

409. *The Analysis of Inorganic Compounds by Paper Chromatography. Part IV.* An Extended Scheme for the Qualitative Analysis of an Unknown Mixture of Cations.*

By F. H. POLLARD, J. F. W. McOMIE, and H. M. STEVENS.

The scheme of analysis described in Part III of this series is extended to include Ce, Li, Mo, Tl, Ti, U, V, and W.

SINCE it is sometimes desirable to analyse for other metals besides the 24 normally included in schemes for qualitative analysis, the procedure described in Part III of this series * has been extended to include Ce, Li, Mo, Tl, Ti, U, V, and W. The chromatograms are prepared with the butanol-benzoylacetone solvent mixture as the mobile phase. If the metals are only present in traces in the original mixture, then it will be necessary to employ some form of concentration technique, *e.g.*, on an ion-exchange column, the important point being that the amount of any particular metal present on the chromatogram must be such that it lies within the sensitivity of the characterising test.

The identification is carried out on individual chromatograms according to the following groups :

- Group A. (i) Ag, Pb, Hg, Tl; (ii) As, Sb.
- Group B. (i) Cr, Ce, Mn, Co, Cu, Ni; (ii) Bi, Fe, (Co), Ti, U, (V).
- Group C. (i) Sn, Sr, Ba; (ii) Cd, Zn, Al, Mg, Ca.
- Group D. Li, Na, K.
- Group E. Mo, W, V.

The R_F values for the additional metals with the butanol-benzoylacetone mobile phase are Ce, 0.01; Li, 0.15; Mo, 0.25; Tl, 0.08; Ti, 0.06; U, 0.25 and 0.94; V, 0.18; W, 0.00, when these elements are run singly, but if they are present in a mixture of cations, the R_F values may be modified by interference.

EXPERIMENTAL.

Dissolution of the Powder.—Three solutions are prepared by boiling portions with (a) 2 ml. of 2N-nitric acid, (b) 2 ml. of 2N-hydrochloric acid, and (c) a small excess of approximately 10% sodium hydroxide solution. Solution (a) is used for Group A, (b) for Groups B, C, and D, and (c) for Group E.

* Part III, *J.*, 1951, 771.

Preparation of the Chromatograms.—Two copies of Sheet I and one copy of II are prepared as described in Part III. Sheet III is prepared with about 8 spots from solution (c). Half of the spots are treated with sulphur dioxide from a siphon, lightly sprayed with 2*N*-hydrochloric acid, and dried. This treatment ensures that excess of alkali is neutralised and cations such as arsenic, antimony, aluminium, zinc, and vanadium will separate on the chromatogram from tungsten, which will remain on the starting line. The other half of the spots provide suitable chromatograms for the application of the test for molybdenum. The colours of spots after the chromatogram has been run and dried often indicate the cations present in the original powder; thus, reddish-brown, iron and/or titanium; yellowish brown, uranium or vanadium; blue, tungsten; green, molybdenum. After spraying the chromatogram with hydrochloric acid and warming: yellow, copper; bright blue, cobalt.

Analytical Reagents.—In addition to those described in Part III, the following are required. Ammoniacal hydrogen peroxide: equal vols. of 20-vol. hydrogen peroxide and ammonia (*d* 0.880); freshly prepared. Potassium ferrocyanide: 5% aqueous solution. Sodium phosphate: equal vols. of 2*N*-disodium hydrogen phosphate solution and concentrated nitric acid. Stannous chloride: 1 g. dissolved in 5 c.c. of warm concentrated hydrochloric acid, to give a clear solution, diluted to 30 c.c. with distilled water; freshly prepared. Tannic acid: 0.5 g. of tannic acid and 1 g. of sodium acetate dissolved in 10 c.c. of warm 60% industrial methylated spirit; freshly prepared.

Analysis of the Chromatograms.—Each strip of chromatogram is analysed separately by a series of consecutive sprayings or treatments as detailed below, and with the precautions given in Part III.

Group A, Ag, Pb, Hg, Tl.—(1) A chromatogram from solution (a), sheet I, is sprayed with potassium chromate, and then held over aqueous ammonia (*d* 0.880). Silver, lead, and mercury are identified as described in Part III, and an orange spot, almost coincident with lead and, like lead, not fading on treatment with sulphur dioxide, suggests thallium Tl. (Bismuth or cerium will sometimes give a yellow spot on the starting line, but this is confirmed in Group B.)

To identify thallium, a second strip from solution (a), sheet I, is sprayed with alkaline hydrogen peroxide and gently warmed. An orange spot (probably Pb_3O_2) suggests lead; black spot (metallic silver), silver; dark brown spot, hydrated peroxide of thallium. The last two can be distinguished from one another by treatment with sulphur dioxide, silver being unaffected while thallium becomes colourless presumably owing to formation of Tl_2SO_4 . (*Note*: Manganese, cobalt, and nickel behave like thallium with respect to alkaline hydrogen peroxide, but these give no distinctive colours with potassium chromate, and brown spots when exposed to ammonia. They are identified in Group B.)

A further confirmation of thallium is obtained by spraying another chromatogram from solution (a), sheet I, with rhodizonic acid and then 2*N*-hydrochloric acid. A purple spot which disappears with hydrochloric acid indicates thallium, while a bright violet spot which persists after the test shows lead.

Occasionally, it has been found that thallium and mercury move together on the chromatogram to an R_F 0.4. This would probably be suspected from the tests with potassium chromate, but to confirm it the following procedure is recommended. The fading of the brown thallium spot with sulphur dioxide on the alkaline hydrogen peroxide-sprayed chromatogram is followed by lightly spraying with ammonium sulphide, and then ammoniacal hydrogen peroxide. The paper is warmed and sulphur dioxide is directed on to the area concerned. Mercury is left as a dark stain, HgS (or HgS and Hg).

Group B.—Sub-group, Cr, Ce, Mn, Co, Cu, Ni. A chromatogram from solution (b), sheet I, is sprayed with sodium hypobromite and warmed. Dark brown spots suggest manganese, cobalt, or nickel, which can be identified as described in Part III, and thallium, already identified if present. A reddish-brown spot suggests iron or titanium, and a blue one copper; these are confirmed at a later stage, as in Part III. Yellow spots at R_F 0.05 indicate chromium, while those of R_F 0 or 0.1 suggest cerium or bismuth. On being sprayed with acidic hydrogen peroxide the chromium spot will turn blue, while those for cerium or bismuth remain unaltered.

To detect cerium, another chromatogram from solution (b) sheet I is sprayed with ammoniacal hydrogen peroxide and warmed. Yellow-orange colours are given by Ce, Bi, Ti, U, Pb, Fe, Co, and Cu. It is possible to distinguish cerium from the others by the facts that its spot does not disappear at 70° while the others do, and it is not discoloured by ammonium sulphide, while the others are darkened.

Sub-group, Bi, Fe, Co, Ti, U, (V). Another chromatogram from solution (b), sheet I, is sprayed with potassium thiocyanate-acetone solution and warmed. A bright yellow spot indicates bismuth (cf. previous observations) or uranium; red, iron or titanium; bright blue, cobalt. The subsequent additional tests for nickel, etc., are performed as in Part III.

A new chromatogram from solution (b) is sprayed lightly with 2*N*-hydrochloric acid, dried, and then sprayed with potassium ferrocyanide. The yellow spot due to uranium on the previous strip will turn dark-brown, while that due to bismuth is unaffected. A brown spot occurring at about R_F 0.25 also indicates uranium. (*Note*: The presence of copper, which gives a red-brown spot at this stage, will have already been established by the rubeanic acid test. Copper gives a black spot with potassium thiocyanate-acetone reagent, presumably owing to the formation of cupric thiocyanate.) Vanadium will form a yellow spot with potassium ferrocyanide, but is confirmed in Group E.

The red spots due to iron and titanium will both form bright greenish-blue complexes after the potassium ferrocyanide treatment. These can be distinguished by spraying a fresh, untreated, chromatogram with the tannic acid reagent, and gently warming. A reddish-purple coloration indicates iron, and a bright orange, titanium. The appearance of a dark blue spot at R_F 0.2 indicates vanadium, but this may be masked by other metals, and confirmation of this is therefore carried out later in Group E. (*Note*: The tannic acid test will not work satisfactorily if the paper is too acid, and this is the reason for the addition of sodium acetate; see above.)

Group C.—The tests described in Part III are carried out. A purple spot may arise with the rhodizonic acid reagent, due to thallium. This fades when treated with the mixed hydrochloric-acetic

acid spray, and can be distinguished from strontium by the previous observations in Group A. Uranium and cerium also give red colours, and may be confused with strontium, except that the uranium spot fades without acid treatment, and the cerium, which behaves very similarly to strontium, has been previously identified. If the concentration of strontium is comparatively low, there may be some difficulty in establishing its presence.

Group D.—Since lithium will give a similar fluorescence to that of strontium, barium, and magnesium in the tests for Group C, it is often advisable to carry out the Group D tests before those of Group C. These tests are performed as in Part III. Lithium gives a fluorescent spot similar to that of sodium with the zinc uranyl acetate reagent, but the R_F values are different, lithium appearing at R_F 0.15, whereas sodium appears at approximately 0.05. Interference by other cations may occasionally upset the R_F values, and so a flame test would probably afford useful additional evidence as to the presence or absence of sodium and lithium.

Group E, Mo, W, V.—Molybdenum. A chromatogram from the solution (*c*), on the portion of sheet III which was not subjected to the sulphur dioxide treatment, is sprayed with the sodium phosphate reagent. On warming to about 40–50° a yellow spot on or near the starting line indicates molybdenum. This is then sprayed with stannous chloride, whereupon the conversion of the spot into a bright blue confirms the presence of molybdenum. (*Note:* Sometimes tungsten spots appear light blue before this test is applied, but the production of the molybdenum-blue is very characteristic.)

Tungsten and vanadium. A chromatogram from one of the solution (*c*) spots, sheet III, which received the preliminary sulphur dioxide treatment, is first sprayed with 2*N*-hydrochloric acid and then dried. It is then sprayed with the kojic acid-oxine reagent and examined over ammonia under the ultra-violet lamp. A very deep yellow fluorescence at about R_F 0.0 or 0.01 indicates tungsten; zinc and aluminium can be identified here, if necessary, by their characteristic fluorescences.

A similar chromatogram, after the 2*N*-hydrochloric acid treatment as described above, is sprayed with the tannic acid reagent. A bright navy-blue spot, usually appearing on warming, at R_F 0.2 confirms the presence of vanadium.

THE UNIVERSITY, BRISTOL.

[Received, March 14th, 1951.]