.c. Mix two solutions, add trace of NaCl , allow to stand 24 hours. Filter.

Acetic acid: 2*N*.

Hydrochloric acid: concentrated and *N*/10.

Nitric acid: *N*.

Phosphoric acid: concentrated.

Oxalic acid: *N*.

Sulphuric acid: concentrated.

Sodium hydroxide: 5*N* and *N*/10.

Ammonia solution: concentrated.

Ammonium carbonate: 5*N*.

do. chloride: saturated

do. phosphate: 5*N*.

Ammonium sulphide : concentrated.

Barium chloride : *N*.

Copper sulphate : *N*/100.

Mercuric chloride : saturated.

Potassium chromate : *N*.

do. cyanide : *5N*.

do. nitrite : *N*.

Sodium acetate : saturated.

do. carbonate : anhydrous.

do. peroxide : solid.

do. phosphate : *2N*.

do. thiosulphate : *N*.

Silver nitrate : *N*.

Stannous chloride : *N* in concentrated HCl.

Starch : solid.

Zinc granulated (free from arsenic) : solid.

Magnesium powder : solid.

Zinc sulphate : *N*.

N = Normal solution containing the molecular weight of the salt in 1000 c.c. of water.

* Solutions of these reagents do not keep well and should be made up as required.

All solutions are made in distilled water unless another solvent is indicated. Alcohol used is 90 % industrial spirit.

TABLE I. Reactions of the Elements.

Reagent	Na	K	Cu	Ag	Au	Mg	Ca	Sr	Ba	Zn	Cd	Hg	B	Al	Tl	Si	Ti	Zr	Sn	Pb	P	V	As	Sb	Bi	SO ₂	Cr	Mo	W	U	Mn	Fe	Co	Ni	
Zinc cyanide	Y	Y	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
Ammon. mercury thiocyanate + ZnSO ₄	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
Ammon. mercury thiocyanate + ZnSO ₄ + tartaric acid	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Stannous chloride	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
Titan yellow	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Dihydroxy tartaric osazone	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Sodium rhodanate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Diphenyl carbazide thiocyanate + AmOH	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Dimethyl amino-benzal thioamide	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Allanate S	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Potassium iodide + Na ₂ S ₂ O ₈	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Potassium persulfate + potassium thiocyanate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hydrogen peroxide	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Phosphomolybdate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Phosphomolybdate acid	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Dithion	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Carbonyl reaction	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Thiourea	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Thioacetamide	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Diphenyl carbazide	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
K ₂ S ₂ O ₈ + SnCl ₄	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
AmS ₂ O ₈ + H ₂ PO ₄ + Ag ₂ SO ₄	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
SO ₂ + H ₂ SO ₄ + Am ₂ SO ₄ + K ₂ O	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Starch + K ₂ Cr ₂ O ₇ + HCl	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Potassium thiocyanate + HCl	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Dimethylglyoxime	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Blk. = Black. Bl = br. Br = Brown. G = Green. Or = Orange. Pk = Pink. Pr = Purple. R = Red. V = Violet. W = White. Y = Yellow.

J. ADAM WATSON: MICRO-CHEMICAL COLOUR REACTIONS.