167. *The Analysis of Inorganic Compounds by Paper Chromatography. Part III. A Scheme for the Qualitative Analysis of an Unknown Mixture of Cations.*

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A procedure is described for the qualitative analysis of unknown mixtures of the following cations, on a series of paper chromatograms prepared with butanol–benzoylacetone as the mobile phase: Pb, Ag, Hg, As, Sb, Cr, Mn, Cu, Co, Ni, Bi, Fe, Sn, Sr, Ba, Cd, Zn, Al, Mg, Ca, Na, K.

Some aspects of the analysis of mixtures of cations by paper chromatography, without any previous chemical separation, have already been discussed (Pollard *et al.*, *J.*, 1951, 470). It was indicated that it was not always possible, and often not necessary, to rely entirely on R_F values for the identification of cations. In this paper we describe a scheme for the use of characteristic reactions, which can be applied even to the identification of cations with similar R_F values and is of general application to any mixture of those cations mentioned below. In some mixtures certain cations may be displaced from their normal positions on the chromatogram, and this effect then assists the analysis.

Briefly, the procedure involves the preparation of a number of similar chromatograms of the mixture to be analysed, using butanol–benzoylacetone (Pollard *et al.*, *loc. cit.*) as the mobile phase for the chromatographic separation. The identification is then carried out on individual chromatograms according to the following groups:

Group A. Pb, Ag, Hg, As, Sb.
Group B. Cr, Mn, Cu, Co, Ni, Bi, Fe.
Group C. Sn, Sr, Ba, Cd, Zn, Al, Mg, Ca.
Group D. Na, K.

It is probable that the same scheme can be used for chromatograms prepared with other solvent mixtures.

EXPERIMENTAL.

Dissolution of the Powder.—Two solutions are prepared by boiling about 0·1-g. portions with (*a*) 2 ml. of 2N-nitric acid, and (*b*) 2 ml. of 2N-hydrochloric acid, respectively. Any dichromate or permanganate anions are converted into cations by adding a few drops of hydrogen peroxide. Each solution, after thorough cooling, is centrifuged to remove any precipitate, and the clear supernatant solutions are used for the analysis. Solution (*b*) will not contain Ag, Pb, Hg^+ cations since these are removed as insoluble chlorides. Any other insoluble salts produced, *e.g.* $BaSO_4$, are brought into solution by a suitable method depending on the substance, and analysed separately.

Preparation of the Chromatograms.—Across a sheet (I) of Whatman No. 1 paper, 40 cm. long and 25 cm. wide, is drawn a line, 8 cm. from one end. At distances about 2 cm. apart, spots of the prepared solutions are placed on the line; the first two from solution (*a*) and the rest from solution (*b*).

Another sheet (II) is prepared in the same way with spots from solution (*b*) only. This sheet is then treated so as to precipitate most of the Mn, Co, and Ni ions present, so that these cations will not move on the chromatogram to any great extent and thus tend to mask the fluorescence of the Zn, Al, Cd, Mg, Ca, Sr, and Ba with the kojic acid–oxine (8-hydroxyquinoline) spray (see later). The treatment consists of two sprayings with sodium hypobromite solution, followed by spraying with 2N-acetic acid. The paper is dried over an electric fire between each spraying.

The two sheets, I and II, after drying, are set up in the same tank for chromatgraphy, and run with butanol–benzoylacetone as the mobile phase until the solvent front is about 5 cm. from the end of the paper. (Details of the arrangement of the tank and the composition of the solvent mixture are given in the previous paper; Pollard *et al.*, *loc. cit.*) The sheets are removed from the tank and dried in a current of warm air. Several chromatograms are thus prepared so that some tests, if necessary, can be done in duplicate.

The two chromatograms corresponding to the spots of solution (*a*) on sheet (I) are cut off. The remainder of the chromatograms are sprayed with 2N-hydrochloric acid to " dampness," and dried at 50—60°. This treatment breaks down any non-ionic complexes present. The sheets I and II are cut into strips containing the individual chromatograms, and each strip is suitably labelled.

Analytical Reagents.—Acidic hydrogen peroxide : equal vols. of 2N-sulphuric acid and 20-vol. hydrogen peroxide.

Alkaline hydrogen peroxide : equal vols. of 2N-sodium hydroxide and 20-vol. hydrogen peroxide.
Ammonium mercuric thiocyanate : 2·7 g. of mercuric chloride and 3 g. of ammonium thiocyanate in 100 ml. of distilled water.
Ammonium sulphide : equal vols. of yellow bench solution and distilled water.
Benzidine : 0·05% (w/v) in 10% acetic acid (v/v).
Copper sulphate : 0·1% (w/v) $CuSO_4,5H_2O$ in distilled water containing 10% (v/v) of 2N-sulphuric acid.
Dimethylglyoxime : 1% in industrial methylated spirit.
Diphenylcarbazide : 1% in industrial methylated spirit.
Fluorescent mixture : 0·1 g. of kojic acid and 0·5 g. of oxine in 100 ml. of 60% alcohol
Gallacetophenone : 1% in 2N-ammonia.
Lead–cobalt nitrate : 5 g. of each salt dissolved together in 100 ml. of water with trace of nitric acid. Dilute hydrochloric acid is then added until a precipitate of lead chloride begins to be formed. The solution is filtered if necessary.
Phosphomolybdic acid : 5% (w/v) in distilled water; kept in a dark bottle.
Potassium chromate : 1 g. in 100 ml. of distilled water.
Potassium nitrite : freshly prepared, saturated solution in 2N-acetic acid.
Potassium thiocyanate–acetone : equal vols. of saturated aqueous potassium thiocyanate and acetone.
Quinalizarin : 0·02% (w/v) in industrial methylated spirit.
Rhodizonic acid : freshly prepared 0·1% (w/v) sodium salt in distilled water.
Rubeanic acid : 0·1% (w/v) in industrial methylated spirit.
Sodium hydrosulphite (dithionite) : freshly prepared 5% (w/v) in distilled water.
Sodium hypobromite : 2 vols. of 2N-sodium hydroxide saturated with bromine, plus 1 vol. of 2N-sodium hydroxide.
Sodium hypophosphite : 5% (w/v) in N-hydrochloric acid.
Sodium nitrite : saturated solution in distilled water.
Zinc uranyl acetate : saturated solution in N-acetic acid.

Analysis of the Chromatograms.—Each strip of chromatogram is analysed separately by a series of consecutive sprayings or treatments as detailed below. It is important not to make the paper too wet by excessive spraying at any stage. It is often an advantage to spray both sides, since spots often appear on the back. Each coloured or fluorescent spot is marked as it is found, to assist comparison of the positions of cations on the chromatograms in the final conclusions.

Group A, Ag, Pb, Hg^{2+} [Most of any Hg^+ present is oxidised by nitric acid in the preparation of solution (*a*)]. (i) A chromatogram from solution (*a*), sheet II, is sprayed with potassium chromate, and then held over ammonia (*d* 0·880). A brick red spot which fades to pale yellow when treated with ammonia indicates Ag. A bright yellow spot which becomes orange with ammonia indicates Pb (an orange-brown spot with $R_F \simeq$ 0·3—0·4, which blackens with ammonia, indicates Hg^+). A blue spot with ammonia, is probably due to Cu. A brown spot with $R_F \simeq$ 0·1—0·2 is probaby Mn or Co as hydroxides. The yellow spot due to Pb shows better contrast if the surrounding potassium chromate stain is destroyed by treatment with sulphur dioxide.

(ii) The strip is now sprayed with 2N-hydrochloric acid, dried, and sprayed with yellow ammonium sulphide when coloured sulphides, etc., are formed, mainly brownish-black. A yellow spot, $R_F \simeq 0{\cdot}2$ is probably due to Cd. A yellow spot $R_F \simeq 0{\cdot}5$, is probably due to As. An orange spot, $R_F \simeq 0{\cdot}1$, probably due to Sb.

The paper is then sprayed with alkaline hydrogen peroxide, warmed over an electric fire, but not dried, and then treated with sulphur dioxide from a siphon, especially where there are dark patches. A dark spot (HgS) at $R_F \simeq 0{\cdot}5$, remaining after this treatment, confirms Hg. The alkaline hydrogen peroxide oxidises all the black sulphides except Hg and usually NiS (which will be nearer the starting line, *i.e.*, $R_F \simeq 0{\cdot}1$; see later tests). If Mn, Co, or Ni is present, it will be precipitated as oxide which is converted by sulphur dioxide into a colourless or faintly coloured spot. Sb is sometimes left as an orange spot, and Cd as a yellow one.

Sub-group. As and Sb. (iii) Another chromatogram obtained from solution (*b*), sheet I, is sprayed lightly with ammonium sulphide. An orange spot, $R_F \simeq 0{\cdot}1$, is probably due to Sb. A yellow spot, $R_F \simeq 0{\cdot}5$, is probably due to As. The spots are marked to distinguish them from any dark sulphides.

The sulphides are dissolved by spraying with concentrated hydrochloric acid and then dried (N.B. : As_2S_3 is not readily dissolved). The paper is sprayed with sodium hypophosphite and held over an electric fire with a thermometer placed directly underneath the paper, and warmed gradually to about 35°. Arsenic shows as a dark brownish spot of $R_F \simeq 0{\cdot}5$. A similar spot for Hg is produced, having $R_F \simeq 0{\cdot}4$, but this has already been identified if present. The strip is now sprayed with phosphomolydic acid and warmed, whereupon Sb is indicated as a " permanent " blue spot, owing to the reduction of the spraying reagent to the " blue " oxide of molybdenum. Any colour caused by residual sulphide fades quickly (10 minutes).

Alternative. Stannous chloride can be used to produce the arsenic stain instead of hypophosphite but, if this is used, the test for Sb has to be done on another chromatogram strip, since the phosphomolybdic acid will be reduced by the stannous chloride if present but is not affected by the presence of hypophosphite.

Group B, Cr, Mn, Cu, Co, Ni, Bi, Fe. (i) A chromatogram from solution (*b*) (sheet I) is sprayed lightly with sodium hypobromite and dried by warming. An orange spot suggests Fe [also with Pb if this has not been completely precipitated when solution (*b*) was prepared]. A blue spot suggests Cu; a dark brown spot, Mn, Co, Ni; a yellow spot, Cr as CrO_4''.

Sub-group, Cr, Mn, Co, Ni. (ii) The strip is now sprayed with acidic (sulphuric acid) hydrogen peroxide; the dark spots due to Mn, Co, and Ni are then slowly converted into faintly coloured sulphates. A Cr spot will become sky blue and then fade quickly ($CrO_4'' \longrightarrow Cr_2O_7'' \longrightarrow$ perchromic acid). A blue Cu spot becomes brown (hydrated copper peroxide) and can be destroyed by spraying it with concentrated hydrochloric acid to " dampness " and then warming over electric fire to remove all the hydrogen peroxide. A confirmatory test for Cr^{3+} as CrO_4'' is to spray the spot with diphenylcarbazide, which immediately becomes purple.

If CrO_4'' is present here, it will interfere with the benzidine test for Mn, which has about the same R_F value, hence it must first be destroyed by reduction with sulphur dioxide to Cr^{3+}; at the same time any NaOBr left on the paper will also be removed. A small excess of benzidine solution is sprayed on the suspected Mn, held over aqueous ammonia (*d* 0·880), and then resprayed with benzidine : a bright blue spot of $R_F \simeq 0{\cdot}1$ indicates Mn (N.B. If excess of benzidine is not used initially, brown MnO_2 may form on exposure to ammonia. If this happens, treatment with sulphur dioxide is repeated, the paper is dried, and the benzidine test repeated).

(iii) The strip is again dried, sprayed with rubeanic acid, and then exposed to aqueous ammonia (*d* 0·880). All other colours produced are ignored except a grey-green spot for Cu, a warm-rusty brown for Co, or a dark Prussian blue for Ni.

Sub-group, Bi, Fe, Co. (iv) Another chromatogram from solution (*b*) (sheet I) is sprayed with potassium thiocyanate–acetone solution. A bright yellow spot indicates Bi; blood red, Fe; bright blue, Co. All these colours are removed by exposure to aqueous ammonia (*d* 0·880), and the paper is then sprayed with excess of dimethylglyoxime, which precipitates the Ni as the very insoluble, red complex which acts as the confirmatory test for Ni and also prevents any interference with the subsequent test for Cu with rubeanic acid, which is then applied as above [see (iii)].

Group C, Sn, Sr, Ba, Cd, Zn, Al, Mg, Ca. The kojic acid–oxine solution is used to spray (1) two chromatograms from sheet I, solution (*b*), and (2) two chromatograms from sheet II, solution (*b*).

Sub-group, Sn, Sr, Ba. The chromatograms from (1) are examined under ultra-violet light after exposure to aqueous ammonia (*d* 0·880), and the positions of the fluorescent spots marked. If a non-fluorescent cation is present, it may produce a region which overlaps the fluorescent spots, or *vice versa*. The cations which produce fluorescence are indicated in the following table (for full details see Pollard *et al.*, Faraday Society Discussion, 1949, no. 1, p. 183).

Cation.	R_F.	Colour.	Brilliance.	Action with acetic acid.
Sn^{2+} and Sn^{4+}	$>0{\cdot}5$	Yellow	++	++
Cd	$<0{\cdot}2$	Yellow	++	—
Zn	$<0{\cdot}2$	Yellow	++	++; sometimes green
Al	$<0{\cdot}2$	Green	+++	+++
Mg	$<0{\cdot}2$	Blue-green	+++	—
Ca	$<0{\cdot}2$	Green	++	—
Sr and Ba	$<0{\cdot}2$	Blue-green	+	—

To confirm the presence of Sn as a yellow fluorescent spot of $R_F > 0{\cdot}5$, the strip is shielded with cardboard above this point, and sprayed with 2N-hydrochloric acid, dried, and then sprayed with phosphomolybdic acid and again warmed. A blue spot due to " blue " molybdic oxide indicates Sn^{2+}. If no blue spot appears it is inferred that the fluorescence is due to Sn^{4+}.

The same chromatogram is then sprayed with rhodizonic acid where other fluorescent spots appeared. The formation of a red spot indicates either Sr or Ba, which can be distinguished by further spraying with a mixture of equal volumes of 2N-hydrochloric and 2N-acetic acid. If the red spot vanishes slowly it is due to Sr but, if the colour becomes a brigher red and permanent, then it is due to Ba (N.B. If a small amount of Pb is present, this will yield a red spot with rhodizonic acid, which becomes violet when sprayed with hydrochloric acid, but in preparing (*b*) it was aimed to remove all the Pb in the original mixture).

Sub-group, Cd, Zn, Al, Mg, Ca. Two chromatograms sprayed with the fluorescent mixture, one from sheet I solution (*b*), and one from sheet II (see above), are examined over aqueous ammonia (*d* 0·880) in ultra-violet light. The position and colour of the fluorescent patches are noted and compared with the above table.

The papers are next sprayed very lightly with glacial acetic acid and again examined under ultra-violet light. Fluorescent spots persisting are due to either Al (green) or Zn (yellow); Cd, Mg, Ca, Sr, and Ba are quenched. A separate, fresh chromatogram from sheet I, solution (*b*), unsprayed with fluorescent mixture, is used to confirm Zn. If Co is absent, the paper is sprayed with copper sulphate and then with ammonium mercuric thiocyanate. The formation of a purple or violet-black spot (sometimes very speckled) after 2—3 minutes confirms Zn. If Co is present, this will interfere and so has to be removed by spraying with potassium nitrite to precipitate the Co as potassium cobaltinitrite. The above test for Zn is applied, followed by sulphur dioxide to reduce any nitrous or nitric acid on the paper. The formation of a purple patch round the yellow potassium cobaltinitrite confirms Zn.

A fresh chromatogram from sheet I, solution (*b*), is sprayed with quinalizarin; a bright violet spot is due to Al or Zn. On subsequent spraying with alkaline hydrogen peroxide, the formation of a bright cornflower-blue spot shows Mg (cf. fluorescent tests).

A yellow fluorescent spot, quenched by acetic acid and giving a yellow sulphide with any of the previous ammonium sulphide sprayings, indicates Cd. This can be distinguished from As by the fact that the arsenic sulphide is darkened (reduction to As) on treatment with fresh sodium dithionite, while CdS is unaffected.

If there is a rather weak fluorescent spot which does not respond to any of the above tests and is not quenched by acetic acid, it is attributed to Ca. This may be confirmed with gallacetophenone, which yields a purple spot (Sr and Ba give similar colours, but these will have already been identified).

Group D, Na, K. A chromatogram from sheet I, solution (*b*), is sprayed with 2N-acetic acid, dried, sprayed with zinc uranyl acetate, and examined under ultra-violet light. A blue fluorescent spot at $R_F \doteqdot 0{\cdot}1$ indicates Na.

The strip is then sprayed with a lead–cobalt nitrate solution, followed by saturated sodium nitrite. The formation, after a few minutes, of the greyish-black triple nitrite of Pb, Co, and K, at R_F 0·1, indicates K. If SO_4'' is present, a preliminary spray of the suspected K area with a saturated aqueous solution of barium nitrate is recommended to precipitate all SO_4'' as barium sulphate. The paper is then dried and sprayed with the necessary reagents to detect K.

This scheme has been tested by several students on a number of analytical mixtures containing up to eight cations associated with a variety of anions. Once the powder has been brought into solution there seems to be no difficulty about identification. As far as we have investigated them, the effect of one cation on another, or the presence of anions like BO_3''', C_2O_4'', and PO_4''', is mainly to modify the relative movements of the cations. Once the chromatograms have been prepared, the time required for identification is usually less than 3 hours; another interesting point is that the dried chromatogram can be kept in the dark for periods up to 3 months before the identification tests are carried out.

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