102. *The Analysis of Inorganic Compounds by Paper Chromatography. Part II. Analysis of Cations and Anions.*

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The application is reported of three solvent mixtures, (A) butanol–water containing benzoylacetone, (B) collidine–water, and (C) dioxan containing antipyrine, to the general qualitative analysis of the 24 cations of the ordinary analysis tables. A large number of mixtures of cations have been chromatographed without being first separated into groups. Various techniques have been used, namely, one-way chromatograms using one, two, or three solvents, either separately or in combination, or two-way chromatograms, using two or three solvents in combination. The methods have been tried with unknown mixtures.

Suitable solvent mixtures for the separation of Cd and Zn; Th and U; K, Ti, V, Mo, and Fe are reported. The separation of Mo from those elements usually associated with it in agricultural analyses is described.

The R_F values for the movement of anions in a solvent mixture, butanol–pyridine–ammonia, are recorded for chloride, bromide, iodide, chlorate, bromate, iodate, nitrite, nitrate, arsenite, arsenate, carbonate, phosphate, chromate, thiocyanate, and sulphate. The separation of certain groups of these anions is reported. The independent movement of anion and cation is noted.

QUALITATIVE analysis based entirely upon filter-paper chromatography, without any previous chemical separation into groups, has been found to be practicable. By using the three solvent mixtures specified above, either singly or together in one-way or two-way processes, a very large number of cationic mixtures containing up to seven or more cations can be analysed. The actual procedure adopted will depend on the mixture to be analysed and the quantity available.

The predictions made from the study of single cations described in Part I (preceding paper) are found to hold for most of the cations when mixed. There are a few instances where interference, which might be classed as displacement, occurs when certain cations are together, *e.g.*, As, Sb, and Sn, or when a very large excess of one salt is present, *e.g.*, $NaNO_3$ with smaller quantities of other cations. Sometimes this slight displacement tends to improve the separation. Even when the cations do not move exactly according to the R_F values for the single cation (see Table I, Part I), there is no serious difficulty about identification, since quite characteristic tests can be applied and the position of most cations can be revealed by the fluorescent spray or ammoniacal hydrogen sulphide (see Pollard *et al.*, *Faraday Soc. Discussions*, No. 7, 1949, p. 186).

The anions originally associated with the cations in the mixture do not seem to be very important since, with the solvent mixtures used, the cations are usually converted on the paper into soluble complexes. Some abnormalities have been observed when phosphates, tartrates, arsenates, or large quantities of ammonium salts are present, but these have not yet been fully studied.

From a study of the movement of single anions described in the Experimental section, we have been able to predict and achieve the separation of a number of mixtures of anions, and also show that the anion associated with the cation does not always move to the same position on the paper as the cation, especially when the latter is Na^+ or K^+. Clearly, this depends on the ionic or covalent nature of the compound.

EXPERIMENTAL.

Apparatus.—Several types of apparatus have been used according to the width of filter-paper (Whatman No. 1) required for the separation, but, in general, the arrangement is exactly similar to that already in use for chromatography of organic compounds. The minimum width of paper for the analysis of a single spot by a one-way procedure was 4 cm., and sheets 27 cm. square were suitable for the two-way method. Thus, glass vessels ranging from 200-c.c. cylinders to tanks, 10 × 13 × 16 in., are used containing a suitably supported glass trough, to hold the organic solvent mixture. Great care is taken to make sure that the vessels are air-tight during an experiment, and variations in temperature are avoided by placing the apparatus in an insulated cupboard.

Preparation of Solvents.—(a) *Butanol mixture.* The benzoylacetone (5 g.) is first dissolved in *n*-butanol (50 c.c.), and then shaken with 0·1N-nitric acid (50 ml.). When equilibrium is attained, the upper layer is placed in the trough, and the aqueous layer put at the bottom of the tank to keep the atmosphere within saturated with vapour.

(b) *Collidine mixture.* 2 : 4 : 6-Collidine is shaken with an equal volume of 0·4N-nitric acid, and when the mixture separates on cooling, the collidine and the aqueous layer are used as above.

(c) *Dioxan mixture.* Antipyrine (1 g.) is dissolved in a mixture of pure dioxan (100 c.c.), concentrated nitric acid (1 c.c.), and water (2·8 c.c.), and this mixture is used in the trough, since no aqueous layer separates, the above forming a homogeneous mixture.

Preparation of Known Mixtures.—Equal volumes of the solution of individual cations (Pollard *et al.*, *loc. cit.*) are mixed according to the mixture of cations required for investigation. Care is taken not to use mixtures which are likely to lead to the precipitation of any of the cations.

Preparation of Unknown Mixtures.—A 2% solution of the unknown mixture is prepared either by dissolving the solid in (i) distilled water and then slightly acidifying it with one or two drops of 2N-nitric acid, or (ii) a few c.c. of 2N-nitric acid or 50% nitric acid and diluting the product to the necessary concentration with distilled water. The pH should be adjusted to about 1. If the unknown mixture will not completely dissolve in the above solvents, then the insoluble portion can be removed by centrifuging and treated separately, while the soluble portion is analysed in the manner described.

Procedure.—(i) *One-way method.* Any number of mixtures can be analysed simultaneously providing that the drops of solution (approx. 0·02 c.c.) are placed at least 4 cm. apart on the starting line, which is pencilled about 8 cm. from the top edge of the paper. Two similar sheets are placed one on each side of the trough, with the top edge dipping into the liquid. Thus, with our largest tank, taking four papers 27 cm. wide, it is possible to analyse seven different mixtures at the same time in quadruplicate.

When a completely unknown mixture is analysed we prefer to chromatograph at least four spots, divide the paper afterwards into strips, spray two with our general reagents, and then use confirmatory tests on the others at the places where, from the information gained from the first strip, we know the cations to be.

For certain groups of cations a single chromatogram with a particular solvent will yield sufficient evidence for a complete analysis, but where the cations are completely unknown, it is possible to obtain three chromatograms separately with the three solvents in different tanks and compare the results. The latter method has been used very successfully for powders similar to those used in analytical courses.

Where the amount of material is strictly limited, it is practicable to separate some cations with the butanol mixture, and then after washing the paper with carbon tetrachloride and drying, to separate others with the dioxan mixture. Only a few such separations have been carried out; the method is capable of further development.

(ii) *Two-way method.* The analysis of one drop (0·02 c.c.) of solution is achieved by separating some of the cations by the collidine, and the others at right angles to the original direction with the butanol mixture. On a piece of filter-paper (27 cm. square) two lines are drawn at right angles, 8 cm. from the edge of the paper. One drop of solution is placed at the point of intersection, and then chromatographed with the collidine mixture. The paper is removed from the tank, washed with carbon tetrachloride, dried in air, and then chromatographed with the butanol mixture run at right angles to the collidine direction.

A still better separation for some cations can be obtained by washing and drying the paper as described above and then running it with dioxan in the same direction as the butanol.

Since two papers can be used in each tank, one of the chromatograms can be tested with the general spraying reagents, and the other used for confirmatory tests.

Results.

Examples of Mixtures separated and identified. (Other possible separations can be predicted from Table I, Part I.)—(I) *One-way, one-solvent mixture chromatograms.* (*a*) With butanol–water containing benzoylacetone : (i) As, Hg, and Pb. (ii) Hg, As, Fe, and one of the following : Ag, Pb, Bi, Al, Cd, Mn, Co, Ni, Ca, Sr, Ba, Mg, K, or Na. (iii) Cu, As, Fe, and one of the following : Ag, Zn, Mn, Co, Bi, Ni, Ca, Sr, Ba, Mg, K, or Na. (iv) Pb, Cd, Cu, As, and Fe. (v) Hg, Bi, Cu, and Cd. (vi) As, Sb, and Sn.

(*b*) With collidine mixture : (i) Pb and Ag or Zn. (ii) Hg and Cd or Zn. (iii) Bi and Cd. (iv) Cu and Hg, or Fe, or Zn. (v) Co and Ni. (vi) Zn, Mn, Co, and Ni. (vii) Ca, Ba, and Sr. (viii) Mg, K, and Na. (ix) Ca, K, and Na. (x) Mg, Ca, K, and Na. (xi) Zn, Mg, Ca, Sr, and Ba. (xii) Mn, Mg, K, and Na. (xiii) Zn, Mg, Ca, K, and Na.

(*c*) With dioxan mixture containing antipyrine : (i) Ag, Hg, and Pb. (ii) Cu, Hg, and Bi, with Ag, or Pb, or Al, or Zn. (iii) Cd, Hg, and Bi, with Al, or Zn, or Co, or Ca, or K. (iv) Fe and Bi. (v) Cu, Bi, and Mn or Ni, or Mg.

The relative positions of the individual cations can be ascertained from Table I (see Part I), except where some interference occurs. All the above move according to the predictions, except for (i) As, Sb, and Sn, where the R_F values after separation with butanol are 0·40, 0·53, and 0·63, respectively, while the individual cations have R_F values of 0·43, 0·0, and 0·54; and (ii) Zn, Mn, Co, and Ni, where the R_F values after separation with collidine are 0·77, 0·75, 0·80, and 0·82 which, with this displacement effect, causes the Zn, Co, and Ni to appear as transverse bands. The separation of Cu and Fe with the dioxan solvent mixture has not been possible owing to displacement; the cationic mixture moves with a common R_F value of 0·4 whilst the individual cations move with the following R_F values : Cu, 0·24 and Fe, 0·09.

It will be observed that the Ag, Hg, and Pb mixture has been separated by both the butanol and the dioxan solvent. The latter gives better and more rapid separations—with Whatman No. 1 in 5 hours, or Whatman No. 54 in less than one hour. The rapid movement of the solvent does not affect the formation of symmetrical concentrated spots.

A further possible adaptation of these methods consists of comparison of three separate chromatograms, using the three general solvent mixtures. The advantage of this is that the three experiments can be run simultaneously in separate tanks with a saving of time, and as some cations move in two or more solvents, confirmatory evidence of the presence of a particular cation can be obtained from the different chromatograms. The collidine solvent mixture furnishes definite evidence of the presence of the following cations : Ag, Al, Fe, Cd, Zn, Na, K, Ca, Ba, and Sr; the butanol mixture containing benzoylacetone of Cu, Cd, As, Sn, Fe; and the dioxan with antipyrine of Ag, Pb, Cu, Cd, Fe, Hg, Bi, Co, and Ni. Where, as with Cd and Zn, Co and Ni, there is likelihood of uncertainty since there is insufficient separation on the chromatogram and the general spraying reagents yield similar spots, it is possible to identify the particular cation by a suitable spot reagent. It is also unlikely that there will be more than eight different cations present in any particular mixture for analysis.

This scheme was tested on 20 unknown mixtures chosen at random from those normally issued to students in the analytical course. The cations were mixed in all kinds of proportions, and associated with many different anions. Sometimes a cation was missed because the amount present was below the sensitivity of the method, and in other cases the presence of certain anions seemed to interfere with the movement of cations. Hence, though this method was not in every analysis completely successful, it can be said that no cation was reported that was not present in the powder though it was possible to miss a cation either through interference or because it was present in extremely small amounts. Methods of overcoming these difficulties are being investigated.

(II) *One-way, two solvents used consecutively on the same chromatogram.* This procedure was tried with a mixture of Al, Bi, and Fe, first chromatographing it with the butanol mixture containing benzoylacetone, washing the paper with carbon tetrachloride, and drying, and then chromatographing it in the same direction with the dioxan mixture containing antipyrine. With the first solvent mixture, Fe moved, leaving the Bi and Al near the starting line, and then with the second solvent the Bi separated from the Al. The R_F values after movement were Fe, 0·95; Bi, 0·6; and Al, 0·06; thus, there was very clear and distinct separation of these three cations. It is possible to apply this technique to many other similar mixtures of cations.

(III) *Two-way, two-solvent mixtures.* First solvent—collidine; second solvent—butanol. Examples of separations achieved : (i) Cu, As, and Fe with any of the following : (*a*) Pb and Zn, (*b*) Pb and Mn, (*c*) Pb, Zn, and Mn, (*d*) Pb, Cu, Mn, (*e*) Al and Cd, (*f*) Al and Mn, (*g*) Al, Cd, and Mn, (*h*) Al, Zn, and Mn. (ii) Al, Cu, Fe, Zn, Ca, and Mg. (iii) Pb, Cu, Cd, Fe, Ca, Sr, Ba. (iv) Bi, Cu, Fe, Co, Mg, K, and Na. (v) Pb, Cu, Fe, Zn, Mn, Ca, and Mg.

The positions of these cations after movement are usually in accordance with the prediction from their movements in the two separate solvent mixtures, and are shown in the scheme below. It has been observed that Cu and Zn always have a higher R_F value in the second solvent (butanol) than would be expected—probably owing to the stability of the respective collidine complexes. Even so, there is no difficulty in identification since it depends not only on the R_F, but also on characteristic tests. There is also a tendency for arsenic not to move in the collidine mixture if certain cations are present, and the alternative positions for it are shown in the scheme (section 1).

The general movement of the cations is along two axes at right angles, and in many cases this provides sufficient separation for analysis. However, it was thought advisable to see if still further separation could be achieved by use of the third solvent. For reasons which are not yet understood the dioxan was not satisfactory in the two-solvent procedure, but from the limited experience gained with the three-solvent procedure it has definite advantages here.

Scheme illustrating two-way separations. The chromatogram is marked into rectangles, by dividing the distances along the axes from the starting point to the respective solvent fronts into ten equal divisions. The rectangle in which the cation is expected to occur is then given by reference to the *x*-axis by letters *A* to *J*, and to the *y*-axis by numbers 1 to 10.

(IV) *Two-way, three-solvent separations.* First solvent—collidine; second solvent—butanol; third solvent—dioxan run in the same direction as butanol.

With a mixture of Al, Bi, Mg, Mn, Cd, and Cu, the separations with this procedure are illustrated in the scheme (section 2). With the first two solvents the cations moved to the positions expected (scheme, section 1); there was almost no separation of Al and Bi. When the third solvent, dioxan, was used, the Bi separated from the Al, and Mg, Mn, and Cd moved to new positions well separated from one another. It would seem, therefore, that for certain groups of cations the three-solvent technique will be quite useful.

The foregoing two-way separations are summarised in the accompanying scheme.

(1) Two-way separations with (*a*) collidine, *x*-axis, and (*b*) butanol containing benzoylacetone, *y*-axis: Al, Bi, Pb, [*A*, 1]; Ba, [*C*, 1]; K, Sr, [*D*, 1] or [*E*, 1]; Na, [*E*, 1]; Ca, [*F*, 1]; Mg, [*G*, 1]; Mn, Cd, [*H*, 1]; Zn(a), [*I*, 1]; As(a), [*A*, 4]; As(b), [*F*, 4]; Hg^{2+}, [*A*, 6]; Cu, [*H*, 8]; Fe, [*A*, 9].

(2) Two-way separations with (*a*) collidine, *x*-axis, and (*b*) benzoylacetone in butanol, followed by antipyrine in dioxan, *y*-axis: Al, [*A*, 2]; Mg, [*E*, 2]; Mn, [*F*, 2]; Cd, [*G*, 3]; Bi, [*A*, 5]; Cu, [*G*, 8].

Special Separations.—Although we have paid rather more attention to the development of a general method of qualitative analysis, certain solvents other than those used in our general procedure have advantages for special separations, and these are described below. All the cations have been detected with our general fluorescent reagent.

Separation of Cd *and* Zn. The best separation of these two cations has been observed with a mixture of butanol, 0·1N-nitric acid, and collidine (5 : 4 : 1). The R_F values were: Cd 0·24, Zn 0·06, and good, symmetrical, concentrated spots were obtained.

Separation of Th *and* U. A mixture of these two cations as nitrates can be separated with a mixture of butanol–N-nitric acid (1 : 1) and 0·5% benzoylacetone. The R_F values for the mixture are: Th 0·03 and U 0·27.

Separation of K, Ti, V, Mo, *and* Fe. A solution of these cations was prepared by mixing equal volumes of 2% solutions of titanium potassium oxalate, vanadium chloride, ferric nitrate, and ammonium molybdate. With a solvent mixture consisting of butanol–N-nitric acid (1 : 1) and 1% acetylacetone, the individual cations were found to have the following R_F values: K 0·07, Ti, 0·60, V 0·20, Mo 0·58, and Fe 0·54, from which one would deduce that a satisfactory separation of Ti, Mo, and Fe is not probable. However, with the mixture of cations the R_F values become K 0·07, Ti 0·55, V 0·17, Mo 0·63, Fe 0·40, which leads to a very satisfactory chromatogram.

Separation of Mo *from other cations.* The importance of molybdenum in agricultural research led us to investigate the behaviour of mixtures containing this element, and we have found that the collidine mixture enables one to separate molybdenum, originally as molybdate, from those elements with which it is usually associated. Its R_F value as an individual ion is 0·24, but it does not always move in the same way with different ions: nevertheless, it can be readily identified.

The following mixtures have been satisfactorily analysed, though the cations do not all move with their normal R_F values, which are quoted in parentheses wherever any marked difference occurs: (*a*) Fe 0; Mo 0·20 (0·24); As 0·60 (0·64); and Co 0·75. (*b*) Pb 0; Mo 0·20 (0·24); K 0·33; Zn 0·76. (*c*) Al 0; Mo 0·18 (0·24); K 0·31; Mg 0·49 (0·64); Cu 0·76. (*d*) Fe 0; Mo 0·19; Ca 0·37 (0·54); Mg 0·47 (0·64); Zn 0·65 (0·75); Co 0·75. All these mixtures give distinct chromatograms and good symmetrical spots; the slight displacements which occur tend to improve the separations.

Separation of anions. (With Mr. A. B. LAW.) A number of suggestions have been made by other workers (*e.g.*, Lederer, *Roy. Aus. Chem. J.*, 1950, **17**, 308) for the separation of certain groups of anions. Using a similar procedure to that described for a study of the individual cations, we have investigated the behaviour of the following anions: chloride, bromide, iodide, thiocyanate, chlorate, bromate, iodate, carbonate, chromate, sulphate, nitrate, nitrite, orthophosphate, arsenite, and arsenate, with a number of different solvent mixtures. We used generally the sodium or potassium salts, and where convenient, the free acid. The solvent mixture was found to be most successful when it was alkaline, and the best movement and spots were obtained with a solvent mixture consisting of butanol, pyridine, and 1·5N-ammonia (2 : 1 : 2). The anions were found to move with the following R_F values: chloride 0·24, bromide 0·36, iodide 0·47, chlorate 0·42, bromate 0·25, iodate 0·09, nitrite 0·25, nitrate 0·40, arsenite 0·19, arsenate 0·05, carbonate 0·06, phosphate 0·04, chromate 0·00, thiocyanate 0·56, sulphate 0·07.

Many reagents were investigated as sprays for their suitability in the detection of anions. The most generally useful reagent was ammoniacal silver nitrate, but certain reagents were particularly good for special groups, *e.g.*, potassium iodide and hydrochloric acid for chlorates, bromates, and iodates.

Mixtures of some of the anions were tried and in all cases the movement and separation were almost the same as for the individual anions; the slight displacements observed, *e.g.*, with NO_3, Br, and I, tended to improve the chromatographic separation. The most successful separations were with the following:

(i) Chloride with iodide, or bromide and iodide, or thiocyanate, or nitrate and thiocyanate. (ii) Bromide with nitrate or thiocyanate. (iii) Iodide with nitrate. The other separations possible with this solvent are apparent from the R_F values.

A test was made to find if the anion moved independently of the cation with nitric acid, hydrochloric acid, sulphuric acid, sodium nitrate, lead nitrate, potassium nitrate, sodium chloride, potassium chloride, sodium sulphate, and potassium sulphate. In all cases the anion moved with the same R_F value, while the cation either stayed on the starting line or moved slightly.

A comparison of the potassium salts of the various anions which moved appreciably showed that, after being sprayed with naphthylaminesulphonic acid and viewed under the ultra-violet lamp, the potassium spot was brightly fluorescent with an R_F of 0·12, while the anions gave black spots and had moved to their normal positions, further down the chromatogram.

Further work is in progress to develop a general procedure for the analysis of groups of anions.

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