Special Applications of Chromographic Contact Printing

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The author describes the use of the method for minerals developed in the zone of oxidation and for certain non-opaque primary species

Synopsis

Chromographic contact printing techniques facilitate the examination of opaque minerals in polished sections during researches concerned with problems of ore-genesis and mineral beneficiation. As non-opaque species are often associated with the opaque it follows that if prints can also be taken from the former a great deal of additional valuable data might accrue.

This paper describes general methods of taking such prints and contains details for obtaining prints—generally by the Simple Contact Method—from many minerals developed in the zone of oxidation and from certain non-opaque primary species.

General

Williams and Nakhla (1950–51) [1] were largely responsible for introducing the English-speaking world to chromographic contact printing techniques. They demonstrated that as these enabled " maps " to be obtained showing the distribution of selected elements in certain minerals exposed at the polished surfaces of ore-specimens and briquetted mill-products, their employment often greatly facilitated the solution of problems relating to ore-genesis and mineral beneficiation.

These workers largely confined their attention to minerals with a metallic lustre, which are, for the most part, conducting and from which prints can be taken by the elegant " electrographic method " ; they and others in the field largely ignored the non-opaque species—particularly those developed in the zone of oxidation—which are non-conducting but from which prints can often be taken by the so-called " simple method." (As the usual methods of taking contact prints are now well known and details are readily available in the paper by Williams and Nakhla (op. cit.), they are not described here. However, annotated, self-explanatory diagrams of the apparatus are included (Figs. 1 and 2).)

The writer's reasons for investigating the taking of prints from non-opaque species—particularly from those developed in the zone of oxidation—are as follows :—

(1) As chromographic contact printing from the opaque ore-minerals has already proved to be of the utmost value to the economic geologist and mineral dresser in their researches, by extension the technique should also prove useful during the study of non-opaque species of economic importance, despite the fact that they can often be identified by skilled personnel employing optical methods. It should also be of value for determining the spatial relationships between certain opaque and non-opaque species occurring in samples of " ore-as-mined " and in mill products. Its application to the examination of primary non-opaque gangue minerals is limited by the fact that many of these are insoluble in those reagents which can be employed when this technique is used.

(2) Whenever chromographic contact printing is used it is important to know whether prints of a given cation will be simultaneously obtained from a given primary mineral and any associated oxidation products. Clearly, if both the primary and the related secondary minerals yield identical results, the print from a sample containing both of these could easily lead to erroneous conclusions. It must, however, be pointed out that when prints of a given cation are obtained from two or more species by precisely the same treatment the intensities of the prints often differ sufficiently for the distribution of each species to be determined with ease. This may be beautifully demonstrated by taking a copper print from a section containing native copper, malachite, and cuprite by attacking for 2 min. with 0·88 ammonia and developing with a 1·0% alcoholic solution of rubeanic acid. Under these conditions the distribution of native

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

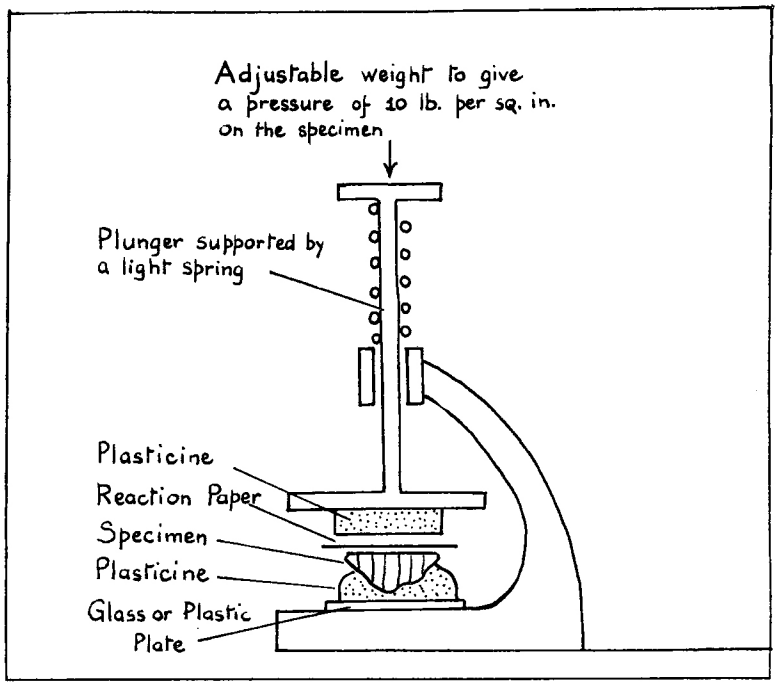

Fig. 1.—Apparatus for Taking Simple Contact Prints.
(*After Williams and Nakhla.*)

copper is indicated by the deepest green (almost black) areas of the print, the malachite by green areas of moderate intensity, and the cuprite by comparatively pale-green areas. It must also be noted that as the vast majority of secondary minerals are non-conducting, if the *rapid* electrographic method is employed to obtain prints of cations from a given primary mineral, no prints (or only very faint ones) are likely to develop from associated oxidation products unless the latter happen to be extremely soluble species such as goslarite, melanterite, or chalcanthite.

Difficulties Associated with the Development of Methods of Taking Prints from Non-opaque Minerals.

Undoubtedly the difficulties associated with the development of methods of taking prints from non-opaque minerals (and most of the minerals deposited in the zone of oxidation are in this category) are considerably greater than those encountered when dealing with the opaque minerals with metallic lustre. These difficulties are as follows :—

(*a*) Most—if not all—of the non-opaque minerals are non-conducting, so that the electrographic method (which produces the best prints) cannot be employed for their examination.

(*b*) The number of different anions and cations encountered in supergene minerals of economic importance is considerably greater than the number of different ions occurring in the economically important opaque hypogene minerals with metallic lustre.

(*c*) Some of the supergene minerals are much less readily attacked by cold dilute solutions of the common reagents than are the parent primary species.

(*d*) It is extremely difficult to obtain samples of many of the minerals developed in the zone of oxidation of sufficient size for satisfactory experimental work.

Methods of Printing Used

A summary of the methods used in the investigation and of the results achieved may be useful here. As most of the species in question are non-conducting, the "simple method"—already described—was used almost exclusively. However, in order to expedite the selection of the most suitable reagents, etc., for taking prints from a given species, attempts were first made to print from heavy streaks of the mineral made on pieces of unglazed porcelain tile. This preliminary work often yielded a great deal of useful information in a surprisingly short space of time, despite the fact that the streak of a given mineral is commonly more reactive than a polished section of it.

As certain minerals from the oxidized zone are only very slightly soluble at room temperature in reagents which can be conveniently used to take contact prints, the possibility of employing heat to facilitate the attack was investigated. Brammall (1920) had earlier employed such a method to take prints from iron oxides.

The method adopted by the present writer is as follows : A piece of cartridge paper—of the type normally used in engineering-drawing classes—is soaked in an appropriate attacking reagent, then lightly pressed between sheets of blotting paper in order to remove the excess reagent. A piece of asbestos paper is placed on a warm hot-plate and on this is placed, in turn, a square of platinum foil, a square of dry cartridge paper of slightly less area than that of the foil, and, finally, the reagent-impregnated paper. The flat surface of the specimen from which a print is to be taken is pressed on to the paper (Fig. 3) and after an appropriate interval—usually a minute—it is removed. The two layers of cartridge paper—which tend to adhere as a result of the above treatment—are then either placed in a suitable developing reagent, or development is carried out by applying a filter paper saturated with an appropriate reagent to the cartridge paper.

Fairly well-defined prints can be taken by this method, which need not be restricted to minerals which are not readily attacked by cold reagents. Indeed, on many occasions this method can be used to obtain information in a very short space of time concerning the spatial distribution of minerals from which prints can be made by utilizing cold reagents and with the added advantage that practically no special equipment is necessary.

The removal of unwanted reagents from the cartridge paper on which a print has been made is considerably more difficult than from gelatin-coated paper and when washed prints are allowed to dry in the air a certain amount of lateral diffusion may take place from the print which, by causing extraneous colour to develop, detracts from the appearance of the finished product.

Methods of taking prints from a considerable number of non-opaque species have been developed as a result of these investigations but there are several important "ore-minerals" for which no means of taking prints of either their anions or their cations have yet been discovered ; of these, one of the most notable is scheelite. Again, only some of the components of some species can be printed. It has not been found possible, for example, to take sodium and calcium prints from supergene minerals, whilst sulphate prints can only be taken from some sulphates. However, if one component of a given species can be printed, that is often sufficient to enable the spatial distribution of the species in the polished section to be determined. Furthermore, if one component of a supergene mineral is established by contact printing, this fact, taken in conjunction with some of the more obvious physical characteristics of the species and of others associated with it, often enable the identity of the mineral in question to be established.

Sometimes it is possible to identify a species largely by the manner in which a print can be taken from it. Thus, chalcanthite is the

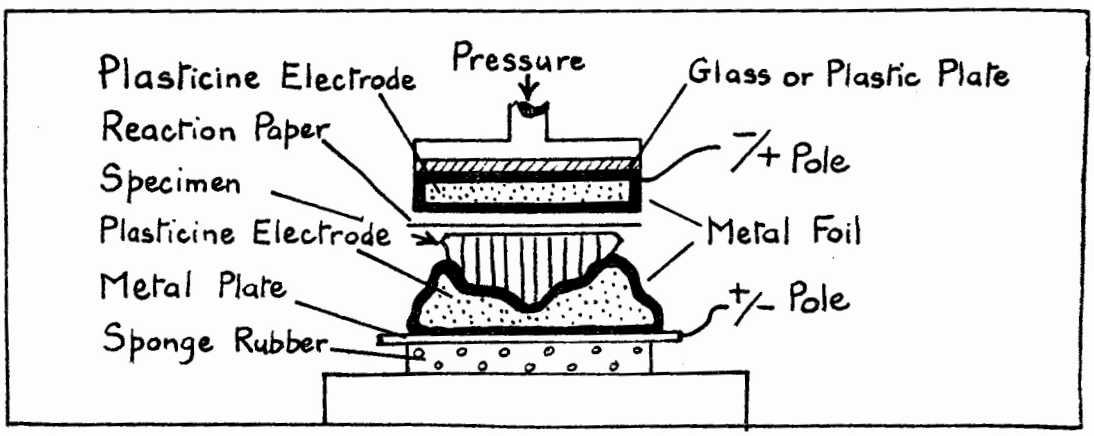

Fig. 2.—Apparatus for Taking Electrographic Contact Prints.

(After Williams and Nakhla.)

only common secondary copper investigated by the writer from which a *strong* copper print can be obtained by employing water as the attacking reagent and a 1% alcoholic solution of rubeanic acid as the developer.

It must, however, be stressed that even if all the components of a given supergene mineral are established by printing and the nature of these is considered in conjunction with physical characteristics of diagnostic value which may be obtained simply by examining a section of the species under the microscope, complete identification may be impossible. Nevertheless, an incomplete identification is often a valuable aid, both to the solution of mineral-dressing problems and to the complete identification of the species in question by extended optical or X-ray methods.

Practical Details of Methods

Prints from Minerals Developed in the Zone of Oxidation and from Certain Non-opaque Primary Species.—Unless stated otherwise, the prints described in this sub-section are simple contact prints taken on gelatin-coated paper by the employment of cold reagents.

Antimony

Minerals Tested.—Cervantite, $Sb_2O_3.Sb_2O_5$ (?) ; valentinite, 4[Sb_2O_3].

Attacking Reagent.—A solution composed of 4 volumes of 20% potassium iodide and 1 volume of 5N.HCl, the duration of attack being 3 min.

Developing Reagent.—Starch solution.

Results.—Both of the species named yield brownish prints which become deep blue on immersion in starch solution. After a short time the prints revert to the brownish colour but the blue is restored on retreatment with starch solution.

Other Notes.

(i) The printing method used is based on the fact that hydriodic acid, which is formed by reaction between potassium iodide and HCl, is oxidized by certain higher metallic oxides—(such as, manganese dioxide, lead dioxide, and antimony pentoxide)—to iodine. The reaction involving antimony pentoxide may be expressed by the following equation :—

$$Sb_2O_5 + 4HI = Sb_2O_3 + 2H_2O + I_2.$$

(ii) Doubtless the reason why a print can be taken from valentinite by this method is because the antimonious ions of the reactive polished surface, together with any which may be liberated as a result of the presence of hydrochloride acid, are rapidly oxidized to the pentavalent state.

(iii) The reaction is based on a test for antimony pentoxide described by Feigl (1947, p. 207).

Further Methods of Printing from Valentinite.—The attacking reagent used in each case consists of a saturated solution of tartaric acid in 6 : 1 HCl, the duration of attack being 3 min.

Developing the Print.

Method (i).—Immerse the paper in a 0·01% solution of Rhodamine B, when a strong purple print is obtained.

(i) Although Rhodamine B reacts only with Sb (V) ions it is a suitable developing reagent in this case because the Sb (III) ions derived from the valentinite oxidize rapidly in the gelatin-layer.

(ii) Mercury, gold, bismuth and tungstates in acid solutions also form purple compounds with Rhodamine B.

(iii) The originator of the test for antimony upon which the above printing method is based is Eegriwe, E. (1927, p. 400).

Method (ii).—First immerse the paper in a 5% solution of phosphomolybdic acid and then hold it in steam, when a blue print develops.

(i) This method is based on a test for *trivalent* antimony ions, which is specific in the absence of stannous ions and which was developed by Feigl and Neuber (1923, p. 382).

Arsenic

(1) *Mineral Tested.*—Arsenolite, 16 [As_2O_3].

Attacking Reagent.—A solution composed of 9 volumes of 5N. NaOH and 1 volume of hydrogen peroxide (20 vols.), the duration of attack being 3 min.

Acidify the paper by immersing it in 5N. acetic acid and then transfer it to a 1% solution of silver nitrate, when a pale-brown print is obtained.

(2) *Minerals Tested.*—Orpiment, 4 [As_2S_3] ; realgar, 16 [AsS].

Reagent for Obtaining a Direct Print.—A solution composed of equal volumes of 5N. NaOH and 1% sodium nitroprusside (see Feigl, F., 1947, p. 298) is used, the printing time being 2 min. A purple print is obtained from orpiment, but not from realgar.

Other Notes.—On warming, sulphides of antimony, tin, tungsten, and molybdenum react with the above reagent forming a purple product, but they will not interfere when orpiment is printed by the above method.

Arsenates and Phosphates

As arsenate-phosphate isomorphous series are of common occurrence, methods of taking arsenate and phosphate prints are conveniently dealt with in the same sub-section.

(1) *Arsenates Tested.*—Bayldonite (Pb, Cu), clinoclasite (Cu), erythrite (Co), mimetite (Pb), olivenite (Cu), pharmacolite (Ca), pharmacosiderite (Fe), tyrolite (Cu, Ca).

Attacking Reagent.—1 : 1 HNO_3, the duration of attack being 3 min.

Developing the Prints.—Neutralize the excess nitric acid in the paper by holding it in ammonia fumes, then immerse it for a minute in 5N. acetic acid. Finally transfer the paper to a 1% solution of silver nitrate.

With the exception of pharmacosiderite, all the species named yield a brown print consisting of silver arsenate when thus treated. The pharmacosiderite print becomes brown during the treatment with ammonia fumes and no further colour change is apparent as the result of the subsequent silver nitrate treatment.

Other Notes.

(i) Pharmacolite yields the strongest print of all the arsenates tested and a good arsenate print may be taken from it simply by subjecting it to a 3-min. attack with 5N. acetic acid followed by development in 1% silver nitrate.

(ii) If the arsenate prints are to be preserved they must be first washed well in water in order to remove the excess silver nitrate.

(iii) It is probable that the method described will enable useful prints to be taken from most, if not all, arsenates which do not contain appreciable amounts of iron.

(iv) An arsenate print may be taken from pharmacosiderite as follows: Print the mineral on cartridge paper impregnated with 1 : 1 nitric acid. After an attack lasting for 3 min. immerse the paper in a solution prepared by dissolving 10 g. of ammonium molybdate in 100 ml. of water and pouring it into 35 ml. of concentrated nitric acid. Finally, remove the paper and hold it over heated wire gauze until steam rises freely from it. A yellow " arsenate print " will appear slowly. If the method is applied to a mineral which is essentially a phosphate a yellow print appears either in the cold or after very slight warming.

(2) *Phosphates Tested.*—Apatite (Ca), autunite (Ca, UO_2), hopeite (Zn), pseudomalachite (Cu), parahopeite (Zn), pyromorphite (Pb), rashleighite (Cu, Al, Fe), tarbuttite (Zn), turquoise (Cu, Al), vivianite (Fe), wavellite (Al).

Attacking Reagent.—1 : 1 HNO_3, the duration of attack being 3 min. and the developing reagent ammonium molybdate solution. For preparation see the note concerning the taking of a phosphate print from pharmacosiderite. With one exception the print obtained by this method is yellow but the intensity varies with the species under test. Vivianite is exceptional in that it gives a blue print.

Other Notes.

(i) To develop the print successfully the paper must remain undisturbed in the molybdate for several minutes; finally it must be lightly washed with water to remove any superficial ammonium phospho-molybdate precipitate.

(ii) The intensity of the print may be increased by gently warming the paper—immediately after bathing it in the molybdate solution—over a hot wire gauze. If the warming is not gentle the test loses its specificity as yellow ammonium arseno-molybdate can then develop rapidly.

(iii) If a piece of filter paper stained with ammonium phospho-molybdate is treated with a solution of benzidine in acetic acid and then subjected to ammonia fumes an intensely blue compound is formed (Feigl, F., 1947, pp. 250–1). It was thought, therefore, that such treatment might improve the phosphomolybdate prints, but trials proved it to be quite unsatisfactory as the whole surface of the gelatin-coated paper became blue.

Taking Anion Prints from Phosphates and Arsenates.—Although the prints taken by the methods described are not always as clearly defined and as intense as might be desired, a considerable amount of useful information can usually be obtained from them.

Barium and Strontium

Minerals Tested.—Witherite, 4[$BaCO_3$]; strontianite, 4[$SrCO_3$].

Attacking Reagent.—N. HCl, the duration of attack being 3 min.

Developing the Prints.—Neutralize the free acid in the paper by holding it in ammonia fumes, then immerse it in a freshly-prepared 0·2% aqueous solution of sodium rhodizonate. (This treatment causes the prints taken from both witherite and strontianite to become reddish-brown.) Bathe the print in 1 : 20 HCl. As a result of this treatment the witherite print becomes red, whilst the strontianite print vanishes.

Other Notes.

(i) Although several other divalent elements react with sodium rhodizonate in neutral or

slightly acid solutions to form coloured rhodizonates, only lead is likely to cause confusion during the application of the above method. Lead ions, just like barium ions, react in acid solution with sodium rhodizonate forming a red salt.

(ii) Barium prints cannot be taken from barite, $4(BaSO_4)$, by the above method, or by any other known to the writer, on account of the insolubility of the mineral.

(iii) In slightly acid solution, lead sulphate—unlike barium sulphate—will react with sodium rhodizonate forming a red compound and this fact may be used to determine, in case of doubt, whether a red print obtained by the above method is due to barium or lead. All that it is necessary to do is to prepare a new print and immerse it in a normal solution of sulphuric acid to precipitate the cations in the gelatin film as sulphates. Then neutralize in ammonia fumes and develop with sodium rhodizonate and 1 : 20 HCl. If a red print develops lead is present.

Bismuth

Minerals Tested.—Bismite, $4[Bi_2O_3]$; bismuth ochre (oxides and carbonates of bismuth); bismutite, $2[(BiO)_2\,CO_3]$.

Attacking Reagent.—1 : 1 HNO_3, the duration of attack being 3 min.

Developing the Prints.—Neutralize the free acid in the paper by holding it in ammonia fumes. Then place the paper in cinchonine-potassium iodide reagent and do not disturb for a few minutes. Finally remove the print and wash it in water. By this method orange-red prints are obtained from all the species named.

Reagent.—Cinchonine-potassium iodide solution. One gram of cinchonine is dissolved by warming it in 100 ml. of water containing a little nitric acid. After cooling, 2 g. of potassium iodide are added.

Other Notes.

(i) Copper and lead interfere because if the former is present iodine is liberated and if the latter is present yellow lead iodide is precipitated.

(ii) The chemical test upon which the method is based was developed by Léger (1889, p. 374).

Chlorine (as Chloride)

Minerals Tested.—Atacamite, $4[Cu_2\,Cl(OH)_3]$; mimetite, $2[Pb_5(AsO_4)_3Cl]$; pyromorphite, $2[Pb_5(PO_4)_2Cl]$; vanadinite, $2[Pb_5(VO_4)_3Cl]$.

Attacking Reagent.—1 : 1 HNO_3, the duration of attack being 3 min.

Developing Reagent.—1% silver nitrate solution. By utilizing this method a white print is obtained from atacamite. This is sufficiently dense to be seen but on exposure to sunlight it becomes purple. The other species listed above, although soluble in 1 : 1 nitric acid, do not yield a chloride print by this method.

Other Notes.

(i) It is probable that the other numerous but rare copper chlorides (see Hey, M. H., 1950, p. 57) would react similarly to atacamite to the above method.

(ii) A method of taking prints from the silver halides is described in the " Silver " sub-section.

Chromium (as Chromate)

Mineral Tested.—Crocoite, $4[PbCrO_4]$.

Reagent.—A mixture composed of equal volumes of 5N. H_2SO_4 and a 1% alcoholic solution of diphenylcarbazide, the printing time being 3 min. The print of the anion so obtained is red to purple and intense.

Other Notes.

(i) The method is based on a test for the chromate ion in lead chromate which was described by Feigl (1947, p. 305).

(ii) A characteristic orange print is obtained directly from crocoite by subjecting it to an attack by 5N. HCl for 3 min.

Cobalt

Minerals Tested.—Bieberite, $8[CoSO_4.7H_2O]$; erythrite, $2[Co_3(AsO_4)_2.8H_2O]$.

Attacking Reagent.—0·880 ammonia, the duration of attack being 3 min.

Developing Reagent.—A 0·1% alcoholic solution of rubeanic acid. Both minerals yield rust-brown prints but that taken from bieberite is the more intense.

Other Notes.

(i) Bieberite yields a good print if water is substituted for ammonia as the attacking reagent but in this case a little ammonia should be added to the rubeanic acid in order to effect the production of a good print. It is also probable that cobalt prints could be taken by this method from the rare species cobalt-chalcanthite, $2[CoSO_4.5H_2O]$; and cobalt-epsomite, $4[(Mg,Co)SO_4.7H_2O]$.

(ii) In ammoniacal solution, copper and nickel ions react with rubeanic acid forming, respectively, olive-green and pale blue salts.

(iii) The method described above of taking prints from the two cobalt minerals is based on a test evolved by Pr. Rây and R. M. Rây (1926, p. 118).

Table 1

Minerals.	*Attacking Reagents.*	*Minutes.*	*Developing Reagents.*	*Colour of the Prints.*
Atacamite, $4[Cu_2Cl(OH)_3]$	0·880 Ammonia	3	Rubeanic acid	Olive-green
Azurite, $2[Cu_3(CO_3)_2(OH)_2]$	0·880 Ammonia	3	Rubeanic acid alpha-Benzoin Oxime	Olive-green Grass-green
Bayldonite, $(Pb, Cu)_7 (AsO_4) (OH)_2.H_2O$	1 : 1 HNO_3	3	Rubeanic acid. (After neutralizing over ammonia.)	Olive-green
Calciovolborthite, $Cu\ Ca\ VO_4OH$	1 : 1 HNO_3	3	Do.	Olive-green
Chalcanthite, $2[CuSO_4.5H_2O]$	Water	3	Rubeanic acid and ammonia	Olive-green
Chrysocolla, Near $CuSiO_3.2H_2O$	1 : 1 HNO_3	3	Ferrocyanide	Brown
Clinoclasite, $4[Cu_3\ AsO_4\ (OH)_3]$	0·880 Ammonia	3	Rubeanic acid	Olive-green
Copper (native), $4[Cu]$	0·880 Ammonia	3	Rubeanic acid	Deep olive-green to black
Cuprite, $2[Cu_2O]$	0·880 Ammonia	3	Rubeanic acid	Olive-green
Cuprodescloizite, $4[Pb\ (Cu, Zn)\ VO_4\ OH]$	HCl (1 : 5) and Rubeanic acid (1% alcoholic solution)	3	Neutralize over ammonia, then immerse in acetic acid	Olive-green
Herrengrundite, $Ca\ Cu_4\ (SO_4)_2\ (OH)_2.3H_2O$	0·880 Ammonia	3	Rubeanic acid	Olive-green
Linarite, $(Pb, Cu)_2\ SO_4\ (OH)_2$	1 : 1 HNO_3	3	Rubeanic acid. (After neutralizing over ammonia.)	Olive-green
Liroconite,	0·880 Ammonia	3	Rubeanic acid	Olive-green
Malachite, $4[Cu_2\ CO_3\ (OH)_2]$	0·880 Ammonia	3	Rubeanic acid alpha-Benzoin Oxime	Olive-green Grass-green
Olivenite, $4[Cu_2\ AsO_4\ OH]$	1 : 1 HNO_3	3	Ferrocyanide	Brown
Pseudomalachite, $Cu_3\ PO_4\ (OH)_3$	1 : 1 HNO_3	3	Rubeanic acid. (After neutralizing over ammonia.)	Olive-green
Turquoise, $Cu\ Al_6(PO_4)_4\ (OH)_8.5H_2O$	1 : 1 HNO_3	3	Do.	Pale olive-green
Turanite, $Cu_5\ (VO_4)_2\ (OH)_4$	1 : 1 HNO_3	3	Do.	Olive-green
Tyrolite, $(Cu, Ca)_5\ (AsO_4)_2\ (OH)_4.7(?)H_2O$	1 : 1 HNO_3	3	Do.	Olive-green

Copper

Little difficulty is experienced in obtaining copper prints from minerals developed in the zone of oxidation provided they contain the element in question in appreciable amounts. For the purpose under discussion 0·880 ammonia usually proves to be the most suitable attacking reagent but sometimes it is necessary to use 1 : 1 nitric acid instead. Numerous reagents are known which are suitable for developing copper prints but the writer usually employs either 1·0% potassium ferrocyanide or a 0·5% alcoholic solution of rubeanic acid. Ferrocyanide causes a brown print to develop but it also forms brown compounds with uranyl and molybdenum ions; further, the reagent reacts with ferric ions forming an intensely blue compound. As stated earlier, rubeanic acid may be used to develop nickel and cobalt prints as well as copper prints. The choice of developing reagent depends, therefore, on the nature of the sample from which the print is to be taken.

Table 1 contains methods of printing copper from specific minerals which have been established—with three exceptions—by the writer. The methods of taking copper prints from native copper and cuprite have been previously described by Gutzeit (1942, p. 439) and from cupro-descloizite by Williams and Nakhla (1950–51, p. 279).

Other Notes.

(i) Whenever ammonia is successfully employed to attack a copper mineral an impermanent, direct blue print is obtained.

(ii) *Alpha-Benzoinoxime.*—A 1% to 5% alcoholic solution of this reagent yields a grass-green insoluble precipitate with copper in ammoniacal solution. Large quantities of other ions which are precipitated by ammonia may

interfere by masking the colour of the copper salt of benzoinoxime (Feigl, F., 1923, p. 2032).

(iii) *Calciovolborthite.*—When a copper print is taken from this mineral by the method noted above and during the neutralization of the excess acid by ammonia, a blue copper print develops which rapidly changes to fox-brown and then darkens. These changes are of considerable diagnostic value as they have not been observed when taking prints from any other mineral by the same process.

(iv) *Chrysocolla.*—A print from a specimen characterized by bands of various shades of pale blue faithfully reproduced the pattern displayed by the sample: The strongest blue bands gave the strongest coloured areas of the print. This suggested that the specimen was, in fact, of a composite nature and was composed of areas of " pure " chrysocolla separated by others composed of intermingled chrysocolla and chalcedony.

Fluorine (as Fluoride)

Minerals Tested.—Cryolite, $2[Na_3Al\,F_6]$; fluorite, $4[CaF_2]$.

Reagent.—Zirconium-alizarin solution and the printing time, 3 min. Both cryolite and fluorite yield pale yellow to white prints on the pink, reagent-stained paper.

Preparation of Reagent.—Dissolve 0·05 g. of zirconium nitrate in a mixture of 50 ml. of water and 10 ml. of concentrated HCl. Mix this with a solution prepared by dissolving 0·05 g. of sodium alizarin sulphonate in 50 ml. of water.

Other Notes.

(i) The fluoride test upon which this method is based was developed by de Boer (1924, p. 404).

(ii) Large amounts of sulphates, thiosulphates, phosphates, arsenates, and oxalates also make the reagent turn yellow (see Feigl, F., 1947, p. 202). However, only readily-soluble sulphate minerals are likely to yield prints by the above method which might be confused with those due to cryolite and fluorite.

Iron

Minerals from which an Iron Print can be taken by Employing Cold 1 : 1 HNO_3 as the Attacking Reagent.

In order to obtain a strong iron print from any of the following minerals an attack lasting for 3 min. is adequate and a 1% to 5% solution of potassium ferrocyanide is an excellent developing reagent; it results in the production of a blue print from pharmacolite $[Fe_5(AsO_4)_3\,(OH)_6.6H_2O]$; pitticite (arsenate and sulphate of iron); scorodite, $8[FeAsO_4.2H_2O]$; or vivianite, $2[Fe_3(PO_4)_2.8H_2O]$.

Other Notes.

It is probable that iron prints could be taken from most of the rarer iron-containing phosphates and arsenates which do not contain other ions capable of forming coloured insoluble ferrocyanides (*e.g.*, symplesite, clinoscorodite, liskeardite, ludlamite, carminite, etc.) by means of the above method.

Method of Taking a Direct Iron Print from Melanterite, $8[FeSO_4.7H_2O]$.

Print for 3 min. on gelatin-coated paper impregnated with a 1% solution of potassium ferrocyanide. A pale blue iron print is obtained which becomes dark blue when the paper is immersed in " 20 volumes " hydrogen peroxide.

Method of Taking Iron Prints from Siderite, $2[FeCO_3)$, and Ankerite $[Ca(Mg, Fe)(CO_3)_2]$.

Attacking Reagent.—1 : 2 HCl, the duration of attack being 3 min.

Developing Reagents.—(*a*) A 1% to 5% potassium ferrocyanide (this gives a blue print) or (*b*) a 5% aqueous solution of the sodium salt of chromotropic acid (this results in a green print, which athough not due to the formation of an insoluble substance is, nevertheless, not removed by prolonged washing in water, nor does it diffuse.

Other Notes.

It is advisable to develop iron prints that are taken from species containing both iron and copper with chromotropic acid as the reagent—unlike potassium ferrocyanide—does not react with the latter element. However, under certain circumstances uranium, silver, mercury, and titanium form coloured compounds with the reagent (Feigl, F., 1947, p. 152).

Method of Taking Iron Prints from Hematite, $2(Fe_2O_3)$, and Limonite.

Iron prints may be taken from both these substances by employing the hot-plate method described earlier. The cartridge paper upon which the print is to be taken is impregnated with concentrated HCl. The attack is continued for 30 sec. to 1 min. and the print is developed with ferrocyanide solution.

(To be concluded.)

Special Applications of Chromographic Contact Printing

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The author describes the use of the method for minerals developed in the zone of oxidation and for certain non-opaque primary species

(*Concluded from the July issue, p. 29*)

Lead

Lead prints may be taken from all the species listed below by employing 1 : 1 HNO_3 as the attacking reagent. Having completed the attack—which should be of 3 min. duration—the excess acid in the paper is neutralized with gaseous ammonia. The print is developed by immersing it in a 0·2% solution of sodium rhodizonate and then either in 1 : 20 HCl or in a buffer solution prepared by dissolving 1·9 g. of sodium bitartrate and 1·5 g. of tartaric acid in 100 ml. of water. The lead print is red or reddish-purple. Barium interferes by forming a similarly coloured rhodizonate.

The method is based on a test for lead which was devised by Feigl and Suter (1942, p. 840).

Minerals Tested.—Anglesite, 4[$PbSO_4$]; bayldonite, $(Pb,Cu)_7(AsO_4)_4(OH)_2.H_2O$; cerussite, 4[$PbCO_3$]; crocoite, 4[$PbCrO_4$]; hydrocerussite, $Pb_3(CO_3)_2(OH)_2$; lead (native), 4[Pb]; leadhillite, $Pb_4SO_4(CO_3)_2(OH)_2$ (?); linarite, $(Pb,Cu)_2SO_4(OH)_2$; mendipite, 4[$Pb_3Cl_2O_2$]; pyromorphite-mimetite, 2[$Pb_5(PO_4)_3Cl$]—2[$Pb_5(AsO_4)_2Cl$].

Other Notes.

Wulfenite.—When wulfenite, 8[$PbMoO_4$], is subjected to the above method of taking prints, anomalous results are obtained. On neutralizing in ammonia fumes a blue print appears. When the neutralized paper is immersed in sodium rhodizonate and then in 1 : 20 HCl a transient pink print develops, but this is quickly replaced by a yellowish-green print when the paper is removed from the acid. Within an hour this print changes through various shades of green to blue. These colour changes are of considerable diagnostic value.

Williams and Nakhla's Methods of Taking Lead Prints from Cerussite and Cuprodescloizite, 4[Pb(Cu, Zn)VO_4.OH]. (See Williams and Nakhla, 1950–51, p. 279.)

The methods employed by Williams and Nakhla for taking lead prints from cerussite and cuprodescloizite—which have been repeated by the writer and found completely satisfactory—are summarized in Table 2.

Table 2

Mineral.		*Attacking Reagents.*	*Duration of Attack (sec.).*	*Developing Reagents.*	*Colour of the Prints.*
Cerussite	(*a*)	$NH_4.CH_3COO$ (40%) + $CH_3.COOH$ (glacial)	45–60	KI + $SnCl_2$ (applied by filter paper)	Yellow
	(*b*)	,,	60	Sodium rhodizonate (applied by filter paper)	Violet
	(*c*)	,,	120	10% Na_2S (applied by filter paper)	Brown
Cuprodescloizite		,,	120	KI + $SnCl_2$	Yellow

Other Notes.

(i) The preparation of the potassium iodide/stannous chloride reagent is as follows: "Stannous chloride solution, prepared from pure tin and concentrated hydrochloric acid, is treated with saturated potassium iodide solution until upon shaking the mixture is converted into a pale-yellow mass. A saturated solution of cadmium nitrate is then added dropwise until the pale-yellow mass dissolves. The reagent is stable in the presence of water" (Vogel, A. L., 1947, pp. 141–2).

(ii) In order to make the KI/$SnCl_2$ reaction specific for lead during the development of contact prints the paper should be held in gaseous ammonia after the attack in order to neutralize any free acid in it. It should then be immersed in dilute sulphuric acid (to convert the lead to the sulphate), thoroughly washed in water, neutralized, and developed in the reagent under discussion which should be freshly prepared.

Hot-plate Method of Taking Lead Prints from Anglesite, Cotunnite, 4($PbCl_2$), and Mendipite.

As anglesite, cotunnite, and mendipite are soluble in hot water, prints can be taken from them by the Hot-plate Method (described earlier), using water as the attacking reagent. The attack should last from 30 sec. to 1 min.

The print, which is developed by bathing the paper first in sodium rhodizonate solution and then in 1 : 20 HCl, is red.

Other Notes.

Although none of the following rare species have been available for this particular aspect of the investigation, it is probable that most, if not all, would yield lead prints if the above method were employed: Daviesite (oxychloride of lead); fiedlerite (chloride or oxychloride of lead); laurionite, 4[PbClOH]; lorettoite, $Pb_7Cl_2O_6$; matlockite, 2[PbFCl]; paralaurionite, Pb Cl OH; penfieldite, Pb_2Cl_3OH.

Magnesium

Minerals Tested.—Brucite, $[Mg(OH)_2]$; dolomite, $[CaMg(CO_3)_2]$; magnesite, $2[MgCO_3]$; periclase, 4[MgO].

Taking Magnesium Prints.—Soak gelatin-coated paper in a 0·1% aqueous solution of Titan Yellow for 3 or 4 min. and then transfer it to 5N. HCl. After about 3 min. lift out the paper, remove the excess reagent from it and take a print in the normal manner. Allow the attack to proceed for 3 min. then develop the print by immersing the paper in 5N. sodium hydroxide. The resultant print—which is vermilion—fades badly in a few hours but may be restored by immersing it in 5N. sodium, hydroxide.

Magnesium prints can be taken from all the species noted by this method.

Other Notes.

(i) The presence of calcium and barium intensifies the reaction but tin, arsenic, bismuth, manganese, and aluminium interfere.

(ii) The Titan Yellow test for magnesium, upon which the method is based, was developed by Kolthoff (1927, p. 254).

Manganese

Gutzeit's Method of Taking Manganese Prints from the Higher Oxides of Manganese. (See Gutzeit, G., 1942, p. 441.)

Attacking Reagent.—Sulphurous acid, the duration of attack being 3 to 5 min.

" The best way to obtain a definite print is to develop the paper in ammonia gas and allow it to oxidize in the air for 5 min.; then treat it with an acetic benzidine solution, which will give a dark blue print."

Developing Reagent.—Dissolve 0·05 g. of benzidine in 10 ml. of concentrated acetic acid and dilute with water to 100 ml.

Williams and Nakhla's Electrographic Method: for psilomelane, $2[(Ba, Mn^{\cdot\cdot}) Mn^{iv}_4 O_8 (OH)_2]$, and pyrolusite, $2[MnO_2]$. (See Williams, D., and Nakhla, F. M., 1951, p. 276 and p. 288.)

The attacking reagent is 1 : 5HCl + H_3PO_4 at 5 V and the duration of attack 20 sec.

Developing the Print.—Expose the paper to ammonia fumes in order to neutralize the acid present and then place it in acetic benzidine solution. This results in the development of a blue print.

Other Notes.

(i) The blue print obtained by either of the above methods rapidly becomes brown.

(ii) The acetic benzidine test is sensitive but not specific, since oxidizing agents and elements which yield auto-oxidizable compounds also give blue compounds when subjected to it.

A Method for Rhodochrosite, $2[MnCO_3]$.

Attacking Reagent.—5N HCl, the duration of attack being 3 min.

Develop exactly as detailed in Gutzeit's method. The resulting print is blue.

Molybdenum and Molybdates

Minerals Tested.—Molybdic ochre (hydrated iron molybdate); wulfenite, $8[Pb Mo O_4]$.

Attacking Reagent.—1 : 1 HNO_3, the duration of attack being 3 min.

Developing the Prints.—Neutralize the excess acid by exposing the paper to ammonia fumes then immerse it in a strong aqueous solution of potassium ethyl xanthate acidified with acetic acid.

Both the species named yield rose to magenta prints by this method.

Other Notes.

(i) The method suffers from the disadvantage that diffusion takes place soon after the print has been developed.

(ii) As stated earlier, the wulfenite print becomes blue when subjected to the ammonia fumes.

(iii) The method is based on a test for the molybdate ion which was developed by Mallowan (1914, p. 73).

Nickel

Minerals Tested.—Annabergite, $2[Ni_3(AsO_4)_2 \cdot 8H_2O]$; morenosite, $4[NiSO_4 \cdot 7H_2O]$.

Attacking Reagent.—0·880 ammonia and duration of attack, 3 min.

Developing Reagent.—A 1·0% alcoholic solution of dimethyglyoxime.

Morenosite gives a strong rose-red nickel

print but the print obtained from annabergite is only pale pink.

Other Notes.

A much more satisfactory nickel print may be taken from annabergite by employing 1 : 1 HNO_3 as the attacking reagent. After an attack lasting for 3 min. either immerse the paper in a 1 : 1 mixture of 0·880 ammonia and 1·0% dimethylglyoxime solution (when a rose-red print appears) or subject it to ammonia fumes in order to neutralize the excess acid and place it in a 1·0% alcoholic solution of rubeanic acid (when a pale blue print develops). As stated earlier, both copper and cobalt also form coloured rubeanates.

Mineral Tested.—Garnierite, $(Ni, Mg)_3 Si_2 O_5 (OH)_4$.

Attacking Reagent.—1 : 1 HCl, the duration of attack being 3 min.

Developing Reagent.—1 : 1 ammonia/dimethylglyoxime (as used in the previous method).

The nickel print obtained by this method is pink.

Other Notes.

It is probable that nickel prints could be taken by this method from other similar nickel-containing silicates such as genthite, alipite, chocolite, etc., and also from bunsenite, 4(NiO); hydroniccite (hydrated oxide of nickel); and nicomelane (a higher oxide of nickel).

Silver

Minerals Tested.—Bromargyrite, 4[AgBr]; chlorargyrite, 4[AgCl]; embolite, 4[Ag(Cl, Br)]; iodargyrite, 2[AgI].

Reagent.—$K_2Ni(CN)_4$/ammonia/dimethylglyoxime. (For the preparation of this reagent and a discussion of the chemistry of the reaction between it and silver halides, see Feigl, F., 1947, pp. 302–303.) Printing time, 3 min.

Rose-red prints are obtained from all the silver species named.

Other Notes.

Doubtless prints of iodembolite, 4[Ag (Cl, Br, I)]; huantajayite, (Na, Ag) Cl; and miersite, 4[(Ag, Cu)I], could also be taken by the method described.

Electrographic Methods. (See Williams, D., and Nakhla, F. M., 1950–51, p. 277.)

(*a*) *Reagent.*—0·880 ammonia, the printing time being 35 sec. at 8 V.

A gray to black print is obtained from native silver.

(*b*) *Attacking Reagent.*—A 2·0% solution of potassium cyanide to which has been added a small quantity of a saturated solution of para-dimethylaminobenzylidene rhodanine. The duration of attack is 30 sec. at 12 V. and the developing reagent 1 : 15 HNO_3. Native silver yields a reddish-violet print.

Other Notes.

The reaction upon which the above method is based was developed by Feigl (1928, p. 38[illegible]. It is not specific for silver as cuprous, gold, mercury, platinum and palladium ions interfere.

Sulphur (as Sulphate)

Minerals Tested.—Anglesite, 4[$PbSO_4$]; anhydrite, 4[$CaSO_4$]; bieberite, 8[$CoSO_4 \cdot 7H_2O$]; chalcanthite, 2[$CuSO_4 \cdot 5H_2O$]; celestite, 4[$SrSO_4$]; goslarite, 4[$ZnSO_4 \cdot 7H_2O$]; gypsum, 8[$CaSO_4 \cdot 2H_2O$]; herrengrundite, $CaCu_4(SO_4)_2(OH)_6 \cdot 3H_2O$; melanterite, 8[$FeSO_4 \cdot 7H_2O$]; morenosite, 4[$NiSO_4 \cdot 7N_2O$]; zippeite, $(UO_2)_2SO_4(OH)_2 \cdot nH_2O$.

Taking Sulphate Prints.—Soak the gelatin-coated paper for a few minutes in a 10% solution of barium chloride and then for a minute in a cold saturated solution of potassium permanganate. Print in the normal manner, allowing the mineral to be attacked for 3 min. Develop the paper by bathing it in tepid N oxalic acid.

A pale-pink print is obtained from all the above minerals except anglesite, celestite, herrengrundite, and zippeite.

Prints from Herrengrundite and Zippeite.

Attacking Reagent.—1 : 1 HCl, the duration of attack being 3 min.

Developing the Prints.—Neutralize the acid in the paper by holding the latter in ammonia gas. Then immerse the paper in a 2 : 1 mixture of barium chloride and potassium permanganate of strengths noted in the method above. Finally, gently agitate the paper in tepid oxalic acid.

Both the species named yield pale-pink sulphate prints.

Other Notes.

(i) By employing the first method sulphate prints can be taken from the more-soluble species.

(ii) The second method, employing an initial acid attack—not necessarily HCl—is likely to be suitable for taking sulphate prints from many of the less-soluble species. However, even this method has not enabled sulphate prints to be taken from anglesite, celestite, and of course barite.

Tungsten and Tungstates

Mineral Tested.—Yttrotungstite from Malaya (tungsten/rare earth oxide ?).

Attacking Reagent.—0·880 ammonia, the duration of attack being 3 min.

Developing the Print.—Immerse for a minute in 5N. HCl and then in a 0·01% aqueous solution of Rhodamine B.

A violet-blue tungsten print develops.

Other Notes.

The test upon which the method is based is by no means specific for tungstates. Mercury, gold and thallium chlorides, basic bismuth chloride, molybdates, and pentavalent antimony ions give colour reactions with Rhodamine B similar to those given by tungstates (Feigl, F., 1947, p. 86).

Tungstate Prints from Scheelite, 8[$CaWO_4$], and Raspite, $PbWO_4$.

All attempts to take tungstate prints from scheelite and raspite have been unsuccessful. Both these minerals have been subjected to attacks of varying duration by HCl and HNO_3 of various concentrations and by mixtures of these acids. Sodium hydroxide and ammonium hydroxide have also been tried. Both the normal and hot-plate methods have been employed and Rhodamine B and stannous chloride have been utilized as potential developing reagents.

Uranium

Minerals Tested.—Autunite, $Ca(UO_2)_2(PO_4)_2.8H_2O$; carnotite, KUO_2VO_4; rutherfordine, $UO_2.CO_3$; zippeite, $(UO_2)_2SO_4(OH)_2.nH_2O$.

Attacking Reagent.—1 : 1 HNO_3 and duration of attack, 3 min.

Developing Reagent.—A 1·0% solution of potassium ferrocyanide.

All the minerals named yield brown prints.

Other Notes.

(i) Under the conditions described many copper minerals yield brown prints which are identical with uranium prints. Therefore, before assuming that a brown print, which has been obtained by the above method, is due to uranium it is wise to compare it with a second print developed with rubeanic acid (as indicated in the Copper sub-section). This procedure will indicate whether or not copper is present and in the presence of copper it will indicate the distribution of both copper minerals and non-copper-bearing uranium minerals.

(ii) A brown print can be taken from torbernite, $Cu(UO_2)_2(PO_4)_2.8H_2O$, by the above method. This brown print is, of course, due to the copper and to the uranyl ions present. However, in the absence of other copper species this method of printing torbernite may be useful for obtaining a record of its distribution in a given sample.

(iii) Iron in a secondary uranium mineral (as in bassetite, $Fe(UO_2)_2(PO_4)_2.8H_2O$), may, by forming blue ferric ferrocyanide, obscure the brown uranium print when the above method is employed.

(iv) According to Tananaeff and Pantschenko (1926, p. 164) interference due to the presence of iron and copper may be overcome when conducting the ferrocyanide test for uranium by the application of potassium iodide and sodium thiosulphate. Attempts to overcome the interference due to copper and iron by applying these chemicals during the production of uranium prints have not been very successful.

(v) The above printing method is an excellent means of determining the distribution of carnotite in samples of yellow sandstone from the Colorado–Utah uranium/vanadium fields.

Vanadium

Minerals Tested.—Descloizite, 4[PbZn VO_4 OH]; vanadinite, 2[$Pb_5(VO_4)_3$ Cl].

Attacking Reagent.—N. H_2SO_4, the duration of attack being 3 min.

Developing Reagent.—A 1·0% solution of 3 : 3′-dimethylnaphthidine in glacial acetic acid.

Both the species named yield reddish-violet prints which disappear after about 24 hours.

Other Notes.

(i) $Cr_2O_7^{--}$ and MnO_4^- ions interfere by forming reddish-violet complexes. However, the colours due to these ions disappear within about 30 min.

(ii) The test for vanadates upon which the above printing method is based was developed by Belcher, Nutten, and Stephen (1951, pp. 430–31).

Minerals Tested.—Calciovolborthite, Cu Ca VO_4.OH; turanite, $Cb_5(VO_4)_2(OH)_4$.

Attacking Reagent.—Tannin/HCl. (Soak the gelatin-coated paper in a 10% aqueous solution of tannin and then in 1 : 5 HCl. Duration of attack, 3 min.

Developing Agent.—Ammonia fumes.

Both minerals yield a gray to black vanadate print. Sometimes the prints lack intensity but this may be corrected by immersing them in the attacking reagents for a few minutes and then subjecting them once more to ammonia fumes.

Other Notes.

(i) Iron interferes by forming a similarly coloured tannin complex but this snag can be overcome by employing phosphoric acid to complex this element.

(ii) This method of printing from vanadates depends on a test devised by Matignon (1904, p. 82).

Williams and Nakhla's Methods. (See Williams, D., and Nakhla, F. M., 1950–51, pp. 279–280.)

Cuprodescloizite.

(*a*) *Reagents for Obtaining a Direct Print.*—1 : 5 HCl or 1 : 5 HNO_3, plus a 1% solution of diphenylamine in acetic acid, the printing time being 90 sec.

Cuprodescloizite yields a green print.

(*b*) *Attacking Reagent.*—1 : 5 HCl *plus* a 10% aqueous solution of tannin, the duration of attack being 1 min.

Developing Agent.—Ammonia fumes.

A black print is obtained.

Vanadinite.

(*a*) *Reagent for Obtaining a Direct Print.*—1 : 5 HNO_3 *plus* a 1% solution of diphenylamine in acetic acid, the printing time being 90 sec.

Vanadinite yields a green print.

(*b*) *Attacking Reagent.*—A mixture composed of 1 : 5 HCl, acetic acid, and a 10% aqueous solution of tannin, the duration of attack being 1 min.

Developing Agent.—Ammonia fumes.

A gray to black vanadium print develops.

Other Notes.

The diphenylamine test is not specific for vanadates: manganese, zinc, and oxidizing agents interfere.

Zinc

Minerals Tested.—Goslarite, $4[ZnSO_4.7H_2O]$; hemimorphite, $2[Zn_4\ Si_2\ O_7(OH)_2.H_2O]$; hopeite, $4[Zn_3\ (PO_4)_2.4H_2O]$; hydrozincite, $2[Zn_5\ (CO_3)_2\ (OH)_6]$; parahopeite, $[Zn_3\ (PO_4)_2.4H_2O]$; smithsonite, $2[Zn\ CO_3]$; tarbuttite, $8[Zn_2\ PO_4\ OH]$; willemite, $6[Zn_2\ SiO_4]$.

Reagent.—A 0·5% solution of diethylaniline which is prepared by dissolving an appropriate quantity of the reagent in a mixture composed of equal volumes of 3% potassium ferricyanide and 3% oxalic acid. The printing time is 3 min.

All the species named yield an orange or brownish-red zinc print.

Other Notes.

(i) It is probable that zinc prints could be taken from most, if not all, secondary zinc minerals by this method. However, the test is not specific for zinc as ions which form coloured precipitates with potassium ferricyanide interfere.

(ii) The reagent should be prepared immediately before taking prints.

(iii) During the taking of prints from secondary zinc minerals the latter become stained with the orange or brownish-red product of the reaction which must be removed by regrinding before further prints are taken. However, the fact that secondary zinc minerals in thin and polished sections can be stained by this reagent may be used as a further rapid aid to their identification.

Minerals Tested.—Aurichalcite, (Zn, Cu $(CO_3)_2\ (OH)_6$ (?); hemimorphite, hydrozincite, smithsonite, tarbuttite.

Chemistry of the Method.—The following method of taking zinc prints from the above species depends on the fact that whilst ammonium (or potassium) mercuric thiocyanate reacts with cupric ions forming a green precipitate and with zinc ions forming a white precipitate, when both cupric and zinc ions are present a purple precipitate is deposited, together with a green or white one, depending on which element is in excess. (See Short, M. N., 1940, pp. 188–91).

Attacking Reagents.—5N. HCl for all the named species excepting tarbuttite, for which 1 : 1 HNO_3 is employed. The duration of attack is 3 min.

Developing the Prints.—The aurichalcite print is developed by bathing it in ammonium mercuric thiocyanate solution. As this species contains both zinc and copper ions a purple print develops at once. This fact serves to differentiate between aurichalcite and the other species noted above.

Zinc prints taken from the other minerals are developed by immersing them in a minimum of very dilute copper sulphate solution (which in a test-tube is aquamarine in colour) and after about 15 sec. adding a considerable excess of ammonium mercuric thiocyanate solution. Prints from all the species under discussion become purple by this treatment.

Reagent. Ammonium mercuric thiocyanate solution.—Dissolve 9 g. of ammonium thiocyanate and 8 g. of mercuric chloride in 100 ml. of water.

Other Notes.

(i) During the development of the prints a certain amount of the green copper compound

is usually deposited on the print, but this is easily removed by washing.

(ii) Under the above conditions cobalt forms a blue precipitate and ferric iron a soluble red compound. Interference due to the latter may be overcome by rinsing the developed print in a solution of ammonium fluoride.

(iii) A very dilute solution of cobalt sulphate (about 0·02%) may be employed instead of copper sulphate in the above method, when the distribution of zinc is indicated by the development of blue prints.

The test depends on the fact that whilst blue cobalt mercuric thiocyanate is precipitated very slowly when ammonium mercuric thiocyanate is added to a very dilute cobalt solution, if zinc ions are also present a blue precipitate is formed immediately (Krumholz, P., and Sanchez, J. V., 1934, p. 114).

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Mineral Processing in Review—II

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A short survey of proceedings at the recent International Congress in Cannes.

(*Continued from the July issue, p. 19*)

Session E : **Gravity Concentration**

This session included six papers, their subjects including pneumatic and hydraulic concentrating machines, jigging, dense media separation, and a mixed gravity-flotation method.

E.18. *A New Apparatus for Pneumatic Separation.* In French, by M. CARTA, C. DEL FA, and G-F FERRARA.

An extension of the French "Lavodune" method, using water as the transporting agent, to the separation of dry sands in an air stream. The apparatus consists of an externally rectangular duct, the inner horizontal walls of which are so formed as to be semi-cylindrical. They thus form eight chambers set axially across the flowline. The upper half can be moved upstream so as to create a labyrinthine structure. Sands in