

100. *Inorganic Chromatography on Cellulose. Part II*. The Separation and Detection of Metals and Acid Radicals on Strips of Absorbent Paper.*

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A method for the separation and detection of a number of metallic ions and acid radicals by extraction with organic solvent mixtures on strips or sheets of absorbent paper is described. Detection is accomplished by spraying the strip or sheet of paper with a solution containing suitable reagents; the presence of individual metals or acid radicals is then made visible as characteristic coloured bands. The following groups of ions have been separated (R.E. = rare earths) :

(a).	(b).	(c).	(d).	(e).	(f).	(g).	(h).	(i).	(j).
Pb ²⁺	As ³⁺	Fe ³⁺	Ni ²⁺	Pt ⁴⁺	R.E. ³⁺	SeO ₃ ²⁻	Li ⁺	Ca ²⁺	F ⁻
Cu ²⁺	Sb ³⁺	Al ³⁺	Mn ²⁺	Pd ²⁺	Sc ³⁺	TeO ₃ ²⁻	Na ⁺	Sr ²⁺	Cl ⁻
Bi ³⁺	Sn ²⁺	Cr ³⁺	Co ²⁺	Rh ³⁺	Th ⁴⁺	—	K ⁺	Ba ²⁺	Br ⁻
Cd ²⁺	—	—	Zn ²⁺	Ir ⁴⁺	—	—	—	—	I ⁻
Hg ²⁺	—	—	Cu ²⁺	Ir ³⁺	—	—	—	—	—
			Fe ³⁺	Ru ⁴⁺					
			UO ₂ ²⁺	Ru ³⁺					
			VO ₃ ⁺	Os ⁴⁺					
			Ti ⁴⁺	Au ³⁺					

The ratio of the distances moved by the ion to that moved by the solvent (R_F value) has been determined in a number of cases. The significance of these measurements is discussed.

WE have already given a preliminary account of the separation of inorganic salts by the technique of paper chromatography employing organic solvents (Report of the Chemistry Research Board 1947, H.M.S.O.; Arden, Burstall, Davies, Lewis, and Linstead, *Nature*, 1948, **162**, 691; Burstall, Davies, Linstead, and Wells, *ibid.*, 1949, **163**, 64; Linstead, *ibid.*, p. 598). Observations made in other laboratories have also recently been described (Lederer, *Nature*, 1948, **162**, 776; Pollard, McOmie, and Elbeih, *ibid.*, 1949, **163**, 292; Lederer, *ibid.*, p. 598; Lacourt, Sommereyns, Degeyndt, Baruh, and Gillard, *ibid.*, p. 999; Lederer, *Anal. Chim. Acta*, 1948, **3**, 476; *idem*, *Science*, 1949, **10**, 115; Osborne and Jewsbury, *Nature*, 1949, **164**, 443).

The following account provides a more detailed description of the qualitative separations carried out in this laboratory; quantitative separations will be the subject of a further paper. Methods of separating the metals constituting the ordinary qualitative analytical groups are described and the isolation of the constituents of mixtures containing some of the less common metals is also included. A few separations of anions have also been achieved. In some cases a particular separation has been extensively studied as to repeatability and interference

* Part I is regarded as the paper by Arden, Burstall, and Linstead (*J.*, 1949, S 311).

by various factors (see, *e.g.*, Part I, *loc. cit.*); in others the method is at a much earlier stage of development.

Paper chromatography has certain advantages over the conventional methods of qualitative inorganic chemical analysis—it is simple and reasonably rapid, costly special apparatus and chemicals are not necessary, and only small quantities of material are required for test purposes. Moreover, the method has proved successful for the separation and detection of groups of metals which are difficult to deal with by existing procedures, *e.g.*, the separation of the platinum metals from one another, of scandium from the rare earths and thorium, and of calcium, strontium, and barium from each other.

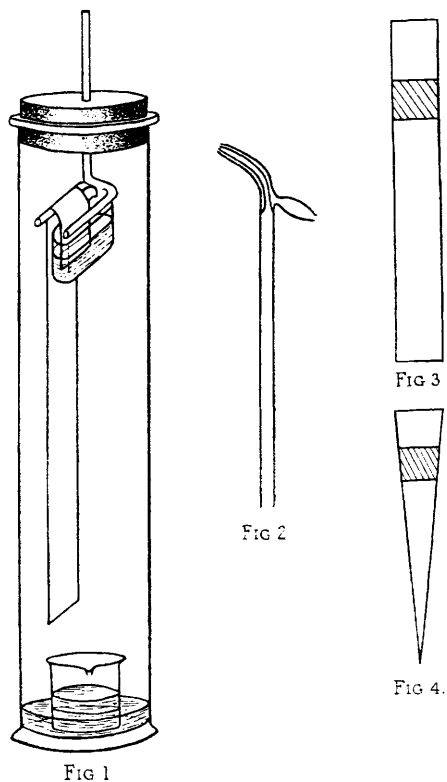
The technique is particularly useful in the separation and detection of groups of elements obtained by some suitable pretreatment of a complex mixture. The well-known analytical groups form a useful division of this kind; the further separation and detection of the elements in these groups can then be conveniently carried out by the methods now described.

It seems quite possible, also, that a complete system of qualitative chemical analysis could be developed on the basis of this new technique. The method is capable of giving good results in the hands of relatively inexperienced chemists. Separations, simple and easy to carry out, include Group IIa (Pb, Cu, Bi, Cd, and Hg), Group IIIb (Co, Ni, Mn, and Zn), the platinum metals and gold. More difficult separations are found in Group IIb (As, Sb, and Sn) and Group IV (Ca, Sr, and Ba). In routine operations such as are employed extensively in industry, the method should be particularly valuable since the conditions can be arranged to cover a particular series of metals or acid radicals and the procedure does not require continuous attention by a chemist.

EXPERIMENTAL.

Nearly all the experiments described in this paper were carried out on paper strips by a procedure which resembles, in general, that employed in similar organic work (Conden, Gordon, and Martin, *Biochem. J.*, 1944, **38**, 224). In view of the general interest of the method in the inorganic field, we give below a description of the technique which has been found most satisfactory over the past 4 years. The apparatus (Fig. 1) consists of a tall glass gas-jar closed with a tight fitting cork or a rubber bung which carries a glass rod to which is attached a glass boat. The boat is suspended about an inch below the bottom of the cork and serves as the container for the solvent employed in the separations. Two side arms are fused to the glass rod above the solvent container and these act as supports for a pair of paper strips, one strip being shown in position in the figure. In order to saturate the atmosphere in the cylinder with respect to the solvent, a layer of the latter is kept at the bottom of the cylinder. In some cases it is also necessary to control the amount of water vapour or acid in the atmosphere and for this purpose a beaker containing water, saturated salt solution, or aqueous acid saturated with solvent is placed on the bottom of the jar. It is advantageous also to maintain fairly constant temperature conditions, and in some cases the whole apparatus is kept in a thermostatically controlled ($\pm 1^\circ$) cabinet or bath.

The method of preparing the paper strip is substantially the same as in the earlier description (Arden, Burstall, Davies, Lewis, and Linstead, *loc. cit.*). A convenient volume (0.05 ml.) of the solution to be tested is placed near one end of a strip of filter-paper. This forms a wet patch about one inch square (Fig. 3) which is usually allowed to dry completely in air although in some cases the degree of drying is dependent on the chemical stability of the salts undergoing separation. In spite of the fact that the original solution is allowed to spread completely across the strip, little trouble has been experienced with edge effects. The strip is then hung vertically in the cylinder with the upper end immersed in the solvent contained in the glass boat. After the solvent has diffused down the paper a sufficient distance to effect a separation, the strip is removed from the cylinder, the solvent is allowed to evaporate, and the presence and position of the salts on the strip are determined by spraying with a suitable reagent. A simple type of atomiser suitable for this purpose is shown in Fig. 2. A large number of inorganic and organic reagents have been used. The criteria applied in choosing a developing reagent differ from those usually employed in selecting a spot-test reagent. It is not



necessary for the reagent to be specific for a certain radical, but it is desirable to have one which will give a delicate test for as many radicals as possible. Some of the reagents found particularly useful in this respect are diphenylthiocarbazone (dithizone), diphenylcarbazide, alizarin, rubanic acid, salicylaldehyde, and morin. In many cases mixtures of two or more of these reagents are advantageous.

In order to obtain repeatable results it is necessary to be certain of constancy in composition of the solvents employed. In many cases, particularly with water-miscible solvents, small variations in the water content will alter considerably the efficiency of a separation. All the solvents used have received a suitable pretreatment which is described later.

The separations described below have been carried out on Whatman No. 1 or No. 3 filter-paper but a number of other papers have been used successfully. The length of the paper strip has varied from about 9 to 18 inches and, although usually this has been about 1 inch in width, it is useful in the detection of small quantities of material to employ a triangular strip as shown in Fig. 4, so that the extracted substance is concentrated in a smaller area of paper.

In the following description of various separations which have been made, a short note of the method recommended for each separation is recorded at the beginning of the appropriate section; this is then followed by a detailed consideration of the behaviour of the metals or acid radicals.

(a) *Analytical Group IIa*: Pb, Cu, Bi, Cd, and Hg. (With D. B. REES EVANS.) *Recommended method.* The metals are present as chlorides and the solvent used is *n*-butyl alcohol saturated with 3*N*-hydrochloric acid.

In earlier work (Burstall, Davies, Linstead, and Wells, *loc. cit.*) it was found that lead, copper, bismuth, cadmium, and mercury can be separated by the use of ethyl *isopropyl* ketone containing 10% (v/v) hydrochloric acid (*d* 1.18). These two liquids are not completely miscible, but one phase is obtained on addition of small amounts of *isopropyl* alcohol or larger amounts of methyl alcohol. Better separations are possible, however, with other solvents described below.

Separation of copper, lead, bismuth, cadmium, and mercury was achieved by using butyl alcohol or amyl alcohol saturated with aqueous hydrochloric acid as solvent. The degree of separation obtained depended on the concentration of the aqueous acid used (Fig. 5). Butyl alcohol saturated with 3*N*-hydrochloric acid was found to give the most efficient separation. It was prepared by shaking together equal volumes of the alcohol and 3*N*-hydrochloric acid, the top layer being used. A solution of the metals in dilute hydrochloric acid was spotted on a strip of paper which had to be at least 18" long to obtain a good separation of copper and lead. The spot was allowed to dry in air for one hour. Use of a wet spot gave wider bands and a more rapid movement of solvent down the strip but did not much affect the R_F values of the five metals. The solvent was allowed to flow for 15–18 hours in an atmosphere saturated with respect to both organic solvent and aqueous phases. After evaporation of the solvent, the strip was sprayed with a solution of dithizone in chloroform. Mercury was detected as a pink band behind the solvent front and was followed by cadmium as a purple band. Although cadmium and mercury were not in the solvent front and each metal was separated from the other, both bands had sharp leading and trailing edges with a width less than that of the original spot. Bismuth appeared as a purple, and copper as a purplish-brown band. Lead, which gives only a weak colour with dithizone, was detected by spraying the top portion of the strip with an aqueous solution of rhodizonic acid; a bright blue band due to lead then appeared just below the copper.

A number of different effects was noted on varying the concentration of the acid with which the butyl alcohol was saturated. As the acidity was decreased, (a) the bands of all five metals became more diffuse (this effect was most marked with bismuth), (b) the R_F value of each cation decreased but to a different extent for each metal. This resulted in a better separation of cadmium and mercury which was partly counteracted by an increase in band width and a decrease in the degree of separation of copper and lead. No complete separation of copper and lead was achieved, even after 18 hours, when acid of strength less than 3*N*. was used. A series of R_F values obtained by using different acidities is shown in Table I. For the purpose of these measurements an R_F value is taken as the ratio of the distance moved by the "centre of gravity" of a band to the distance moved by the solvent.

TABLE I.

Variations in R_F values with change in acid concentrations.

Solvent.	Cu.	Pb.	Bi.	Cd.	Wet solvent front.	Hg.
Satd. with H ₂ O	0.04, 0.04	0.05, 0.05	0.50, 0.49	0.60, 0.62	0.65, 0.66	0.73, 0.74
Satd. with 1 <i>N</i> -HCl ...	0.08, 0.08	0.12, 0.11	0.55, 0.52	0.66, 0.63	0.70, 0.68	0.76, 0.78
Satd. with 2 <i>N</i> -HCl ...	0.13, 0.11	0.17, 0.12	0.57, 0.54	0.69, 0.66	0.72, 0.69	0.76, 0.76
Satd. with 3 <i>N</i> -HCl ...	0.20, 0.20	0.27, 0.27	0.60, 0.58	0.77, 0.77	0.79, 0.79	0.81, 0.81

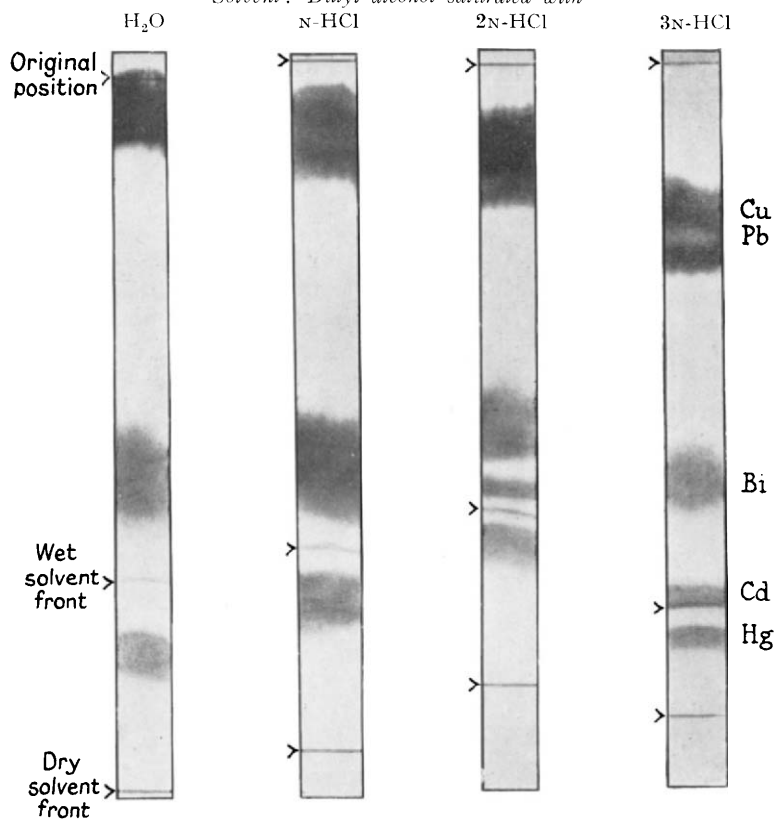
Two solvent phases exist on the paper strip, an upper area in which the paper is saturated with water and below that a region of dry solvent. When the solvent contained both hydrochloric acid and water the upper wet phase was strongly acid, but the lower dry phase was almost free from acid. The boundary between these two phases was not easily detected until the strip was sprayed with a suitable reagent, but on spraying the strip with dithizone or diphenylcarbazide solution a band of what appeared to be cadmium was found just in front of the main cadmium band. A similar band was obtained when a blank strip of paper was used and did in fact mark the position of the wet solvent boundary. The material causing the colour has not been identified but appears to be organic rather than inorganic since it gives a negative test for metals such as copper and iron normally found in cellulose. The position of the wet solvent front was also found by taking advantage of the difference in acidity of the two phases and spraying the strip with a suitable indicator. The R_F value of the wet solvent front was measured in a number of cases and is recorded in Table I.

As the concentration of aqueous acid used was increased above 3*N*-hydrochloric acid the bismuth and

FIG. 5.

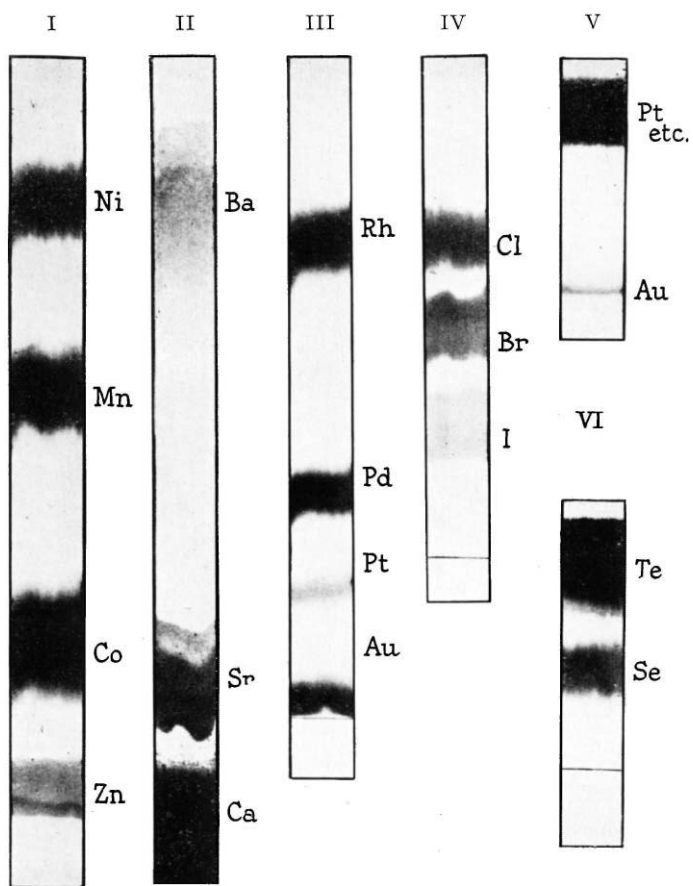
Group IIa.

Solvent: Butyl alcohol saturated with
N-HCl



[To face p. 518.]

FIG. 6.



lead bands were displaced backwards towards the copper whereas the cadmium band moved forward towards the mercury. The use of butyl alcohol containing 10% (v/v) of hydrochloric acid (d 1.18) resulted in mercury and cadmium being found in a mixed band. Copper and bismuth also formed a mixed band but lead was now in a separate band behind the copper. In order to get repeatable figures for R_F values it was essential that the atmosphere be completely saturated with respect to butyl alcohol and aqueous acid phases. Well-separated bands of bismuth, cadmium, and mercury were often obtained when at the beginning of a run the atmosphere was incompletely saturated, but results were not accurately repeatable. As an aid to maintaining a constant atmosphere the temperature was controlled at 22°. The R_F values appeared to be fairly independent of the concentration of each of the metals, of the total concentration of metals, and of the acid concentration of the original solution. Bismuth was more affected by such factors than the other metals. A difference in R_F values was noted in tests with varying times of solvent diffusion. Table II gives R_F values obtained with butyl alcohol saturated with aqueous acid of different strengths. The effect of time of running is noticeable in each case but agreement between duplicate strips is good. Unless otherwise stated, the amount of copper, bismuth, cadmium, and mercury was 100 μ g. of each metal, and 40 μ g. of lead were used.

TABLE II.

 R_F Values using butyl alcohol + 3N-HCl.

Metal.	Time of run.							
	7 hrs.		8 hrs.		15 hrs.		16 hrs.	
Cu	0.10		0.21	0.21	0.24	0.25	0.25	0.25
Pb	0.24		—	—	0.30	0.30	—	—
Bi	0.56		0.58	0.60	0.69	0.70	0.74	0.73
Cd	0.71		0.69	0.70	0.87	0.89	0.89	0.88
Hg	0.80		0.73 *	0.75 *	0.91	0.92	0.92 *	0.92 *

* Only 10 μ g. of Hg present. R_F Values using butyl alcohol + 2.5N-HCl.

Metal.	Time of run.							
	5 hrs.		8 hrs.		16 hrs.		16 hrs.	
Cu	0.15	0.17	0.15	0.16	0.18	0.19	0.19	0.19
Bi	0.55	0.54	0.58	0.55	0.63	0.63	0.62	0.62
Cd	0.66	0.66	0.67	0.65	0.73	0.73	0.73	0.72
Hg	0.73	0.72	0.77	0.75	0.79	0.78	0.78	0.76

 R_F Values using butyl alcohol + 2N-HCl.

Metal.	Time of run.							
	5 hrs.		8 hrs.		16 hrs.		16 hrs.	
Cu	0.15	0.13	0.13	0.13	0.16	0.15	0.14	0.14
Bi	0.53	0.52	0.54	0.54	0.60	0.58	0.58	0.58
Cd	0.62	0.61	0.64	0.62	0.70	0.68	0.67	0.64
Hg	0.70	0.71	0.73	0.74	0.75	0.75	0.74	0.72

TABLE III.

 R_F Values with different solvents prepared with 2.5N-HCl.

Metal.	Method (a).		Method (b).		Method (c).	
Cu	0.17	0.18	0.19	0.20	0.16	0.15
Pb	0.25	0.25	0.27	0.27	0.20	0.20
Bi	0.59	0.63	0.63	0.65	0.64	0.62
Cd	0.68	0.73	0.75	0.76	0.75	0.73
Hg	0.74	0.80	0.79	0.80	0.81	0.79

The term "butyl alcohol saturated with hydrochloric acid" is capable of several interpretations, but from the R_F values given in Table III it will be seen that no significant difference is made to the separation when three different methods are used for saturating the solvent: (a) by shaking together equal volumes of acid and butyl alcohol, (b) by shaking two volumes of acid and one of butyl alcohol, (c) by adding acid to butyl alcohol until two phases just do not separate.

A similar pattern in the results was obtained by using amyl alcohol in place of butyl alcohol. The optimum concentration of aqueous hydrochloric acid used for saturating the alcohol was again 3N. A similar two-phase effect was observed, as was found with butyl alcohol. One marked difference obtained with amyl alcohol was an absence of separation between copper and lead. A large number of variations in the solvent mixture was tried in order to achieve a separation but without success.

As the acid concentration was increased beyond 3N, the same closing up of the bands (already described for butyl alcohol) was observed. If the hydrochloric acid concentration was raised until the amyl alcohol contained 20% (v/v) of hydrochloric acid (d 1.18), lead was obtained as a separate band above the copper. The R_F values obtained on using amyl alcohol which had been shaken with an

equal volume of 3*N*-hydrochloric acid are given in Table IV. Temperature was again controlled at 22° and time of running was 18 hours.

TABLE IV.

R_F Values using amyl alcohol + 3*N*-hydrochloric acid.

Metal.	Cu.	Bi.	Cd.	Hg.
<i>R_F</i> value	0.07, 0.07	0.36, 0.36	0.63, 0.64	0.70, 0.72

Copper, bismuth, cadmium, and mercury have been separated from lead by using methyl alcohol containing 5% (v/v) of concentrated hydrochloric acid as solvent. The solution of the metals in dilute hydrochloric acid was spotted on a strip and allowed to dry thoroughly in air. The copper, bismuth, cadmium, and mercury travel in mixed diffuse bands with mercury in the solvent front, while the lead moves much more slowly. A lower concentration of hydrochloric acid in the solvent results in a diffuse lead band, whereas higher concentrations cause the lead to move sufficiently fast to overlap the copper.

Another separation of Group IIa metals has been achieved by using pyridine. Bismuth, copper, cadmium, and mercury have been separated in that order. Lead and bismuth remained in the original spot while mercury was just in front of, but overlapping, the cadmium. The original solution of the metals in dilute hydrochloric acid was spotted on a paper strip and then made alkaline by exposure to ammonia vapour. A better separation was achieved by this method than by leaving the original spot acid.

(b) *Analytical Group IIb*: As, Sb, and Sn. (With N. F. KEMBER.)—*Recommended method.* The metals are present as their lower chlorides and the solvent consists of a mixture of acetylacetone saturated with water, with 0.5% (v/v) of hydrochloric acid (*d* 1.18) and 25% (v/v) of acetone.

A very large number of solvents have been examined for the separation of arsenious, antimonous, and stannous chlorides. Many solvents gave a clear-cut separation of antimony and tin from arsenic, but few have been found capable of completely separating antimony and tin. Development with gaseous hydrogen sulphide was used in early tests as a means of detecting the arsenic, antimony, and tin bands; it then appeared possible to separate antimony and tin with a number of solvents. The use of a chloroform solution of dithizone, which was a more sensitive spot test, showed that, while most of the tin appeared to be in a concentrated band separated from antimony, a small amount of tin tailed back to the front edge of the antimony. The separation of arsenic, antimony and tin using ethyl acetate (Burstall, Davies, Linstead, and Wells, *loc. cit.*) suffers from the same disadvantage. The best conditions for obtaining repeatable results with ethyl acetate were as follows. The original solution of the metals in dilute hydrochloric acid was spotted on to a paper strip and allowed to dry in air for 1 hour. The strip was then tested as already described with ethyl acetate saturated with water in an atmosphere of ethyl acetate and water vapour. After evaporation of the solvent the strip was sprayed with a solution of dithizone in chloroform. The arsenic was detected as a very sharp, narrow, yellow band, while the antimony was lower down the strip in a wider reddish band with sharp front and rear edges, and the tin formed a purple band, with a sharp front edge and a trailing rear edge well behind the solvent front. Similar results were obtained with methyl acetate and methyl propyl ketone. Various modifications were tried in order to obtain a better tin band, *e.g.*, (a) addition of ethyl acetoacetate to ethyl acetate, (b) the use of methyl acetate in an atmosphere of chloroform vapour, (c) addition of chloroform to methyl acetate, (d) addition of various concentrations of hydrochloric acid and water to : methyl propyl ketone : methyl propyl ketone-acetone mixtures; methyl acetate-acetone mixtures, etc. A good separation of all three metals was sometimes obtained, but results with respect to the tailing of the tin band were difficult to repeat. Of the alcohols tried, butyl alcohol saturated with water gave the best separations. Antimony and tin were well separated from arsenic, which formed a more diffuse band than that obtained with esters or ketones. Both antimony and tin furnished very narrow bands which, in an atmosphere saturated with the solvent, were very close together or just touching. Addition of hydrochloric acid to the alcohol resulted in overlapping of the antimony and tin bands. Good bands were obtained for all three metals on using ethyl ether saturated with water, but again the antimony and tin bands touched. Other solvents examined include: acetone, methyl ethyl ketone, cyclohexanone, isopropyl ether, "Cellosolve" and its derivatives, pyridine, 2 : 2'-dichlorodiethyl ether, methyl isobutyl ketone, dioxan, formic acid, acetic acid, triacetin, and ethylene dichloride.

Acetylacetone gave the best separation of tin and antimony so far achieved. Separations were first obtained by using acetylacetone saturated with water. There was a tendency, also found with other solvents, for a small amount of tin to remain behind in the original spot. To prevent this effect 0.5% (v/v) of hydrochloric acid (*d* 1.18) was added to the solvent together with 25% (v/v) of acetone. The acetone was added in amount sufficient to enable the hydrochloric acid and acetylacetone to form a clear solution. The acetylacetone was freshly distilled, and the fraction of b. p. 137–141° was collected. This fraction was saturated with water, and to 7.5 ml. of the saturated solvent were added 0.05 ml. of concentrated hydrochloric acid and 2.5 ml. of dry acetone. A solution of arsenious, antimonous, and stannous chlorides in dilute hydrochloric acid (2–4*N*.) was spotted on a paper strip and allowed to dry in air for 15 minutes. The experiment was then run with this solvent for one hour (solvent movement 15 cm.) in an atmosphere saturated with respect to a saturated solution of acetylacetone in water. The complexes formed with acetylacetone were extremely stable, particularly the one formed with tin. Accordingly, the following method was used to develop the bands: the strip was removed from the extraction vessel, and the solvent allowed to evaporate for several minutes. Before the strip was completely dry it was sprayed with a chloroform solution of dithizone and then allowed to dry thoroughly. The tin was found in the solvent front and had a diffuse trailing edge. The antimony formed a wider band with a sharp front and slightly diffuse rear edge; approximate *R_F* value 0.5. The arsenic was present in a very narrow band; *R_F* value approx. 0.2.

(c) *Analytical Group IIIa*: Fe, Al, and Cr.—*Recommended method.* The metals are present as chlorides and the solvent used is glacial acetic acid containing 25% (v/v) of dry methyl alcohol.

Although the separation of iron from aluminium and chromium can be carried out easily with a large number of solvents, the separation of aluminium from chromium was more difficult. A convenient solvent for the separation of iron as ferric chloride from aluminium and chromic chlorides was acetone containing hydrochloric acid. The acid concentration was not critical but acetone +10% (v/v) of hydrochloric acid (d 1.18) produced a narrow band of iron in the solvent front with little movement of aluminium and chromium. Increase in the acid or water content of the acetone resulted in increased movement of aluminium and chromium but always in overlapping bands. A large number of solvents were tested for the separation of aluminium and chromium including: methyl, ethyl, isopropyl, butyl, and amyl alcohols, methyl propyl ketone, ether, isopropyl ether, "Cellosolve," "Carbitol," ethyl acetate, and pyridine. These solvents were tested with varying concentrations of water and hydrochloric acid and in mixtures of these liquids. Separation of aluminium and chromium was not obtained although movement of both metals often took place. In all these experiments the original solution consisted of a solution of ferric, aluminium, and chromic chlorides in dilute hydrochloric acid. Chromium as chromate or dichromate was extremely soluble in organic solvents but reduction to chromic chloride occurred, resulting in a diffuse band of chromium stretching from the solvent front to the original spot.

Aluminium as the trichloride was extracted in the solvent front by aqueous acetic or formic acid solutions (Lacourt *et al.*, *loc. cit.*). With glacial acetic acid, aluminium and chromium moved slightly and together, and iron was extracted in a band some way behind the solvent front. As the concentration of water in the solvent was increased, so did the rate of movement of the three metals, the movement of aluminium being much greater than that of chromium and iron. If a mixture of equal volumes of glacial acetic acid and water was used as solvent, aluminium was found in the solvent front, with iron in a separate band just behind the aluminium, and chromium still further behind, but only just separated from iron. By adjusting the water concentration it was possible to obtain a separation of chromium, aluminium, and iron in that order, proceeding down the strip. Such a separation was achieved by the use of acetic acid containing 10% (v/v) of water but the bands were all very diffuse.

The same type of variation in movements obtained with acetic acid-water mixtures was also obtained with acetic acid-methanol and acetic acid-ethanol mixtures. With these mixtures better bands were obtained and there was less tendency for the formation of the double bands of chromium and iron often obtained with aqueous acetic acid. The best separations were obtained with glacial acetic acid containing 25% (v/v) of dry methyl alcohol. The test solution of iron, aluminium, and chromium chlorides was prepared in 5*N*-hydrochloric acid, spotted on to a paper strip, and allowed to evaporate to dryness in air. Use of a solution containing insufficient free hydrochloric acid gave incomplete extraction and double-band formation of iron. The experiment was allowed to run for 12 hours in an atmosphere saturated with respect to the mixed solvents. A further improvement in the separation was obtained by maintaining a low humidity in the extraction chamber, *e.g.*, by keeping a saturated solution of potassium carbonate in the bottom of the vessel. In order to detect the position of the bands, the solvent was allowed to evaporate and the strip was cut lengthwise into two portions. One portion was sprayed with an alcoholic solution of alizarin, made alkaline by exposure to ammonia vapour, and then warmed. Aluminium appeared as a red band well separated from a purple band due to iron, which was some way behind the solvent front. The other portion of the strip was sprayed first with aqueous sodium peroxide solution and then with a solution of benzidine in acetic acid. Chromium was indicated as a bright blue band just behind the aluminium.

Unsuccessful attempts at separation were made when the nitrates of iron, aluminium, and chromium were used with solvents containing nitric acid or potassium thiocyanate.

(d) *Analytical Group IIIb*: Ni, Mn, Co, and Zn. (With Miss J. N. CLARKE.)—*Recommended method.* The metals are present as chlorides, and the solvent used is acetone containing 5% (v/v) of water and 8% (v/v) of hydrochloric acid (d 1.18).

To obtain a separation of nickel, manganese, cobalt, and zinc (Fig. 6; Strip I) a solution of the metals in dilute hydrochloric acid was spotted on to a paper strip and allowed to dry in air. The solvent consisted of acetone containing 5% (v/v) of water to which was added 8% (v/v) of hydrochloric acid (d 1.18). A solvent movement of about 25 cm. was allowed in an atmosphere saturated with respect to the solvent. The solvent was allowed to evaporate and the strip exposed to ammonia vapour and then sprayed with a mixture of alizarin, rubeanic acid, and salicylaldehyde in alcohol. Nickel was detected as a blue band which had just moved from the original spot. Manganese formed a brownish band below the nickel, whereas cobalt formed a brown band below manganese and zinc was in the solvent front. Approximate R_F values were: Ni, 0.07, Mn 0.3, Co 0.6, Zn 0.9.

The separation of nickel, manganese, cobalt, copper, and iron by using a mixture of methyl propyl ketone, acetone, and hydrochloric acid has been reported by Arden *et al.* (*loc. cit.*), and the application of this separation to the quantitative estimation of these metals will be described in another paper.

(e) *Analytical Group IV*: Ca, Sr, and Ba.—*Recommended method.* The metals are present as chlorides, and the solvent used is pyridine containing 20% (v/v) of water and 1% (w/v) of potassium thiocyanate.

This mixture of metals has not proved easy to separate. The use of solvents alone or containing water or acid was not effective with the chlorides or nitrates. With potassium thiocyanate in certain solvents some success was achieved, and of these solvents pyridine containing 10–20% of water (and 0.5–1.0% of thiocyanate) proved the best. An aqueous solution of the alkaline-earth metals as chlorides was spotted on the paper strip and allowed to dry in air. Extraction was allowed to proceed for 5–6 hours which gave a run of about 20 cm. The atmosphere in the cylinder was saturated with respect to pyridine, and the relative humidity was also controlled between 65 and 80% by having at the bottom of the cylinder a beaker containing either saturated ammonium nitrate or ammonium chloride solution. After the paper had been dried, the separated salts were developed with alizarin to identify the calcium and with sodium rhodizonate to reveal barium and strontium. The calcium occurred just behind the solvent front, with the strontium a little way above the calcium (Fig. 6; Strip II). Under the best conditions the movement of barium is slight, but in some cases, particularly on warmer days if the temperature is not controlled, there is a tendency for the barium to move downwards towards the

strontium. This movement is often irregular and appears to be connected with the movement of the strontium, for it decreases or stops once the calcium and strontium are separated from the barium.

(f) *Analytical Group V: Li, Na, and K. Recommended method.* The metals are present as their chlorides in neutral solution and the solvent used is methyl alcohol.

Only preliminary work has been carried out on the separation of the alkali metals and so far only lithium, sodium, and potassium have been examined. With an aqueous solution containing 100 μg . of each of the metals as chlorides, in 0.05 ml. of solution, separations were obtained with methyl alcohol as solvent. The position of the alkali-metal bands was found by spraying with a mixed solution of silver nitrate and fluorescein and then drying the strip. Three chloride bands were detected, lithium some distance behind the solvent front, sodium about half-way between the original position and the solvent front, and the potassium band just below the original position.

(g) *The Platinum Metals: Pt, Pd, Rh, Ir, Ru, Os, and Au.—Recommended method.* The metals are present as their chlorides or sodium chloro-salts and the solvent used is methyl ethyl ketone containing 30% (v/v) of hydrochloric acid (d 1.18).

Several methods of separation of the platinum metals have been achieved depending on the solvent used and on the valency states of the metals in solution. In order to maintain standard conditions, a chloride solution was prepared by fusing gold, palladium, platinum, rhodium, and iridium chlorides with sodium peroxide. A second mixture also included ruthenium and osmium. The melt was dissolved in water and acidified with hydrochloric acid. The chloride solution was spotted on a paper strip and allowed to dry thoroughly in air. For the subsequent detection of the metals, stannous chloride was found to be a suitable developing reagent for platinum, palladium, gold, and rhodium. A more sensitive reagent was a mixture of stannous chloride and potassium iodide solutions. The strip was warmed gently for the full development of the rhodium colour. Iridium was reduced to the colourless trichloride by stannous chloride. A good spot test was not found for iridium, but reoxidation to the brown tetrachloride was found to be fairly satisfactory. A solution of thiourea in 5*N*-hydrochloric acid was used to test for ruthenium and osmium, and the strip was warmed to develop the colours fully. The work has been mainly directed to the separation of gold, platinum, palladium, iridium, and rhodium and only a small number of experiments have included ruthenium and osmium. A number of solvents separated gold, platinum, iridium, and osmium from rhodium provided that the rhodium was present as sodium chlororhodite (Na_3RhCl_6); rhodium chloride (RhCl_3) is soluble in a number of organic solvents. Acetone +5% of hydrochloric acid (d 1.18) has been found particularly satisfactory provided that the ketone is dry and freshly distilled. The rhodium was left in the original spot, and gold, platinum, palladium, iridium, and osmium were obtained in overlapping bands, gold being in the solvent front. If, in the absence of gold, the original solution was reduced with sulphur dioxide, platinum, palladium, and osmium were still extracted from rhodium with acetone +5% (v/v) of hydrochloric acid (d 1.18) but iridium and ruthenium then remained with the rhodium.

Iridium tetrachloride moved together with the platinum band with all the solvents investigated, but in the presence of an organic solvent containing hydrochloric acid the tetrachloride was reduced or partly reduced to the trichloride. Iridium trichloride behaved similarly to sodium chlororhodite. This reduction of Ir^{IV} to Ir^{III} increased as the concentration of hydrochloric acid in the organic solvent increased. With acetone containing 5% (v/v) of hydrochloric acid (d 1.18) the extraction of iridium tetrachloride from rhodium was practically complete with little or no reduction to the trichloride. The presence of an oxidising agent such as sodium chlorate further aided the extraction by preventing reduction. Ruthenium was extracted by acetone +5% (v/v) of hydrochloric acid (d 1.18) as a wide diffuse band stretching from solvent front to original spot. If sulphur dioxide was first passed through the ruthenium chloride solution, the resulting solution was not extracted by the acetone solvent but remained with rhodium and tervalent iridium. The reduction of the chloride solution of the mixed platinum metals with sulphur dioxide first gave a clear solution, but in a short time a precipitate was formed. This deposit was shown to be due to insoluble ruthenium and osmium compounds. The reduced solution of platinum, palladium, and iridium chlorides was stable.

The separation of rhodium, iridium, platinum, palladium, and gold into four bands, one of which contained both rhodium and iridium, using methyl propyl ketone +30% (v/v) of hydrochloric acid (d 1.18) has already been reported (Burstall *et al.*, *loc. cit.*). The separation of silver, copper, palladium, platinum, and gold by using butyl alcohol saturated with *n*-hydrochloric acid has also been recorded by Lederer (*Nature*, 1948, **162**, 776). Methyl ethyl ketone containing 30% (v/v) of hydrochloric acid (d 1.18) has been used in place of methyl propyl ketone with satisfactory results (Fig. 6; Strip III). Either of the ketonic solvents rapidly reduced Ir^{IV} to the comparatively immobile Ir^{III} which moved with rhodium. With less than 30% (v/v) of hydrochloric acid (d 1.18) in methyl ethyl ketone, Ir^{IV} was partly extracted from the rhodium band owing to incomplete reduction. With methyl propyl ketone containing less than 30% (v/v) of hydrochloric acid (d 1.18) double bands of platinum were formed. On addition of ruthenium and osmium to the system, ruthenium was found with the rhodium and iridium, while osmium was found between, but not completely separated from, the gold and the platinum. The behaviour of ruthenium and osmium was similar with both ketonic solvents.

A number of R_F values were measured and shown to be fairly constant (Table V) providing conditions were sufficiently standardised. The solvent was prepared by dissolving 30 ml. of concentrated "AnalaR" hydrochloric acid (d 1.18) in 70 ml. of methyl propyl ketone or methyl ethyl ketone and the atmosphere of the separation vessel was saturated with respect to the solvent. The solution of platinum metals in 2*N*-hydrochloric acid was spotted on a paper strip and dried for 1 hour.

The solvent was freshly made up each day, since, when kept for a long time with acid, both ketones undergo some decomposition and darkening. The normality of the concentrated hydrochloric acid is likely to vary, but this will not affect the separation although some alteration in R_F values will be observed.

For the separation of rhodium and iridium after removal of gold, platinum, and palladium with either ketonic solvent, the test was run first with methyl propyl ketone or methyl ethyl ketone +30% (v/v) of hydrochloric acid (d 1.18), the solvent was allowed to evaporate, and the strip then sprayed with

an oxidising agent, *e.g.*, chlorine water. After drying, the strip was re-run with acetone containing 5% (v/v) of hydrochloric acid (d 1.18). This second extraction removed the iridium in the new solvent front, which was then allowed to move to a point between the rhodium and palladium bands.

A number of other solvents have been found to give successful or partly successful separations. "Carbitol" or "Cellosolve" containing 20% (v/v) of hydrochloric acid (d 1.18) gave a separation of gold, platinum, palladium, and rhodium into 4 bands; "Cellosolve acetate" containing hydrochloric acid (d 1.18) gave similar results, but in all three cases quadrivalent iridium was found with the palladium band.

A graduated series of results was obtained on using the alcohols with 20% (v/v) of hydrochloric acid (d 1.18). These mixtures being used, the separation improved on ascending the series, methyl, ethyl, butyl, amyl. With amyl alcohol, separation of gold, platinum, palladium, and rhodium into four bands was obtained, but the platinum and palladium bands remained in contact. Iridium was reduced by the amyl alcohol solvent as already described for the ketonic solvents. With butyl alcohol saturated with 2*N*-hydrochloric acid a good separation of rhodium, platinum, palladium, and gold was obtained but iridium was found in a disperse band stretching from the gold to palladium.

(h) *Separation of Gold from the Platinum Metals.—Recommended method.* The metals are present as their chlorides, and the solvent used is ethyl ether containing 2% (w/v) of dry hydrogen chloride and 7.5% (v/v) of dry methyl alcohol.

TABLE V.
R_F Values of platinum metals.

Operator.	Solvent.	Time of run, hrs.	<i>R_F Values.</i>					Wt. of each metal present, μ g.	
			Au.	Os.	Pt.	Pd.	Rh and Ir.		Ru.
A	COMeEt + 30% HCl	16	0.91	—	0.76	0.56	0.06	—	50
"	"	16	0.91	—	0.78	0.56	0.05	—	25
"	"	8	0.95	0.92	0.84	0.61	0.09	0.09	50
"	"	8	0.97	0.93	0.84	0.60	0.09	0.08	25
B	"	16	0.95	—	0.84	0.64	0.17	—	50
"	"	16	0.97	—	0.85	0.65	0.17	—	25
"	"	8	0.97	—	0.83	0.65	0.16	—	50
"	"	8	0.97	—	0.82	0.62	0.15	—	25
A	COMePr + 30% HCl	16	0.91	—	0.75	0.53	0.11	—	50
"	"	16	0.92	—	0.75	0.52	0.10	—	25
"	"	8	0.96	0.89	0.81	0.56	0.11	0.07	50
"	"	8	0.96	0.91	0.81	0.56	0.11	0.07	25
B	"	8	0.98	—	0.80	0.57	0.17	—	50
"	"	8	0.98	—	0.80	0.57	0.15	—	25

A useful quick method for the detection of small amounts of gold in chloride solutions of the platinum metals has been discovered. The solvent consisted of ethyl ether containing 1–2% (w/v) of dry hydrogen chloride to which was added 7.5% (v/v) of dry methyl alcohol. This mixture extracted gold in a narrow band in the solvent front, while the platinum metals remained in the original spot (Fig. 6; Strip V). By using this solvent it was found possible to detect 1 μ g. of gold in several hundred times the amount of each of the platinum metals.

Several practical difficulties have been observed. In experiments with pure gold chloride solution, it was found that when an aqueous solution was allowed to evaporate to dryness on filter-paper, some of the gold salt was reduced to the metal and was not subsequently extracted. A solution in fairly concentrated (>2*N*.) hydrochloric acid, however, could be evaporated to dryness on a paper strip without reduction to the metal and subsequent extraction was complete. With a 12-hour gap between the drying and running of a strip, partial reduction to gold occurred even with use of concentrated hydrochloric acid. In all work with solutions containing gold chloride, therefore, the original solution was made acid with hydrochloric acid and after being spotted on a paper strip was allowed to dry in air for 1 hour and then run with solvent. The methyl alcohol was added to the solvent in order to increase the efficiency of extraction, by decreasing the rate of movement of ether which was too fast for complete extraction of the gold chloride. Addition of too much methyl alcohol brought about partial reduction of the auric chloride. Increase in the concentration of dry hydrogen chloride in the solvent to 4% (w/v) also caused reduction, but variation in the concentration between 1 and 2% (w/v) was without effect. The test was run in an atmosphere of solvent vapour, but the extreme volatility of the solvent made constant atmospheric conditions difficult to maintain. A number of modifications and different solvents were tried in order to overcome this disadvantage, but either the platinum metals moved or the gold was extracted in a band which tailed badly. An example of a solvent which produced tailing was glacial acetic acid containing 4% (v/v) of hydrochloric acid.

(i) *Separation of Mercury from other Metals.* (With Miss M. N. JENKINS.)—*Recommended method.* The metals are present as their chlorides and the solvent used is methyl acetate containing 3% (v/v) of methyl alcohol and 10% (v/v) of water.

The separation of mercury by using tetrahydrofuran as solvent has already been reported (Arden *et al.*, *loc. cit.*). Methyl acetate was found to be a suitable and more readily available solvent for the extraction of mercury as chloride from the following metals: lead, copper, bismuth, cadmium, arsenic, antimony, iron, aluminium, chromium, nickel, cobalt, manganese, and zinc. A number of other solvents including ethyl acetate and methyl propyl ketone also gave good results. Mercuric chloride is

soluble in a large number of organic solvents but is exceptional in that the partition coefficient between most solvents and water falls off rapidly as the acidity of the aqueous layer is increased. Methyl acetate extracts mercuric chloride under widely differing conditions but the width of the mercury band and its position relative to the solvent front vary considerably with small changes. Mercury was extracted in a very narrow band in the solvent front by the following method.

The test solution, which should not contain more than 5% (v/v) of hydrochloric acid (d 1.18) and must have pH <2, was spotted on a paper strip and allowed to evaporate for 10–15 minutes. The solvent was methyl acetate with 10% (v/v) of water and 3% (v/v) of methyl alcohol or the constant-boiling mixture of methyl acetate and methyl alcohol with an added 7% (v/v) of water. The solvent was run in an atmosphere saturated with respect to the vapour of a saturated solution of methyl acetate in water and the temperature was kept constant at 22°. The solvent moved sufficiently far in 20–30 minutes to effect a complete separation. After the solvent had been allowed to evaporate, the strip was made alkaline by exposure to ammonia vapour and sprayed with an alcoholic solution of diphenylcarbazide; mercury was then indicated by a blue band in the solvent front. Two solvent phases were clearly distinguishable on the strip; an upper aqueous phase containing impurities, and a dry solvent phase with the mercury in the front edge. The extent to which water could usefully be added to the solvent was controlled by the behaviour of the upper wet phase. As the amount of water in the solvent was increased the extraction of mercury was improved, but if the amount of water added was increased beyond a definite limit, which varied with temperature, only one aqueous phase was obtained on the strip and all the metals present moved down to the solvent front. The amount of water permissible decreased with increase in temperature. The original spot was not allowed to dry over a prolonged period in order to avoid the formation of basic salt which retained the mercury. It was possible to detect with ease 1 μ g. of mercury by this method in the presence of a large excess of other metals. Some interference in the extraction of mercury was noted with concentrations of copper in the test solution exceeding 10% (w/v) but the extraction was largely independent of the ratio of mercury to copper.

(j) *Separation of Selenium and Tellurium.* (With N. F. KEMBER.)—*Recommended method.* The metals are present in dilute nitric acid solution, and the solvent used is dry butyl alcohol containing 40% (v/v) of dry methyl alcohol.

The following method has been developed for the separation of selenium and tellurium. A solution of the elements as selenite and tellurite in dilute nitric acid was spotted on a paper strip and allowed to dry thoroughly in air. The strip was treated with a solvent consisting of a mixture of 60% (v/v) of dry butyl alcohol and 40% (v/v) of dry methyl alcohol, in an atmosphere saturated with respect to the solvent vapour and with a relative humidity maintained at 50%. The solvent was allowed to diffuse 8–10 cm. down the strip (approx. 2 hours). After evaporation of the solvent, the strip was developed by spraying with stannous chloride solution. The tellurium which had moved only slightly from the position of the test sample was indicated as a black band, whereas selenium formed an orange band half-way between the solvent front and the original spot position (Fig. 6; Strip VI). The lower limit of detection for selenium, with the normal 1" wide strip and stannous chloride as developer, was 5 μ g., but 1 μ g. was detected in 1000 μ g. of tellurium by using a triangular strip. This separation was also obtained with test solutions consisting of tellurate and selenate in dilute nitric acid, but more difficulty was experienced in detecting the position of the bands. Sulphate, if present, did not affect the separation but remained with the tellurium. The original spot on the paper strip had to be thoroughly dry, otherwise excessive tailing of tellurium occurred; moreover, both alcohols in the solvent mixture must be dry. Increase in the percentage of methyl alcohol in the solvent mixture gave more rapid extraction of selenium in a narrower band but excessive forward tailing of tellurium was also obtained. The humidity of the extraction vessel was controlled at approximately 50% by means of a saturated solution of calcium nitrate kept in the bottom of the container. Variation in the humidity was found to alter the extraction in the following ways: (a) Increase in humidity gave more complete extraction of selenium. (b) At relative humidities >30%, slight movement of tellurium took place; this increased as the humidity was raised. (c) The relative movement of selenium decreased as the humidity was increased. (d) "Edge effects" for selenium decreased as the humidity was raised.

The conditions chosen for extraction therefore represent a compromise.

(k) *Separation of Thorium, Scandium, and the Rare Earths.* (With N. F. KEMBER.)—*Recommended method.* The metals are present as nitrates, and the solvent used is tetrahydrofuran containing 5% (v/v) of water and 10% (v/v) of nitric acid (d 1.42).

The separation of scandium from the rare earths on a column of cellulose by aid of an ethyl ether-nitric acid mixture has already been briefly reported (Burstall *et al.*, *loc. cit.*). A solvent containing diethyl ether is not suitable for use with the paper-strip technique, but tetrahydrofuran was found to be a suitable solvent, after addition of water and nitric acid, for the separation of scandium and thorium from each other and from the rare earths, on the same strip.

A solution of the rare earths, thorium, and scandium in dilute nitric acid was spotted on a paper strip and dried thoroughly in air. The solvent, consisting of tetrahydrofuran containing 5% (v/v) of water and 10% (v/v) of nitric acid (d 1.42), was allowed to diffuse about 15 cm. down the paper strip. By controlling the relative humidity of the atmosphere at about 80% with a saturated solution of ammonium chloride in the bottom of the extraction vessel, a narrow and concentrated band of scandium was obtained. The solvent was allowed to evaporate, and the strip placed for about 10 minutes in an atmosphere of ammonia. The strip was sprayed with an alcoholic solution of alizarin and finally with *N*-acetic acid; thorium was then detected as a violet-blue band with a sharp front edge about 0.6 cm. behind the solvent front. Scandium formed a more diffuse band about 2.5 cm. in front of the rare earths which moved only slightly from the original position of the test spot. With alizarin the rare earths gave a similar colour to thorium but a redder tint was obtained with scandium. By this method 1 μ g. of scandium was detected in 1000 μ g. of the rare earths.

Scandium was also separated from the rare earths by using methyl acetate containing 10% (v/v) of water and 5% (v/v) of nitric acid (d 1.42) as solvent. The strip was allowed a solvent run of 25 cm.; scandium was then found in a similar position to that obtained with tetrahydrofuran but in a narrower

band. Thorium, however, was detected as a more diffuse band between scandium and the solvent front.

(1) *Separation of F, Cl, Br, and I.* (With D. B. REES EVANS.)—*Recommended method.* The acid radicals are present as their sodium salts and the solvent used is pyridine containing 10% (v/v) of water.

The anions, fluoride, chloride, bromide, and iodide, have been separated as their sodium salts by using pyridine or acetone as solvent. The acetone used contained 20% (v/v) of water, and the pyridine was AnalaR pyridine, with 10% (v/v) of added water. Separations were not affected by a variation of $\pm 2.5\%$ in the water concentration of the solvents. The test solution, consisting of a neutral aqueous solution of sodium chloride, bromide, and iodide (the sodium salts were found preferable to the potassium salts), was spotted on a paper strip and allowed to dry in air. The strip was run in an atmosphere saturated with solvent vapour for $1\frac{1}{2}$ —2 hours. The solvent was allowed to evaporate from the strip which was then sprayed with a mixture of silver nitrate and fluorescein solutions. On drying, the halides appeared as three characteristic dark bands, which when viewed under ultra-violet light appeared as dark areas on a fluorescent background (Fig. 6; Strip IV). Strips one inch wide being used, it was possible to detect 1 $\mu\text{g.}$ of bromide and 4 $\mu\text{g.}$ of chloride or iodide in 0.05 ml. of original solution by this method. With a triangular strip, 1 $\mu\text{g.}$ of chloride or iodide per 0.05 ml. of test solution was detected. Separations were carried out in which 1—10 $\mu\text{g.}$ of one or two of the halides have been detected in the presence of 10 times the quantity of either one or both of the others. No difficulty has been experienced in dealing with concentrations up to 200 $\mu\text{g./0.05 ml.}$ of each of the halides.

A more limited study has been made of the behaviour of fluoride. Sodium fluoride was added to the original solution of sodium chloride, bromide, and iodide. Strips were run with both the acetone and the pyridine solvent. The position of the fluoride band was detected by spraying with zirconium-alizarin reagent. For this purpose each strip was cut in two longitudinally; one part was then sprayed with silver nitrate-fluorescein reagent and the other with zirconium-alizarin solution. When pyridine was used as solvent the fluoride remained in the original spot. With the acetone solvent the fluoride moved but still remained separated from the chloride band. With this solvent a trace of fluoride was left in the original spot. Use of a wet spot overcame this disadvantage but R_F values were not then repeatable. R_F Values obtained by using a dry spot were fairly constant with both solvents as indicated below:

Radical.	R_F Values for halides.							
	Acetone + 20% (v/v) H_2O .				Pyridine + 10% (v/v) H_2O .			
Fluoride	—	—	0.26	0.24	—	—	0.00	0.00
Chloride	0.50	0.53	0.51	0.49	0.25	0.22	0.23	0.24
Bromide	0.62	0.62	0.62	0.60	0.47	0.47	0.47	0.47
Iodide	0.77	0.77	0.77	0.76	0.72	0.70	0.72	0.71

(m) *Miscellaneous Separations.* (With N. F. KEMBER.)—In addition to readily recognised groups of metals the separation of a number of special mixtures of metals has been examined, as follows:

(1) The separation of nickel, manganese, cobalt, copper, and iron (of interest in analysis of steel) has been studied, the solvent being either acetone or methyl ethyl ketone mixtures with hydrochloric acid. (2) In parallel experiments, using the same solvents, the separation of uranium, vanadium, and titanium has been explored.

For this purpose two solutions were prepared, one containing nickel, manganese, cobalt, copper, and iron in dilute hydrochloric acid, and another containing uranium, vanadium, and titanium, also in dilute hydrochloric acid. A portion of each solution was placed upon a separate paper strip and allowed to dry in air; the solvent was then allowed to run down both strips for a distance of 15 cm. A series of approximate R_F values obtained with different solvents are shown in Table VI. It can be seen that nickel, manganese, cobalt, copper, and iron have been separated with methyl ethyl ketone + 8% (v/v) of hydrochloric acid (d 1.18), and uranium has been extracted from vanadium and titanium with a variety of solvents.

Two lines drawn between a pair of R_F values in the table indicate that the two metals concerned are in bands which overlap. One line indicates that the bands just touch. The abbreviations D or VD written after an R_F value indicate that the band is diffuse or very diffuse. Where two R_F values are given for the same metal then the metal is in a double band.

With methyl ethyl ketone as solvent two phases were obtained on the paper strip; acetone, although miscible with water, also gave two phases. With both solvents the phases consisted of a lower dry solvent phase, in which the acid concentration was low, and an upper phase of aqueous solvent in which there appeared to be an acidity gradient, the strip being most acid at the top and becoming progressively less acid nearer the solvent front. The approximate position of the interphase boundary was measured and the R_F value is recorded with those of the metals in Table VI. It appears to be directly related to the proportion of acid and water in the solvent, the ratio of the wet to dry solvent phase increasing as the concentration of acid is increased and falling off as the water content is increased. The position of the interphase boundary is important in that copper tends to split into two bands, a main band in the wet solvent phase and a weaker band in the dry solvent phase. If, however, the R_F value of the interphase boundary is sufficiently high, copper is found only in the wet solvent phase. The behaviour of uranium is also unusual in that it is sometimes found in the wet solvent phase and at others in the dry solvent phase.

During a study of the double band formation of copper it was noticed that the acid ketonic solvents used extracted a certain amount of copper and iron from the filter-paper. After runs on blank sheets and strips of paper, a band of iron was detected in the solvent front and some way behind a band of copper was obtained. Further investigations are being made to extract this soluble inorganic material without interfering with subsequent chromatographic separations.

TABLE VI.

 R_F values with different solvents.

Solvent.	COMe ₂ +5% (v/v) H ₂ O + 5% (v/v) HCl.		COMe ₂ +10% (v/v) H ₂ O + 5% (v/v) HCl.		COMeEt +6% (v/v) HCl.	COMeEt +8% (v/v) HCl.	COMeEt +5% (v/v) H ₂ O + 8% (v/v) HCl.	COMeEt +10% (v/v) H ₂ O + 10% (v/v) HCl.	COMeEt +10% (v/v) H ₂ O + 5% (v/v) HCl.
	Metal.								
	Strip 1.								
Ni	0.09	<u>0.12</u>	<u>0.01</u>	0.01	0.01	<u>0.01</u>	<u>0.10</u>	<u>0.005</u>	
Mn	0.21	<u>0.20</u>	<u>0.13</u>	0.18	0.18	<u>0.13</u>	<u>0.13</u>	<u>0.01</u>	
Co	0.43	<u>0.27</u>	<u>0.42D</u>	0.54	0.54	<u>0.30</u>	<u>0.21</u>	<u>0.04</u>	
Cu	0.61, 0.80	0.63, 0.92	<u>0.65VD</u>	0.71	0.71	<u>0.72VD</u>	0.53, 0.70D	0.26, 0.39	
Fe	0.97	0.97	<u>0.90</u>	0.93	0.93	0.91	0.90	0.70VD	
	Strip 2.								
Ti	—	<u>0.17</u>	—	—	—	—	<u>0.10</u>	<u>0.02</u>	
V	0.18	<u>0.17</u>	0.07	0.14	0.14	0.09	<u>0.12</u>	<u>0.03</u>	
U	0.65	0.81	0.76	0.87	0.87	0.73	0.62	0.30	
R_F value of interface...	0.64	0.64	0.50	0.82	0.82	0.72	0.64	0.37	

(3) *Separations with Butyl Alcohol.*—The solvent butyl alcohol saturated with 3N-hydrochloric acid, used for the separation of the metals of the analytical group IIa, has been employed in a number of other separations. The members of the following pairs of metals are mutually interfering, when undergoing estimation on the polarograph: copper and bismuth, vanadium and iron, uranium and molybdenum, and lead and antimony; but, as may be deduced from the R_F values in the table below, separation is possible by using butyl alcohol saturated with 3N-hydrochloric acid. A chloride solution of the metals is treated as described in Section (a) (p. 518). After suitable development, copper, vanadium, uranium, and lead are found on the top portion of the strip, above the iron band below which the bismuth, molybdenum, and antimony bands are located. The individual members of each of these groups of four metals may then be estimated by the polarograph since the other three metals present will not interfere.

 R_F Values with butyl alcohol + 3N-hydrochloric acid.

Metal	V	Cu	Pb	U	Fe	Mo	Bi	Sb
R_F value	0.18	0.19	0.23	0.26	0.42	0.53	0.57	0.78

Enhanced Colours.—It has been noticed that when a strip is sprayed with developing reagent before all the solvent has evaporated, the colours obtained are often very much more intense, than those obtained normally with the reagent and the radical after solvent has been removed, *e.g.*, arsenic, antimony, and tin with dithizone in chloroform in the presence of ethyl acetoacetate, scandium and the rare earths with alizarin in the presence of methyl acetate, gold and the platinum metals with stannous chloride in the presence of various "Carbitol" derivatives, the halides with silver nitrate and fluorescein in the presence of pyridine.

It is thought that this effect may have application in increasing the sensitivity of "spot" tests. The opposite effect has also been noticed. It is then often necessary to warm the strip for some time after developing it to allow the colour reaction to proceed.

Preparation of Solvents.—*Acetone.* Refluxed with solid potassium hydroxide and permanganate for 1 hour; the fraction, b. p. $56^\circ \pm 0.5^\circ$, was used.

Methyl ethyl ketone. As acetone. The fraction, b. p. $79.5\text{--}79.7^\circ$, was used.

Methyl n-propyl ketone. As acetone. The fraction, b. p. $99\text{--}102^\circ$, was used.

Methyl alcohol. Redistilled, b. p. 63° .

n-Butyl alcohol. Dried over calcium; b. p. $116.5\text{--}117.5^\circ$.

Amyl alcohol and pyridine. Both of AnalaR brand.

Ethyl acetate. Shaken with saturated calcium chloride solution, dried (CaCl_2), and distilled; b. p. $76.5\text{--}77.5^\circ$.

Methyl acetate. Either the constant-boiling mixture with methyl alcohol, b. p. 54° , was used, or the ester was dried (CaCl_2) and distilled, the fraction of b. p. $56.5\text{--}58^\circ$ being used.

Ethyl ether. Refluxed with alkaline permanganate, distilled, dried (CaCl_2), and fractionated. The solvent used was free from peroxide and had a water content of less than 1%.

Tetrahydrofuran. As ethyl ether; the fraction of b. p. $79\text{--}80^\circ$ was used.

DISCUSSION.

Measurement of R_F Values.—The method used for measuring R_F values requires explanation. The original solution was placed along a pencilled line ruled across the paper strip. The

distance moved by an element was considered to be the distance between this line and the "centre of gravity" of the band formed by the element; this was compared with the movement of the solvent measured from the same line. This method of measurement was simple but suffered from several disadvantages; no indication was given of the width of a band, without which an R_F value can be misleading, *e.g.*, using amyl alcohol as solvent the R_F values for cadmium and mercury were very close but the bands were so narrow that separation occurred, whereas with the same amounts of lead and copper and the same solvent, a difference in R_F values was obtained, but without separation, the lead forming a narrow band in the forward area of a wide copper band. An alternative method of measurement would be to give the R_F values for the front and the rear boundary of each band; this, however, would be difficult for those bands with diffuse boundaries. When two liquid phases are obtained on a paper strip there is some advantage to be gained from using the aqueous phase front (Lederer, *Nature*, 1948, 162, 776) as a reference point for the calculation of R_F values, but in many cases the position of the phase front has been very indeterminate and in others only one phase appeared to exist.

Constancy of R_F Values.—Providing close control of all the variables is maintained, constant R_F values are obtained. The necessity for such close control would be a disadvantage in routine applications but, as found with amino-acids (Conden *et al.*, *loc. cit.*), relative rates of movement are constant with less control. Thus, one band on a strip can usually be identified by its position relative to known bands. Again, the large number of characteristic "spot" tests available for the detection of inorganic radicals diminishes the necessity for accurate measurement of R_F values. Constancy of solvents, temperature, and saturation of the atmosphere being assumed, a number of factors were found to affect R_F values, *viz.* :

(a) The presence of other anions. This is very common. A good example is the presence of chloride in separations carried out with nitrate solutions.

(b) The acidity of the original solution. This effect has been reported by Lacourt *et al.* (*loc. cit.*), and variations have been found although the original solution was first allowed to evaporate. The cause may be due to the need for acid in the formation of a complex soluble in the organic solvent complex, *e.g.*, gold chloride. On the other hand, the presence of acid may tend to prevent complex formation, *e.g.*, the extraction of mercury with methyl acetate from a strongly acid solution.

(c) The time of running of a strip. This factor is not important in all cases but is important in certain separations. In the separation of copper, lead, bismuth, cadmium, and mercury with butyl alcohol saturated with 3*N*-hydrochloric acid, R_F values increase with the time of running and this coincides with a decrease in the rate of movement of the solvent front. The reason for these changes is not known with certainty but several points may be relevant. At the beginning of a run, the paper is in equilibrium with the prevailing laboratory atmospheric conditions but after some twelve or more hours in an atmosphere saturated with respect to butyl alcohol and dilute hydrochloric acid the strip has absorbed so much water vapour that difficulty is often found in detecting the exact position of the solvent front. It is this increase in water content of the cellulose which undoubtedly accounts for the decrease in the rate of movement of the solvent front. A further variable which has not, so far, been investigated is the esterification of the butyl alcohol.

(d) The presence and concentration of other cations. A few cases of interference by one metal on the extraction of another have been observed. This appears to be due to complexation formation or to the amphoteric properties of one of the metals.

The Formation of Two Phases.—The following explanation is put forward to correlate all the facts observed. Consider a solvent containing water passing down a strip of paper. The cellulose will absorb water from the solvent until an equilibrium is set up. Since the affinity of cellulose for water is much higher than that of most organic solvents, equilibrium is reached when the solvent is almost dry and the cellulose almost saturated with water. This will result in a clearly defined wet area of strip, and further down the strip there is an area of dry solvent. If now the percentage of water in the solvent is progressively increased, the ratio of area of wet phase to area of dry phase increases. This type of behaviour was observed on adding increasing quantities of water to the constant-boiling mixture of methyl acetate and methyl alcohol used for the extraction of mercury.

A solvent containing hydrochloric acid as well as water may next be considered. In some cases the presence of hydrochloric acid in the solvent increases its affinity for water. At the same time there is partition of hydrochloric acid between the water in the cellulose and the solvent. The net result is that the solvent competes more effectively with the cellulose for the

water and travels further down the strip before losing all its water. This results in (1) a hydrochloric acid gradient in the wet part of the strip and a very low concentration of hydrochloric acid in the dry phase (both these effects can be noted in separations with acetone, hydrochloric acid, water mixtures); (2) a lower concentration of water in the wet phase area of the strip than that obtained when using an organic solvent containing water only; (3) a larger ratio of wet to dry phase on the strip. The last two points are supported by the behaviour of a number of solvents, *e.g.*, butyl alcohol, amyl alcohol, or methyl propyl ketone, with increasing hydrochloric acid content. The concentration of water in the paper underlying the wet phase decreases with increase of hydrochloric acid concentration until it is very difficult to detect the exact position of the interphase boundary. This change is accompanied by an increase in wet/dry phase ratio which continues until only one phase is obtained. These observations are illustrated by the behaviour of platinum on extraction with methyl propyl ketone containing hydrochloric acid.

Band Width.—Those salts which have a high solubility in organic solvents tend to be extracted in the solvent front. When this occurs, *e.g.*, mercuric chloride with methyl acetate, gold chloride with a mixture of ethyl ether and hydrochloric acid, and ferric chloride with acetone-hydrochloric acid mixtures, the width of the band in the solvent front is usually very much less than the width of the original spot. When two phases exist on a paper strip, a similar decrease in band width is sometimes noticed if a metal tends to travel just above the inter-phase boundary, *e.g.*, arsenious chloride with ethyl acetate-water mixtures. A somewhat different case arises when cadmium and mercury chlorides are extracted with butyl alcohol saturated with 3*N*-hydrochloric acid. Both form bands narrower than the original spot and neither is in the solvent front, although the cadmium is probably just above the interphase boundary. The second case is explicable if a soluble metallo-complex is formed only in the presence of a definite excess of water or acid concentration.

Further work is necessary to explain the other two cases.

It is hoped to devise more general separations when further basic knowledge of the behaviour of different salts with various solvents has been obtained.

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