INORGANIC CHROMATOGRAPHY

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Chromatography has been simply defined as " those processes which allow the resolution of solute mixtures by selective fixation and liberation on a solid surface or support with the aid of a fluid streaming in a definite direction ".[1] A great variety of chromatographic systems is possible; thus, many different materials have been used as the solid surface or support, usually called the adsorbent, while the fluids, or solvents, employed include aqueous solutions, organic solvents, and even gases. An exact classification of all the variations is not possible, but an arbitrary division into four groups may be made, according to the mechanism by which the solute is fixed or adsorbed on the adsorbent. The classification has to be arbitrary since many solutes are retained on an adsorbent by more than one process. The four types of adsorbent which will now be considered are: (*a*) Surface-active adsorbents, which include such materials as activated alumina. (*b*) Bound or supported liquids; these give rise to partition chromatography, the most popular form being paper chromatography, where the supported liquid is water in the cellulose and the solute undergoes partition between this phase and the solvent. (*c*) Chemically reactive solids; these give rise to adsorption by means of direct chemical combination with the solute to form recognised compounds. (*d*) Ion-exchange materials; these may be considered as particular examples of chemically active solids.

To whom should go the honour of having performed the first chromatographic separation is still a matter of discussion; there is, however, no doubt that the first major publication on the subject was by F. Goppelsroeder, a student of C. F. Schönbein,[2] who in 1861 noticed, on dipping filter-paper into an aqueous solution of an electrolyte, that the water rose to a greater height than did the dissolved salt. Moreover, he found that different solutes rose to different heights up the filter-paper. These observations formed the basis of many years of work by Goppelsroeder, who studied the behaviour of organic compounds under similar conditions and ultimately published his results in Dresden in 1910 in a book entitled " Kapillaranalyse ". As may be gathered from this title, Goppelsroeder attributed his separations to capillary forces acting in the paper. That this is not the full story has been explained by F. Feigl, who has elaborated and developed the ideas of Schönbein and Goppelsroeder into the well-known technique of " Spot Tests ".[3] Adsorption of the solute by the filter-paper does play an important part in many separations of this type.

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[1] L. Zechmeister, " Progress in Chromatography, 1938—1947 ", Chapman & Hall, London, 1950.

[2] *Pogg. Ann.*, 1861, **114**, 275.

[3] " Chemistry of Specific Selective and Sensitive Reactions," English transl., R. E. Oesper, Academic Press Inc., New York, 1949.

Similarly, to whom to attribute the first chromatographic separation by a truly adsorptive process is still a matter of argument, but here again there is little doubt that the first major contribution came from the botanist, M. Tswett.[4] The technique by which he was able to separate the components of chlorophyll and the isomers of carotene has been described fully many times and will not be further dealt with here. A jump of some 37 years is necessary to arrive at the first application of Tswett's technique to inorganic separations. It was shown by G. M. Schwab and K. Jockers [5] that, when a solution of metal salts, of suitable pH, was filtered through a column of alumina, the metals were precipitated in a series of sharply-defined zones and always in a definite order. The reader is referred to any one of a number of text books [1, 6, 7, 8, 9] for a full description of these early experiments together with details of the first chromatographic separation of inorganic anions.

The growth of inorganic chromatography has been characterised by a tendency to lag behind developments in organic chromatography. Partition chromatography was devised initially for the separation of amino-acids [10] and it was used in the separation of a number of other organic materials before it was applied to inorganic separations. Ion-exchange materials were initially prepared for the exchange of inorganic ions, but the number of applications of ion-exchange chromatography to organic separations probably equals if not exceeds the applications to inorganic separations. One field is, however, peculiar to inorganic separations. It was introduced by H. Erlenmeyer and H. Dahn,[11] who discovered the possibility of separating inorganic mixtures on columns prepared from organic precipitation reagents, such as hydroxyquinoline. This appears to have no application so far in organic separations.

There is now evidence of a growing interest in inorganic chromatography and a realisation of its possibilities, so it is to be hoped that the lead, long held by organic chromatography, may be somewhat reduced.

Surface Active Adsorbents

The study of the separation of inorganic ions on alumina, initiated by G. M. Schwab and his co-workers, was continued over a number of years.[12] It was shown that the length of an adsorption zone was proportional to the

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[4] " Chromophylls in the Plant and Animal World " (Warsaw, 1906), Academic Press, New York, 1949.

[5] *Angew. Chem.*, 1937, **50,** 546.

[6] L. Zechmeister, " Principles and Practice of Chromatography ", English transl., A. L. Bacharach and F. A. Robinson, Chapman & Hall, London, 1941.

[7] T. I. Williams, " An Introduction to Chromatography ", Blackie & Son, London, 1946.

[8] H. Cassidy, " Adsorption and Chromatography ", Interscience Publishers, New York and London, 1951.

[9] H. H. Strain, " Chromatographic Adsorption Analysis ", Interscience Publishers, New York and London, 1941.

[10] A. J. P. Martin and R. L. M. Synge, *Biochem. J.*, 1941, **35,** 1358.

[11] *Helv. Chim. Acta,* 1939, **22,** 1369.

[12] G. M. Schwab and G. Dattler, *Angew. Chem.*, 1937, **50,** 691 ; 1938, **51,** 709 ; G. M. Schwab and A. N. Ghosh, *ibid.*, 1939, **52,** 666 ; 1940, **53,** 39.

concentration of the material present and thus it is possible to carry out an approximately quantitative estimation. By using columns of 1—2 mm. diameter and specific spot-test reagents, micro-amounts of an ion present in a large volume of solution can be detected. The ions present are concentrated by the adsorption process into a narrow zone and with the aid of a suitable reagent a sensitivity of detection equal to that of normal spot tests is obtained. The application of alumina chromatography to the general analysis of an unknown mixture is difficult because of the lack of separation between several pairs of metals. It is, however, possible to separate the individual metals of an analytical group after separation into groups by the conventional methods.[13] More recently, the separation of the platinum metals on alumina has been investigated.[14] It is claimed that extremely sharp separations can be obtained, the order of increasing adsorption being Rh, Pd, Pt, Ru, and Ir, but certain conditions with regard to the age of the test solution and absence of interfering metals must be fulfilled. Thus the platinum group can be separated from Pb, Cu, Zn, and Ni, but in the presence of iron, mixed complex formation gives rise to complicated chromatograms.

The separation of organometallic complexes on columns of alumina has been demonstrated. It has been claimed [15] that one part of cobalt in 2×10^9 parts can be detected by the addition of a chloroform solution of the complex of the metal with β-nitroso-α-naphthol to an alumina column. After being washed with a small amount of alcohol, the cobalt complex is visible as a red band at the top of the column. The cobalt complex with Nitroso-R-salt has been utilised in the determination of cobalt in carbon steels.[16] A solution of the salt was added to a suitably buffered solution of the steel. After addition of perchloric acid, the solution was passed through a column of alumina, which had been pretreated by washing with M-perchloric acid. The excess of reagent and iron salts was washed through the column with hot nitric acid. The cobalt complex was finally eluted with M-sulphuric acid.

A number of mechanisms have been proposed to explain the separation of inorganic ions on alumina. Technical alumina invariably contains sodium aluminate as an impurity and adsorption has been supposed to be due to cation exchange between the sodium and adsorbed ion.[12] Again, technical alumina has an alkaline reaction, and it has been suggested that precipitation of basic salts occurs.[12] Both carbonates and bicarbonates are normally present in technical alumina, and precipitation of basic carbonates may take place.[17] Although all three of these reactions probably occur when technical alumina is used, they are not essential, since separations are equally possible on sodium-free alumina. The possibility of exchange between cations and aluminium ions has been proposed,[12] but since the

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[13] H. H. Fillinger and L. A. Trafton, *J. Chem. Educ.*, 1952, **29**, 285.
[14] G. M. Schwab, *Discuss. Faraday Soc.*, 1949, **7**, 170.
[15] R. O. Bach and A. A. Garmendia, *Anal. Asoc. Quim., Argentina*, 1951, **39**, 11.
[16] J. A. Dean, *Anal. Chem.*, 1951, **23**, 1096.
[17] G. Siewert and A. Jungnickel, *Ber.*, 1943, **76**, 210.

position of aluminium adsorption in the chromatographic series has been located between lead and cadmium this does not explain adsorption of ions lower in the list. Other mechanisms suggested include : amphoteric adsorption by alumina, giving rise to both anionic and cationic exchange ; preferential adsorption of ions which then bind the ion of opposite charge by equivalent secondary adsorption and molecular adsorption.[18]

Considerable practical evidence has been given in support of a theory of hydrolytic adsorption.[19] This suggests that the hydrolysis of a metallic salt according to the equation

$$M^{\cdot\cdot} + H_2O \rightleftharpoons M(OH)^{\cdot} + H^{\cdot}$$

is encouraged by the removal of hydrogen ions by aluminium-ion—hydrogen-ion exchange, thus :

$$Al_2O_3 + 6H^{\cdot} \rightleftharpoons 2Al^{\cdot\cdot\cdot} + 3H_2O$$

The liberated aluminium salt is then adsorbed as a basic salt :

$$2Al^{\cdot\cdot\cdot} + 2H_2O \rightleftharpoons 2Al(OH)^{\cdot\cdot} + 2H^{\cdot}$$

Since the alumina is in excess the process goes to completion. This theory explains the observed separations and with a few exceptions the order of adsorption of metals is the same as the order for the degree of hydrolysis of the metallic salts. The order of adsorption is also the same as the order of ionic potential values, the reciprocal of dialysis coefficient values, and the reciprocal of diffusion coefficients ; moreover the most highly hydrated cations are the most strongly adsorbed. This agreement is explained by the fact that co-ordinated water molecules in an aquo-complex are orientated with the hydrogen atoms directed outwards. The opposite type of polarisation occurs with water adsorbed on alumina and the hydrogen atoms are directed towards the oxygen molecules of the adsorbent. Thus the suitably polarised water molecules of the aquo-complexes will be readily adsorbed by the alumina. Further, the degree of polarisation of the molecules will increase with the ionic potential, which is in agreement with the correlation between ionic potential values and degree of adsorption.

In addition to work on columns of alumina, separations have been carried out on paper impregnated with alumina.[20, 21] The paper is prepared by soaking it in sodium aluminate solution, allowing it to dry, and then soaking it in sodium hydrogen carbonate solution. The paper is finally washed for several days in distilled water and then allowed to dry. About 0·1 ml. of test solution is sucked up to a height of 1—3 cm. on a strip of paper, which is then treated with water until the water rises to a height of about 10 cm. The same type of separation as is obtained on columns of alumina occurs, and the order of adsorption is identical. If the paper is pretreated with dilute nitric acid, separation of anions may be obtained, as with columns of alumina similarly treated. The zone length is directly proportional to the concentration, but different ions give different zone lengths. In general, for ions of the same valency, zone length increases

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[18] P. W. M. Jacobs and F. C. Tompkins, *Trans. Faraday Soc.*, 1945, **41,** 388, 395, 400.

[19] L. Sacconi, *Discuss. Faraday Soc.*, 1949, **7,** 173.

[20] H. Flood, *ibid.*, p. 190.

[21] Y. Oka and A. Murata, *Sci. Rep. Res. Inst. Tôhoku Univ.*, 1951, *A*, **3,** 82.

with decreasing adsorption properties. Increase in valency results in increasing zone lengths and the zone length is to some extent affected by the anion present. A disadvantage of the separations on alumina is that separation is only into zones. In most cases there is some overlapping of zones and even in the best separations the zones remain in contact. It is possible to obtain clear cut and absolute separations by addition of complexing agents to a mixture of cations. The undissociated molecules are not adsorbed on alumina, with the result that addition of a complexing agent to a mixture of cations will permit separations depending upon the relative stability of the complexes formed. Thus a solution of glycine added to a copper solution will result in a mixture of unadsorbed copper glycinate molecules and adsorbable copper ions, giving two bands in the chromatogram. If the amount of glycine is sufficient to form a complex $[CuGl_2]$ with the whole of the copper, none of the copper is adsorbed. This may be used for the determination of copper by a method known as a chromatographic titration. To aliquots of the unknown copper solution are added known amounts of glycine, and the solutions are chromatographed. By extrapolation of the adsorbed copper zones to zero length, the equivalent amount of glycine, and hence the unknown copper concentration, may be calculated. If two metals are present in solution and the stability constants of their complexes with glycine differ sufficiently, complete separation of the two metals may be achieved. Thus on chromatographing a mixed solution of nickel and cobalt in the presence of a suitable concentration of glycine, two completely separated zones are obtained, one of cobalt, which has moved little from its original position, and another of nickel, which has migrated some way along the paper.

Another modification of Schwab's technique, due to J. E. Meinhard and N. F. Hall,[22] uses a thin film of alumina mixed with an adhesive on a microscope slide as adsorbent. Spots of test solution are applied to the film and the chromatogram of concentric rings is examined under the microscope.

Other metallic oxides have been used as adsorbents, including chromic oxide,[23] which was claimed to give better results than alumina but has not proved a popular adsorbent.

Zinc sulphide has been used as an adsorbent [24] for the separation of copper and cadmium. Since this separation is almost certainly dependent upon the formation and relative stability of the sulphides of the two metals, it ought perhaps to be included with the separations described in the next section, carried out on chemically active solids.

Partial separation of the isotopes of neon has been achieved by chromatographic separation on charcoal at the temperature of liquid nitrogen.[25] The work was undertaken in order to test equations derived for the behaviour of two solutes (which gave non-linear isotherms) in the region of the frontal interboundary. Best results were obtained by immersing the charcoal

[22] *Anal. Chem.*, 1949, **21,** 185.

[23] H. Goto and Y. Kakita, *J. Chem. Soc. Japan*, 1942, **63,** 120.

[24] J. M. Bach, *Anal. Asoc. Quim., Argentina*, 1937, **183,** 55.

[25] E. Glueckauf, K. H. Barker, and G. P. Kitt, *Discuss. Faraday Soc.*, 1949, **7,** 199.

column in liquid nitrogen and then filling it with helium. Neon was then passed through the column and replaced the less-adsorbed helium and advanced with a self-sharpening front boundary. Enrichment factors of up to 15 were obtained on quantities of the order of a milligram, but it is not suggested that the method could be readily used on a larger scale. The result of varying experimental conditions could be forecast by consideration of the theoretical equations, and theoretical and practical values for " theoretical plate " height were in close agreement.

Chemically Reactive Solids

A type of chromatography which so far appears to have been confined to the inorganic field was introduced by Erlenmeyer and Dahn in 1939.[11] They employed as adsorbent " oxine " (8-hydroxyquinoline) diluted with at least its own weight of an inert material such as starch or Kieselguhr. On adding a solution of cations of preadjusted pH to a column of the adsorbent and washing with a buffer solution separation of the mixture into a number of zones occurred. Each zone had the distinctive colour of the hydroxyquinoline complex of the metal concerned. The order of adsorption proceeding down the column has been given by G. Robinson [26] as VO_3^-, Mn^{++}, WO_4^{--}, Ag^+, Cu^{++}, Bi^{+++}, Ni^{++}, MoO_4^{--}, Al^{+++}, Co^{++}, Zn^{++}, Mg^{++}, Fe^{+++}, UO_2^{++}. The same worker has shown that the technique may be applied to quantitative analysis. If carefully controlled conditions, particularly with regard to pH of the test and wash solutions, are used, the length of zone produced is reproducible and proportional to the concentration of metal present. The method has been used for the analysis of both zinc and silver brazing alloys. When dealing with the first, an upper green zone due to copper was obtained, below which were two yellow zones, the top one due to nickel and the lower one to zinc. The colours of the lower zones were sufficiently alike to make measurement of the length of the zinc zone impossible, but advantage was taken of the fact that the zinc complex gives a bright green fluorescence in ultra-violet light. With the silver alloy tested, an upper yellow zone due to silver was obtained, separated from a yellow zinc zone by a green zone due to copper. Far less satisfactory results were obtained when an attempt was made to apply the method to the analysis of ferrous alloys. The large concentration of iron led to the formation of the intensely black ferric complex. Efforts to wash the complex through the column led to a spreading of the colour throughout the column, thus masking the presence of other cations. On using a slightly acid (pH 3) wash solution, a much speedier movement of the ferric complex was obtained, but the wash solution dissolved sufficient of the oxine to ruin the zones due to other metals. This solubility of the adsorbent in slightly acid solutions is a limiting factor which prevents a much wider application of the technique. A clear picture has not been given of the mechanism by which zoning of cations in these columns occurs. It may be due to a combination of two factors, difference in affinity of oxine for oxine salts and difference of solubility of the oxine salts in water. It is significant that the order of

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[26] E. Glueckauf, K. H. Barker, and G. P. Kitt, *Discuss. Faraday Soc.*, 1949, **7**, 195.

adsorption is very similar to the order of stability of the oxine complexes in acid solution.

Separations on columns of oxine are confined to those metals which form insoluble oxine complexes (oxinates), but other organic reagents have been employed as adsorbents. Sodium, potassium, magnesium, and ammonium ions have been separated on columns of violuric acid.[27] All give violet to brick-red colours with the reagent. A compound column containing 4-hydroxyimino-5-oxo-3-phenyl*iso*oxazoline in the upper half and violuric acid in the lower half has been employed for the quantitative separation of sodium and potassium.[28] With the aid of a column of dimethylglyoxime it is possible to detect traces of nickel in the presence of large amounts of cobalt, iron, and even palladium.[29] The nickel is retained as a red complex at the top of the column, while the other metals are washed through. These separations on columns of reactive chemicals suffer from the same major disadvantage as a separation on alumina, namely, that they are not complete. Even in the best cases, where clearly defined zones are obtained, the zones are in contact with each other. This disadvantage was overcome by P. P. Hopf,[30] who used, as adsorbent, filter paper which was impregnated first with starch or peptised alumina and then with an organic reagent. Thus he was able to show that, on placing a drop of an aqueous solution containing manganese and iron on a piece of paper impregnated with alumina and formaldoxime hydrochloride, complete separation took place. On making the paper alkaline with ammonia vapour a central spot due to manganese was observed, separated by a blank zone from a coloured ring due to iron. Using a formula suggested by Flood, Hopf was able to apply the method to quantitative analysis. Flood had shown that the radius of a spot formed by a solute was a function of its concentration plus a constant for the paper, from which Hopf deduced the expression :

$$\frac{a}{b} = \frac{r_1^2 - r_2^2}{r_3^2 - r_4^2} K_{ab}$$

for a binary mixture. This was derived from the equations :

$$a = \pi(r_1^2 - r_2^2)K_a \quad \text{and} \quad b = \pi(r_3^2 - r_4^2)K_b$$

K_{ab} being put for K_a/K_b, where a = concentration of first substance and r_1 and r_2 are bounding radii of the annular zone which it forms, b = concentration of second substance and r_3 and r_4 are bounding radii of the annular zone which it forms, and K_a and K_b are constants which may be determined by an experiment on a solution of known concentration. The method was also utilised in the analysis of ferromolybdenum alloys by using paper impregnated with alumina and 8-hydroxyquinoline, and for the separation of ammonium and potassium salts by using paper impregnated with starch and violuric acid.

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[27] H. Erlenmeyer and W. Schroenauer, *Helv. Chim. Acta*, 1941, **24**, 878.

[28] H. Erlenmeyer and J. Schmidlin, *ibid.*, p. 1213.

[29] F. Burriel Marti and F. Pino-Perez, *Anal. Chim. Acta*, 1949, **3**, 468.

[30] *J.*, 1946, 785.

Partition Chromatography

The number of separations of inorganic materials achieved by chromatographic means has been greatly increased by the application of partition chromatographic techniques to mixtures of inorganic salts. In the organic field, partition separations have been carried out with a number of adsorbents such as cellulose, powdered rubber, silica gel, and Celite, but for inorganic substances attention has been almost totally confined to cellulose. The reader is referred to a recent booklet for an excellent review of the use of cellulose in both organic and inorganic chromatography.[31] The cellulose has been used both in sheet form and as a powder, and the solvents employed have been organic liquids usually containing water and often a mineral acid. To improve separations various compounds capable of complexing inorganic salts have been added to the solvents.

In their preliminary experiments, Martin and his co-workers attempted to separate the acetyl derivatives of the amino-acids by partition chromatography on silica gel.[10, 32] This was only partly successful and they later introduced a technique employing cellulose as the adsorbent.[33] In this method the aqueous test solution is applied to a small area near one end of a strip of filter-paper and allowed to dry. The strip is then suspended vertically with the end nearest the test spot dipping into a solvent container. Both solvent and strip are enclosed by a sealed jar in order to maintain constant atmospheric conditions. The solvent diffuses down the strip, passes through the spot of test solution and carries with it, at differential rates, the inorganic materials present. After the solvent has moved sufficiently far to achieve a separation of the mixture, the position of the cations or anions on the strip may be found by spraying the strip with a suitable spot-test reagent. A modification of this system, originated by Williams and Kirby,[34] has also proved popular with a number of investigators. For this technique a sheet of filter-paper is rolled to form a cylinder, which can be stood on end in a solvent container. The test solution is applied as spots a few cm. up from the lower end of the cylinder. Again the whole apparatus is enclosed by some suitable vessel to maintain constant atmospheric conditions. In this case diffusion of the solvent is upward and separation into a series of spots takes place. A third technique, due to L. Rutter,[35] has been used in which a circular disc of filter-paper is employed. Two parallel cuts about 2 mm. apart are made from the circumference to the centre of a disc of filter-paper. The strip of paper thus formed is bent down at right angles to the disc of paper, thus forming a " tail ". The test solution is applied as a spot to the centre of the filter-paper, which is then placed in a horizontal position supported by the edge of the bottom half of a Petri dish. The " tail " is allowed to dip into a solvent receptacle contained

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[31] J. N. Balston and B. E. Talbot, " A Guide to Filter Paper and Cellulose Powder Chromatography ", H. Reeve Angel & W. & R. Balston Ltd., 1952.

[32] A. H. Gordon, A. J. P. Martin, and R. L. M. Synge, *Biochem. J.*, 1943, **37**, 79.

[33] R. Consden, A. H. Gordon, A. J. P. Martin, and R. L. M. Synge, *ibid.*, 1944, **38**, 224.

[34] R. J. Williams and H. Kirby, *Science*, 1948, **107**, 481.

[35] *Nature*, 1948, **161**, 435 ; *Analyst*, 1950, **75**, 37.

by the Petri dish, and paper and dish are covered by the second half of the dish. The solvent rises up to the tail of filter-paper and spreads radially through the test spot. A chromatogram is formed in which the inorganic ions are found as a series of concentric annuli. Use of the upward or downward diffusion method seems largely a matter of personal choice for the operator. Rutter's technique is employed when a quick qualitative result is required.

These methods of separation, using sheets of filter-paper, are limited in the amount of material which can be dealt with in any one experiment. The maximum amount of material normally dealt with is of the order of 1 mg., although a few cases have been described where by virtue of the special properties of the material being dealt with or by using wide strips, up to 0·15 g. of metal has been employed. By using a column of cellulose pulp there is theoretically no reason why the amounts of material separated should have any limitations, since it is quite practicable to use very large columns. Workers at the Chemical Research Laboratory have, in fact, carried out separations on up to ½ kg. amounts of metal. In using a cellulose column [36, 37] the cellulose is packed in pulp form into a glass tube containing the organic solvent mixture to be used during the separation. The aqueous solution containing the material solution is transferred to the top of the column, and the solvent passed through. In order to avoid clogging of the column and undesirable wall effects, the test solution is often transferred to the top of the column by first absorbing it on a wad of cellulose and then transferring the mixture. The separated metals are collected in suitable fractions in the eluate solvent solution. In such experiments concentration of excess of water at the top of the column is likely to be high at the beginning of the run. To prevent mechanical carry down of the water between the cellulose and glass walls of the tube it has been found advantageous to treat the inner surface of the glass tube with a water repellant such as dimethyldichlorosilane or other suitable silane. Use of cellulose columns has a number of advantages over the use of more classical adsorbents. The metal is obtained in eluate solvent solution ; it is not necessary to extrude the adsorbent and wash the metal from a particular zone. Any residual metallic salts in the column can normally be removed by washing through with water or dilute acid. In the few cases of particularly strong adsorption, complete recovery can be effected by ashing the cellulose.

Apart from the technique and apparatus used, the approach to inorganic partition chromatography has varied with different workers. One group have concentrated on separating the metals of previously isolated groups of metals, another has concerned itself with the separation of a large number of metals in an unknown mixture. A further type of separation is that of one metal from a very large number of others. A few inorganic salts have exceptionally high solubilities in organic solvents, and advantage has been taken of these peculiarities to produce highly specific separations. Thus uranium has been tested for in solutions of minerals in nitric acid by using

[36] F. H. Burstall, G. R. Davies, and R. A. Wells, *Discuss. Faraday Soc.*, 1949, **7**, 179.
[37] F. H. Burstall and R. A. Wells, *Analyst,* 1951, **76**, 396.

a paper-strip technique.[38] The most satisfactory results were obtained with 2-methyltetrahydrofuran as solvent, but good separations were obtained with the simple ester ethyl acetate. In both cases water and nitric acid were added to the solvent and uranium was extracted in a narrow band in the solvent front. Most other metals remained in the original test-spot, or moved only slightly. By cutting out the portion of the strip containing the uranium, ashing, and determining the uranium in the ash, the separation was shown to be quantitative [39] and the method has been used for the determination of uranium in minerals and ores. Uranium has also been extracted quantitatively on a larger scale from a variety of minerals by using a cellulose column with ethyl ether containing nitric acid as solvent.[37] Mercuric chloride is extremely soluble in a number of organic solvents, but unlike other inorganic salts its solubility decreases as the concentration of acid added to the solvent increases. By using as solvent a mixture of methyl acetate and water, mercuric chloride has been separated from a wide range of metals, many of which are themselves extracted by the same solvent in the presence of hydrochloric acid, both in strip [40] and column experiments.[36] By using butyl alcohol saturated with N-hydrochloric acid thallic chloride has been separated quantitatively [41] from a number of metals. Here advantage was taken of the fact that the thallium salt moved in the solvent front, by tapering the paper strip and collecting the first few drops of solvent to drip from the end. The metallic salt was thus isolated in a small volume of solvent. A similar technique has been adopted for the quantitative separation of gold by a paper-strip method.[42] Auric chloride is very soluble in a number of organic solvents but there is a strong tendency for it to be reduced to the metal, particularly in the presence of an organic solvent and cellulose. This has been prevented by the use of ethyl acetate containing nitric acid as solvent. The test solution was prepared in dilute hydrochloric acid and applied to a paper strip. The gold chloride was extracted in a narrow band in the solvent front, and providing the solvent was saturated with water, separation was achieved from all metals with the exception of uranium, antimony, and tin. The solubility of ferric chloride in organic solvents is well known, and various solvents may be used for the paper-strip separation of iron from other metals. Mixtures of ketones with hydrochloric acid extract ferric chloride particularly efficiently. With simple mixtures of acetone containing hydrochloric acid very sharp separations from titanium, nickel, lead, aluminium, manganese, cobalt, etc., have been obtained. With higher ketones the list of metals from which separation is possible, grows rapidly.

The extreme insolubility of some inorganic salts in organic solvents makes it possible to carry out the opposite type of separation from that just described. By choice of a suitably polar solvent a large number of metals

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[38] T. V. Arden, F. H. Burstall, and R. P. Linstead, *J.*, 1949, S 311.

[39] J. A. Lewis and J. M. Griffiths, *Analyst*, 1951, **76**, 388.

[40] F. H. Burstall, G. R. Davies, R. P. Linstead, and R. A. Wells, *J.*, 1950, 516.

[41] J. R. A. Anderson and M. Lederer, *Anal. Chim. Acta*, 1950, **4**, 513.

[42] N. F. Kember and R. A. Wells, *Analyst*, 1951, **76**, 579.

may be extracted, leaving the required insoluble salt still in the original position of the test-spot or at least near the top of the strip. Thus many metals may be separated from lead as their chlorides with methyl alcohol containing dilute hydrochloric acid. Similarly, the extreme insolubility of nickel, aluminium, and titanium salts in a number of organic solvent mixtures has permitted the ready extraction of other metals from them. Advantage of the insolubility of nickel salts has been taken in the determination of impurities in nickel-plating baths.[43] An aliquot of the plating solution was extracted in a column of cellulose with acetone containing hydrochloric acid. Six metals, iron, manganese, cobalt, copper, zinc, and cadmium, were quantitatively recovered and estimated in the eluate solution. This separation is particularly interesting in that the test solution was in sulphuric acid but the extracted metals were eluted as their chlorides. The mass of nickel sulphate was slowly converted into the chloride by the hydrochloric acid in the solvent and free sulphuric acid appeared in the eluate.

Considerable success has been achieved in the separation of groups of metals, and the metals of each of the groups of the routine qualitative analysis tables have been separated on paper strips.[40] In some cases the study of the separation of one particular group has been extended to include metals not present in the group. The metals of Group IIA, lead, copper, bismuth, cadmium, and mercury, have been separated as their chlorides with butyl alcohol saturated with 3N-hydrochloric acid as solvent, and the behaviour of the additional metals vanadium, uranium, iron, molybdenum, and antimony with the same solvent has been studied.[40] It was found that vanadium moved with copper, uranium with lead, antimony with bismuth, and molybdenum moved very close to bismuth but a clear separation of iron between copper and bismuth was obtained. A number of naturally occurring groups or pairs of metals are separated only with difficulty by normal methods. Many of these have been separated by paper-strip technique. Thus aluminium, indium, gallium, and zinc [44] have been readily separated as their chlorides with butyl alcohol containing 20% of concentrated hydrochloric acid. The platinum metals Pt and Pd, together with Au, Ag, and Cu, have been separated with butyl alcohol, saturated with N-hydrochloric acid [45] and both methyl propyl ketone and ethyl methyl ketone containing concentrated hydrochloric acid have been used in the separation of Au, Pt, Pd, Ir, and Rh mixtures.[40] By suitable choice of solvent and acid radical the members of the following pairs have been separated: aluminium and beryllium,[46] zirconium and hafnium,[49] and selenium and tellurium.[40] Scandium and thorium have been separated from each other and from the rare earths.[40] Separation of the alkali metals and alkaline earths on paper strips has been studied by a number of workers.[40, 47, 48] Although separations have been achieved, location of the

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[43] F. H. Burstall, N. F. Kember, and R. A. Wells, *J. Electrodepositors Tech. Soc.*, 1951, **27**, 261.

[44] T. V. Arden, F. H. Burstall, G. R. Davies, J. A. Lewis, and R. P. Linstead, *Nature*, 1948, **162**, 691.

[45] M. Lederer, *ibid.*, p. 776.

[46] G. H. Osborn and A. Jewsbury, *ibid.*, 1949, **164**, 443.

metals on the strips has given some difficulty. Violuric acid has been used to test for Li, Na, K, Be, Mg, Ca, Sr, and Ba after separation of the acetates with ethyl alcohol containing acetic acid.[47] More recently, thiovioluric acid has been introduced [48] as a more sensitive reagent than violuric acid. The metallic salts fluoresce strongly, and since in this particular separation the areas of the spots vary linearly with the quantity of ion present, quantitative estimations of the cations has been possible.

There are a number of disadvantages in using a fluoride system for paper-strip separations, but with metals such as niobium and tantalum the advantages of a fluoride solution are obvious. By using a Polythene apparatus, it has proved possible to separate niobium and tantalum from a number of metals and from each other on paper strips, ethyl methyl ketone containing hydrofluoric acid being used as solvent.[49]

The R_F value for an element, defined as the ratio of the distance moved by the element to that moved by the solvent front, conveniently describes its behaviour. Reasonably constant R_F values are obtained if sufficient precautions are taken to standardise conditions. The R_F values of some 40 elements have been determined by Lederer,[50] using the solvents : ethyl alcohol plus 10% v/v 5N-HCl, *iso*propyl alcohol plus 10% v/v 5N-HCl, butyl alcohol saturated with N-HCl, and amyl alcohol saturated with 2N-HCl. These form a useful list which can be consulted to ascertain whether the metals present in a given mixture can be separated with a particular solvent. With few exceptions, the R_F values for a metal decrease as the molecular weight of the alcohol used increases. With mixed alcohol solvents the R_F values obtained were less than the mean value for the individual alcohols. The R_F values for a large number of metals in butyl alcohol saturated with N-hydrochloric acid have been compared [51] with values obtained with butyl alcohol containing hydrogen bromide and with butyl alcohol–nitric acid mixtures. These results emphasise the importance of the nature of the acid radical in most of these separations. On using the nitrate-containing solvent, uranium was the only metal of those tested which showed appreciable movement. With a solvent containing either hydrochloric or hydrobromic acid appreciable movement was observed with all those metals which readily form chloride or bromide complexes. E. C. Martin [52] has measured R_F values for a number of metals with butanol containing thiocyanic acid, using Rutter's technique. Others from the same laboratory [53] have measured R_F values for 22 metals, using diethyl ether saturated with N-HCl, N-HBr, N-H_2SO_4, or N-HNO_3 as solvents. The only metals to give significant movement with all four solvents were arsenic, antimony, and tin.

Workers at Bristol University have made considerable progress in working out a separation scheme, which can be applied directly to any unknown

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[47] H. Erlenmeyer, H. von Hahn, and E. Sorkin, *Helv. Chim. Acta*, 1951, **34,** 1419.

[48] H. Seiler, E. Sorkin, and H. Erlenmeyer, *ibid.*, 1952, **35,** 120.

[49] Chemical Research Laboratory, unpublished work.

[50] *Anal. Chim. Acta*, 1951, **5,** 185.

[51] M. Lederer, *ibid.*, 1950, **4,** 629.

[52] E. C. Martin, *ibid.*, 1951, **5,** 511.

[53] J. R. A. Anderson and A. Whitley, *ibid.*, 1952, **6,** 517.

mixtures of metals.[54, 55] They have preferred to use nitrates, which are relatively insoluble in organic solvents, and induce solubility by the addition of strong complexing agents such as benzoylacetone. Two different procedures have been described for the identification of an unknown mixture. In the first, three separate chromatograms are run using the following mixed solvents : butanol–water–benzoylacetone, collidine–water, and dioxan–antipyrine. The metals are identified by their R_F values and by their characteristic reaction to spot tests. In some cases two-dimensional chromatography is employed. In this process one solvent is run normally down a sheet of paper on which the test solution has been placed in an upper corner. The paper is then turned through 90°, and after the solvent has been allowed to dry off, a second solvent is allowed to diffuse down the paper. In a few cases the process is repeated with a third solvent. In the second separation procedure, a series of chromatograms are run with the butanol–water–benzoylacetone mixture. A systematic testing of the chromatogram with a series of spot test reagents then enables the unknown mixture to be identified.

The behaviour of the oxine complexes of a number of cations has been studied by carrying out separations on strips of paper impregnated with 8-hydroxyquinoline.[56] The paper was prepared by treating it with an alcoholic solution of the oxine reagent and then allowing it to dry. The solvents tested included pyridine, chloroform, acetone, and methyl, ethyl, *n*-propyl, *iso*propyl, and *n*-butyl alcohols, and a number of separations were shown to be possible. Together with R_F values, the workers in this field have listed a number of corresponding S, or spreading factor values. If A is the initial band width and B_i the final band width for a cation i, then $S_i = B_i/A$. By a consideration of both R_F and S values it is possible to predict whether a complete separation of two metal zones is possible. The interesting observation has also been made that cations may be divided into two groups, those whose R_F values increase as the chain length of the alcohol used as solvent is increased, and those whose R_F values decrease, which supports the supposition that two types of 8-hydroxyquinoline complex may be formed. Separation of those metals which form chelate complexes with oxine has also been attempted [57] by using butanol containing 20% (v/v) of 12N-hydrochloric acid. A solution of the oxinates of the metals in dilute hydrochloric acid was applied to a paper strip, which was then run with the butyl alcohol solvent. Although good separations were obtained, it appears from the R_F values, that the metals were in fact separated as their chloride complexes rather than as their oxinates. The chelated compounds undergo decomposition in the presence of the acid in the solvent, and the oxine is found in a separate band (R_F value 0·5).

Use of a specific complexing agent has been applied to the separation of one metal from a group of others. Thus bismuth has been extracted with

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[54] F. H. Pollard, J. F. W. McOmie, and I. I. M. Elbeih, *J.*, 1951, 466, 470.

[55] F. H. Pollard, J. F. W. McOmie, and H. M. Stevens, *J.*, 1951, 771.

[56] D. E. Laskowski and W. C. McCrone, *Anal. Chem.*, 1951, **23**, 1579.

[57] W. A. Reeves and T. B. Crumpler, *ibid.*, p. 1576.

acetone containing nitric acid from admixture with lead and copper after complexing the cations with diallyldithiocarbamidohydrazine.[58] Copper has been extracted quantitatively on a paper strip from a number of other metals, butanol saturated with 2N-ammonia and dimethylglyoxime [59] being used as solvent.

In addition to these separations on a column scale, to which reference has already been made, a variety of other metals have been handled on the larger scale made possible by the use of a cellulose column. The separation of zirconium from hafnium has been carried out [60] by using ethyl ether containing nitric acid as solvent. The separation was not quantitative, but by the use of large columns capable of dealing with 100 g. of zirconia it was possible to prepare substantial amounts of hafnia-free zirconia. Other separations which have been performed on an analytical scale include the extraction of thorium and scandium from minerals and ores with ethyl ether–nitric acid mixtures,[61, 62] the removal of zinc from solders by extraction with butanol containing 2% v/v HCl (*d* 1·18),[63] and the separate extraction of both niobium and tantalum from a variety of minerals.[64, 65, 66] For this last separation, which was carried out in the presence of free fluoride, a Polythene tube replaced the normal glass column. The test material was prepared in dilute hydrofluoric acid solution and the tantalum was extracted with ethyl methyl ketone saturated with water; the niobium was subsequently extracted with ethyl methyl ketone containing 12½% of hydrofluoric acid (40% aqueous). The only interference came from tungsten, which is partly extracted with the niobium. A simple separation which might readily be applied to quantitative analysis is the extraction of vanadium and molybdenum from titanium.[67] Both metals have been readily separated by using acetone containing 2% v/v HCl (*d* 1·18) as solvent. Ketonic solvents have also been used for the separation of the platinum metals, rhodium, iridium, palladium, and platinum.[68]

Mixtures of anions have been separated by procedures similar to those employed for cations. Solutions of the sodium salts have normally been employed in order to avoid interference but in most cases only the anionic part of the salt moves. The cations remain in the original spot or move only little. One group of workers have used pyridine containing water for the separation of fluoride, chloride, bromide, and iodide.[40] Another has separated chloride, bromide, iodide, and thiocyanate with butyl alcohol saturated with 1·5N-ammonia.[69] A third group has measured the R_F values

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[58] M. M. Singh and J. Gupta, *J. Sci. Ind. Res. India*, 1951, **10**, *B*, 289.

[59] J. R. A. Anderson and M. Lederer, *Anal. Chim. Acta*, 1951, **5**, 396.

[60] Chemical Research Laboratory, unpublished work.

[61] N. F. Kember, *Analyst*, 1952, **77**, 78. [62] A. F. Williams, *ibid.*, p. 297.

[63] J. R. Bishop and H. Liebmann, *Nature*, 1951, **167**, 524.

[64] F. H. Burstall, P. Swain, A. F. Williams, and G. A. Wood, *J.*, 1952, 1497.

[65] A. F. Williams, *ibid.*, p. 3155.

[66] R. A. Mercer and A. F. Williams, *ibid.*, p. 3399.

[67] Chemical Research Laboratory, unpublished work.

[68] D. B. Rees-Evans and R. A. Wells, in the press.

[69] M. Lederer, *Science*, 1949, **110**, 115.

of chloride, bromide, iodide, chlorate, bromate, iodate, nitrite, nitrate, arsenite, arsenate, carbonate, phosphate, chromate, thiocyanate, and sulphate, employing a solvent mixture of butyl alcohol, pyridine, and 1·5N-ammonia in the proportions 2 : 1 : 2.[54] The separation and estimation of borate from silicate and molybdate by means of acetone plus concentrated hydrochloric acid has been described.[70] Following the work by C. S. Hanes and F. A. Therwood [71] on the separation of the phosphoric esters, other workers have described the separation of ortho-, pyro-, meta-, and poly-phosphates. Acid solvents have been used; thus one group of investigators have used a 70 : 30 : 5 mixture of *iso*propyl alcohol, water, and trichloroacetic acid,[72] another has favoured an aqueous butanol–acetic acid mixture.[73] The separations have also been carried out with alkaline solvents, *e.g.*, a 40 : 20 : 39 : 1 mixture of *iso*propanol, *iso*butanol, water, and ammonia (*d* 0·880).[72] By using as solvent a mixture consisting of equal volumes of *n*-butanol, dioxan, and N-ammonia the separation of phosphates, phosphites, and hypophosphites has been demonstrated.[74]

Cellulose has proved to be a very convenient adsorbent on which to carry out partition separations, but other materials have been used. The complexes of a number of metals with 8-hydroxyquinoline have been separated on a column of silica gel.[75] The oxinates were adsorbed on the column from a solution in chloroform and eluted with a mixture of chloroform and ethyl alcohol. The order of adsorption was found to be : Cu > Co > Fe > Al > Bi > Ni > Pb. By elution with chloroform containing 1% of ethyl alcohol it was possible to obtain a complete separation of copper, nickel, and cobalt. Silica gel columns have also been used for the separation of zirconium and hafnium.[76] On passage of a 1·5% solution of mixed zirconium and hafnium tetrachlorides in methyl alcohol through a silica gel column, the hafnia is preferentially adsorbed and it has been shown possible to recover 60 g. of zirconia containing 0·1% of hafnia from 455 g. of the mixed materials with the aid of a column consisting of 290 g. of the silica adsorbent.

The principles of electromigration have been combined with those of chromatography to produce separations of inorganic ions. The technique was introduced by G. Haugaard and T. D. Kroner [77] for the separation of amino-acids and has been named electro-chromatography. While the solvent was allowed to diffuse down a sheet of paper bearing the amino-acid mixture, a potential gradient was applied across the paper at right angles to the flow of solvent. The negatively charged acids moved towards the anode and the basic acids towards the cathode, thus producing a two-dimensional

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[70] A. Lacourt, G. Sommereyns, and M. Claret, *Mikrochem. Mikrochim. Acta*, 1951, **38**, 444.

[71] *Nature*, 1949, **164**, 1107.

[72] J. P. Ebel and Y. Volmar, *Compt. rend.*, 1951, **233**, 415.

[73] T. Ando, J. Ito, S. Ishi, and T. Soda, *Bull. Chem. Soc. Japan*, 1952, **25**, 78.

[74] A. Bonnin and P. Sue, *Compt. rend.*, 1952, **234**, 960.

[75] L. B. Hilliard and H. Freiser, *Anal. Chem.*, 1952, **24**, 752.

[76] R. S. Hansen and K. J. Gunnar, *J. Amer. Chem. Soc.*, 1949, **71**, 4158.

[77] *Ibid.*, 1948, **70**, 2135.

separation. Using a similar technique, H. A. Strain [78] has demonstrated the separation of inorganic ions. Separation of inorganic ions by electromigration on filter-paper has been achieved by a number of workers,[79–85] but the combination of this technique with chromatography has introduced a number of new possibilities. Not only is it possible to carry out more difficult separations, but the process may also be made continuous. An electrochromatographic cell has been designed by Strain for this purpose.[86] A sheet of filter paper 0·1″ thick was clamped between two glass plates held vertically. Two electrodes, consisting of fine platinum wire, were inserted along the vertical edges of the paper. At the top of the glass plates was arranged an electrolyte holder so that electrolyte flowed continuously down the whole width of the paper. With the voltage applied, a solution of the mixture to be separated was continuously applied to the centre of the top edge of the sheet of paper. As the test solution was carried down the sheet by the flow of electrolyte, varying transverse movement of the ions present took place and diverging zones of the separated ions were formed. By a suitable arrangement of " collecting wicks " at the bottom of the strip it was possible to collect the electrolyte solution in portions containing the separated ions. A variety of electrolytes has been suggested for different separations. Thus conditions for the separation of large amounts of phosphate from calcium have been given. The electrolyte, 0·1M-lactic acid, was allowed to flow through a 12-inch wide cell at the rate of 150 ml. per hour. A mixture of calcium chloride and phosphoric acid in 1N-hydrochloric acid constituted the original solution. A potential of 300 v, giving a current of 150 milliamp., was applied. For a full discussion of the technique the reader is referred to a report by the U.S. Atomic Energy Commission.[87]

Ion Exchange

Since the discovery by J. T. Way [88] in 1850 of the ion-exchange properties exhibited by materials of the aluminosilicate type, substances capable of undergoing ion exchange have been used for a wide variety of purposes. These include the concentration of dilute solutions, removal of interfering ions, chromatographic separations, the study of complexes, determination of activity coefficients, and use as catalysts for organic reactions. A thorough review of the whole field of ion exchange appeared in an earlier Review,[89] and the reader is referred to this and to a number of excellent

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[78] H. H. Strain and J. C. Sullivan, *Anal. Chem.*, 1951, **23,** 816.

[79] H. J. McDonald, M. C. Urbin, and M. B. Williamson, *Science*, 1950, **112,** 227.

[80] K. A. Kraus and G. W. Smith, *J. Amer. Chem. Soc.*, 1950, **72,** 4329.

[81] M. Lederer and F. L. Ward, *Australian J. Sci.*, 1951, **13,** 114.

[82] M. Lederer, *Nature*, 1951, **167,** 864.

[83] M. Lederer and F. L. Ward, *Anal. Chim. Acta*, 1952, **6,** 355.

[84] J. R. A. Anderson and M. Lederer, *ibid.*, p. 472.

[85] H. H. Strain, *Anal. Chem.*, 1952, **24,** 356.

[86] T. R. Sato, W. P. Norris, and H. H. Strain, *Anal. Chem.*, 1952, **24,** 776.

[87] *Idem*, Office of Tech. Services, Dept. of Commerce, Washington, D.C. ; U.S.A.E.C. Document ANL 4724 (1951).

[88] *J. Roy. Agric. Soc.*, 1850, **11,** 313.

[89] J. F. Duncan and B. A. J. Lister, *Quart. Reviews*, 1948, **2,** 307.

reviews [90–93] and text books [8, 94, 95] for a detailed treatment of the theory and practice of ion exchange. The present discussion is confined to the use of ion exchange in inorganic chromatography, and deals with the principles and observations which have been utilised in obtaining separation of various substances with the aid of ion-exchange materials. Although a few chromatographic separations have been studied on naturally occurring and synthetically prepared siliceous materials, *e.g.*, zeolites and permutites, and others have been attempted on ion-exchange materials prepared by the sulphonation of coal, most interest has been concentrated on synthetic resin ion exchangers. The first cation exchanger of this type was prepared by B. A. Adams and E. L. Holmes [96] by the condensation of phenols with formaldehyde. The product yielded insoluble resin containing ionisable hydroxyl groups capable of ion exchange. The same workers produced anion-exchange resins by condensation of polyamines with formaldehyde. Since this early work, the search for stable resins having a high capacity has led to the production of a wide variety of exchangers. Cation exchangers combining the properties of physical and chemical stability with high capacity have been produced by nuclear sulphonation of polymeric aromatic hydrocarbons, and most of the recent work on the separation of cations by ion exchange has been carried out on materials of this type. The study of anionic separations has received great impetus from the introduction of strongly basic anion exchangers of high physical stability. The stability of the earlier weakly basic anion exchangers, which relied upon primary, secondary, or tertiary groups for their ion-exchange properties, left much to be desired. The new materials containing quaternary ammonium functional groups are strong bases and have a relatively high chemical and physical stability.

The general equation for the equilibrium between univalent ions on an exchanger and in solution may be written

$$\mathrm{RA} + \mathrm{B}^{\pm} \rightleftharpoons \mathrm{RB} + \mathrm{A}^{\pm}$$

where R is the insoluble resin ion. By the mass law

$$a_{\mathrm{RB}}a_{\mathrm{A}^{\pm}}/a_{\mathrm{RA}}a_{\mathrm{B}^{\pm}} = K \quad . \quad . \quad . \quad . \quad (1)$$

If the solutions are dilute, the ratio of activities in solution may be replaced without much error by the ratio of concentration and (1) becomes

$$[\mathrm{RB}]\gamma_{\mathrm{RB}}/[\mathrm{RA}]\gamma_{\mathrm{RA}} = K_1[B^{\pm}]/[\mathrm{A}^{\pm}] \quad . \quad . \quad . \quad (2)$$

where γ_{RB} and γ_{RA} are the activity coefficients of the ions A and B in the resin phase. Since the ionic strength in the resin is constant, $\gamma_{\mathrm{RB}}/\gamma_{\mathrm{RA}}$ may be assumed nearly constant over a wide variation in the ratio [RB]/[RA] and (2) becomes

$$[\mathrm{RB}]/[\mathrm{RA}] = K_{\mathrm{A}\rightarrow\mathrm{B}}[\mathrm{B}^{\pm}]/[\mathrm{A}^{\pm}]$$

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[90] R. Kunin, *Anal. Chem.*, 1949, **21,** 87.

[91] *Ibid.*, 1950, **22,** 64. [92] *Ibid.*, 1951, **23,** 45. [93] *Ibid.*, 1952, **24,** 64.

[94] F. C. Nachod, " Ion Exchange ", Academic Press Inc., New York, 1949.

[95] R. Kunin and R. J. Myers, " Ion Exchange Resins ", John Wiley & Co. Inc., New York, 1950.

[96] *J. Soc. Chem. Ind.*, 1935, **54,** 1T; B.P. 450,308, 450,309 (1934).

$K_{A \to B}$ may be termed the affinity coefficient and gives a measure of the relative affinity of the resin for the ions A and B. By a similar argument an expression for the more general case of multivalent exchange may be derived. The affinity coefficients of a number of cations relative to hydrogen and of a series of anions relative to chloride have been measured.[97–100] The numerical values obtained vary with the type of functional group and the degree of cross-linking of the resin but the order of affinities remains the same. In general, the higher the charge on a cation the more strongly it is adsorbed, and for ions of the same charge resin affinity increases with decrease of hydrated ionic radius. At the present moment it is not possible to make a similar generalisation correlating anion size with order of adsorption.

Consideration of the difference in affinities leads to the simplest type of chromatographic analysis, named by A. Tiselius [101] frontal analysis. If a solution containing a mixture of ions having different affinity coefficients is passed through a column of ion-exchange resin, in sufficient quantity to exceed the exchange capacity of the resin, the least adsorbed ion " breaks through " the column first. This has been made the basis of a number of inorganic separations, although generally the method has proved more useful in the organic field. A solution containing 0·1N-KCl and 0·1N-NaCl was passed through a column of cation exchanger in the hydrogen form,[102] and the effluent solution was collected in fractions and analysed for hydrogen, sodium, and potassium. At first, hydrogen ion was displaced at a concentration of 0·2N, *i.e.*, equal to the total influent. Sodium, having a lower affinity than potassium, then broke through and its concentration in the effluent rose rapidly to 0·2N, *i.e.*, it was displaced by the potassium. Later, potassium appeared in the effluent and its concentration increased to 0·1N, at which point analysis of input and effluent solutions was the same. In a similar manner copper and zinc have been separated [103] in sulphate solution by passage through a column of cation exchanger having carboxylic functional groups. The less adsorbed zinc appeared in the effluent first and continued to be displaced by the copper. B. A. J. Lister attempted to use this method for the separation of zirconium and hafnium.[104] He passed a solution of mixed zirconyl and hafnyl nitrates in N-sulphuric acid through a column of a high-capacity cation exchanger. The experiment was not a complete success since small amounts of hafnium and zirconium were detected in the effluent almost from the beginning. Hafnium continued to be extracted at the same concentration for some time after the break-through of zirconium until finally there was a rapid increase in concentration. The net effect was that a considerable amount of zirconium was recovered with a much reduced hafnia content but a complete separation was not obtained.

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[97] G. E. Boyd, J. Schubert, and A. W. Adamson, *J. Amer. Chem. Soc.*, 1947, **69**, 2818.
[98] B. H. Ketelle and G. E. Boyd, *ibid.*, p. 2800.
[99] R. Kunin and R. J. Myers, *ibid.*, p. 2874.
[100] R. M. Wheaton and W. C. Bauman, *Ind. Eng. Chem.*, 1951, **43**, 1088.
[101] *Arkiv Kemi, Min. Geol.*, 1940, *B*, **14**, No. 22.
[102] Anon., Chemistry Research, 1951, D.S.I.R., p. 92.
[103] E. J. Breton and A. W. Schlecten, *J. Metals*, 1951, **3**, 517.
[104] *J.*, 1951, 3123.

This may have been due to the presence of colloidal and anionic complexes, which are formed in nitrate solutions of both metals.

One of the earlier separations carried out with the aid of ion exchange was the partial separation of the isotopes of lithium by T. I. Taylor and H. C. Urey.[105] This was again a frontal-analysis experiment carried out by passing a solution of lithium chloride down a column of natural zeolite. A more efficient separation was obtained by Glueckauf *et al.*,[25] who used a column of Zeo-Carb H-I, ground and sieved to a grain size of $1{\cdot}5 \times 10^{-3}$ cm., and passed through it a solution of lithium acetate. In the first fractions of effluent collected the ^{6}Li isotope content had been reduced from 7·5 to $< 1{\cdot}0\%$. Other examples of separation by frontal analysis have been reviewed previously.[89]

A further type of chromatographic separation has been termed displacement development. The mixture is adsorbed from solution on to a resin and then displaced with a reagent more strongly retained by the resin than any component of the mixture. The most strongly adsorbed material displaces less strongly adsorbed materials, each component of the mixture in turn displacing less readily adsorbed components. If the volume of effluent is plotted against concentration, a stepwise diagram is obtained in which each step as it emerges consists of one pure component, all components moving through the column at the same rate. Little use has been made of the technique as yet for inorganic separations.

By far the most used method of separation is that of elution development. The mixture to be separated is adsorbed in a narrow band at the top of a resin column and is then desorbed by passing down the column a solution of another ion, which has a lower affinity coefficient than the components of the mixture, and which is already adsorbed on the major portion of the column. The components of the mixture separate to an extent depending upon their distribution coefficients and on the nature of the adsorption isotherm for each material. The distribution coefficient, at equilibrium, of an ion has been defined [106] as $K_d = (M_S/\text{mass of resin})/(M_L/\text{volume of liquid})$, where M_S and M_L are the fractions of the ion on the solid resin and in the liquid phase. If the volume of effluent solution is plotted against concentration of solute an elution curve is obtained. In cases of low concentration where a linear isotherm is obeyed the elution curve is of the Gaussian type provided that the column is run sufficiently slowly for equilibrium conditions to have been approached. In more concentrated solutions the Langmuir, and less frequently the Freundlich, isotherm applies and the shape of the elution curve alters accordingly. Thus a common result is a sharpening of the front edge and trailing of the back edge of the elution curve.

This simple type of elution analysis can be illustrated by reference to the separation of the alkali metals. The first success was a partial separation [107] of Na, K, Rb, and Cs, in that order, obtained by adsorbing the mixture on a column of Dowex 50 (sulphonic acid-type cation exchanger) and elution

[105] *J. Chem. Phys.*, 1938, **6**, 429.

[106] E. R. Tomkins and S. W. Mayer, *J. Amer. Chem. Soc.*, 1947, **69**, 2859.

[107] W. E. Cohn and H. W. Kohn, *ibid.*, 1948, **70**, 1986.

with 0·15N-hydrochloric acid. Later, in experiments with two-component mixtures, sodium was completely separated from potassium by elution with 0·1N-perchloric acid,[108] and sodium was separated from magnesium by elution with either this acid or 0·1N-hydrochloric acid.[109] By use of radioactive tracers a complete separation [110] of the four metals Na, K, Rb, and Cs was achieved by first eluting Na and K with 0·1N-hydrochloric acid and then Rb and Cs with N-acid. A fine piece of work by W. Rieman *et al.*[111] has placed the separation of Li, Na, and K on an analytical basis, and the method has been applied to the routine estimation of alkali metals in silicates.[112] The elution was carried out with 0·7N-hydrochloric acid on a column of colloidal Dowex 50, and the behaviour of a number of other metals was studied. Cadmium was eluted before lithium, and mercury before cadmium; beryllium was eluted with the potassium, and lead, zinc, and manganese were eluted between potassium and magnesium. Other workers [113, 114] investigated the separation of the alkali metals, and a mixture of Li, Be, and Al has been separated,[115] 0·1N-HCl being used to elute the lithium, 0·05N-$CaCl_2$ to elute the beryllium, and 4N-HCl to remove the aluminium.

This type of separation, depending upon the selectivity of the exchanger for a number of ions, has also been utilised in the separation of anions.[116] The halides F, Cl, Br, and I have been separated on a column of Dowex 2 (strong base exchanger) by elution with M-sodium nitrate, the pH of which had been adjusted with sodium hydroxide to 10·4.

The scope of elution analysis was greatly increased by the introduction in 1947,[117] by workers for the Manhattan Project, of the use of complexing agents as elutriants. If two cations in solution compete for a resin an equilibrium is set up, in which the amount of each ion on the resin phase depends upon its activity and upon its relative affinity for the resin. If now a complexing agent, which will strongly complex one of the ions, is added to the system, the concentration of that ion in the solution will be greatly reduced and the equilibrium will move in favour of the adsorption of the second ion. This reasoning was applied to the separation of the rare earths, alkaline earths, fission products, and transuranic elements on cation-exchange resins. The eluting agent was a suitably buffered solution of citric acid. For a tervalent rare-earth ion adsorbed on the ammonium form of a cation exchanger two reactions are involved:

$$3NH_4R + M^{+++} \rightleftharpoons MR_3 + 3NH_4^+ \quad . \quad . \quad . \quad (1)$$

$$M^{+++} + 3H_2Cit^- \rightleftharpoons M(H_2Cit)_3 \quad . \quad . \quad . \quad . \quad (2)$$

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[108] G. Kayas, *Compt. rend.*, 1949, **228**, 1002.

[109] R. Bouchez and G. Kayas, *ibid.*, p. 1222.

[110] G. Kayas, *J. Chim. Phys.*, 1950, **47**, 408.

[111] J. Beukenkamp and W. Rieman III, *Anal. Chem.*, 1950, **22**, 582.

[112] R. C. Sweet, W. Rieman III, and J. Beukenkamp, *ibid.*, 1952, **24**, 952.

[113] H. Kakihana, *J. Chem. Soc. Japan*, 1951, **72**, 255.

[114] R. Wickbold, *Z. anal. Chem.*, 1951, **132**, 401.

[115] M. Hondo, *J. Chem. Soc. Japan*, 1950, **71**, 118; 1951, **72**, 361.

[116] R. W. Attenberry and G. E. Boyd, *J. Amer. Chem. Soc.*, 1950, **72**, 4805.

[117] *Ibid.*, 1947, **69**, 2769—2881.

The distribution of the rare earth between resin and solution will depend upon the equilibrium constants for these reactions. Citric acid gives three ions in solution, H_2Cit^-, $HCit^{--}$, and Cit^{---}, according to the pH and thus the concentration of the rare-earth ion will depend on the pH of the solution. At any one pH value the rare-earth ion will exist as a mixture of several citric acid complexes, so equation (2) is an approximation. However, if 5% citric acid solution is used as eluting agent, optimum separation of the rare earths is obtained with the pH between 2 and 3. In this range citric acid is almost completely in the H_3Cit and H_2Cit^- forms, so the most probable rare-earth complex is $M(H_2Cit)_3$. Those cations which form the strongest citrate complexes are also those for which the resin has the lowest affinity, so that complexing elution accentuates minor differences in adsorption and improves the separation. The use of citrate eluting agents for the separation of cations has been described and reviewed on numerous occasions.[94, 118, 119] Papers continue to appear describing attempts to simplify, increase the scale, extend the scope, or improve the degree of separation for rare earths and other metals by use of citrate solutions. A mixture of titanium, zirconium, and thorium has been separated[120] by elution from a column of colloidal Dowex 50 with a 1% solution of citric acid buffered to pH 1·75. Zirconium was the first to be eluted, followed by titanium. The eluting agent was then changed to 0·05M-diammonium hydrogen citrate in order to elute thorium in a reasonable volume. From measurement of distribution coefficients the predominant complexes over the pH range 1·59 → 5·39 were calculated to be $TiCit_2^{-2}$, $ThCit_2^{-2}$, $ZrO(HCit)_2^{-2}$ (at lower pH values) and $ZrOCit^-$ (at higher pH values). Other factors being equal, the sharpness of ion-exchange separation increases with decrease of resin particle size. To obtain optimum and repeatable results for the separation of titanium, zirconium, and thorium, it was necessary to use a resin sieved to a mesh size of 100—120. Strict control of temperature ($25° \pm 0{\cdot}1°$) was also necessary. In general, the effect of increased temperature is to increase the rate of exchange, with resultant increase in the sharpness of elution peaks. The high affinity of cationic resins for thorium has suggested[121] a method of separation of the rare earths from this element. The rare earths can be eluted from a cation exchanger with a 10% citric acid solution buffered to pH 3. Thorium is retained and can be subsequently eluted with 6N-sulphuric acid.

The adsorption of the rare earths from citrate solution on an anion-exchange resin indicates the presence of anionic complexes of the rare earths. Tracer quantities of promethium and europium were adsorbed[122] from solution in 0·0125M-citric acid, buffered to pH 2·1 with hydrochloric acid, on a column of Dowex 1. They were then eluted differentially with a further portion of the same solution. A similar separation of the oxalate

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[118] L. L. Quill, *Record Chem. Progress*, 1950, **11**, 151.

[119] R. Bock, *Angew. Chem.*, 1950, **62**, *A*, 375.

[120] W. E. Brown and W. Rieman III, *J. Amer. Chem. Soc.*, 1952, **74**, 1278.

[121] P. Radhakrishna, *Anal. Chim. Acta*, 1952, **6**, 351.

[122] E. F. Huffman and R. L. Oswalt, *J. Amer. Chem. Soc.*, 1950, **72**, 3323.

complexes of zirconium and niobium has been achieved.[123] The resin was again Dowex 1, and after adsorption from oxalic acid solution (0·1—0·4M) the metals were eluted, zirconium first, with a 1M-hydrochloric acid solution, 0·01M with respect to oxalic acid.

At first sight the separation of zirconium and hafnium on a cation-exchange resin by elution with dilute acid might appear to be completely due to differences in adsorption affinity, but further study has shown it to be due to complex formation. If the two metals are eluted from a cation exchange with 3—6N-hydrochloric acid [124] separation occurs and the hafnium is extracted first. In an experiment [125] using 2·8 g. of the mixed oxychloride, 42% of the HfO_2 was recovered at better than 99·9% purity. Elution with N-sulphuric acid [126, 127] also produced a separation but in this case zirconium was extracted first, well in advance of the hafnium. The ease with which zirconium forms anionic complexes with sulphuric acid is well known. As will be shown later, it also forms negatively charged complexes in concentrated hydrochloric acid solution. Elution with nitric and perchloric acids produced no separation, but whereas the rate of elution of both metals with nitric acid was similar to that obtained with hydrochloric and sulphuric acids, both metals were extracted much more slowly with perchloric acid, indicating little complexing in perchloric acid solution. B. A. J. Lister has described experiments [126] in which 95—98% of the zirconia containing 0·01% of hafnia has been recovered from 20 g. of zirconyl nitrate, having an original hafnia content of 1·5%.

K. A. Kraus and G. E. Moore [128] have also separated zirconium and hafnium on an anion-exchange column, making use of their negatively charged fluoride complexes. Elution with a mixture of 0·5M-HF and 1·0M-HCl extracted zirconium first but a complete separation was not obtained. E. A. Huffman and R. C. Lilly [129] also studied the same separation and investigated the effect of varying the hydrochloric acid concentration over the range 0·15—0·6M and the hydrofluoric acid concentration over the range 0·01—0·6M, but in no case obtained a complete separation. This work on the fluorozirconates and fluorohafnates was extended to include a study of the separation of niobium, tantalum, and protactinium and the separation of all three from zirconium.[130] The elution constants for the four metals were measured with elutriants containing varying quantities of HCl and HF. The elution constant, E_D, was defined as dA/V_1 where d is the distance (cm.) a band maximum moves after the passage of V ml. of eluting solution through a column of A cm.² cross-section. It was found that for HCl concentrations of 0·2—9M and HF concentration of 0·1—5·0M the order of elution constants was Pa > Nb > Ta. Variation in the acid concentration outside these limits could bring about changes in the order

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[123] R. E. Wacker and W. H. Baldwin, U.S.A.E.C., ORNL-637, N.S.A., 1950, **4**, 469.

[124] K. Street and G. T. Seaborg, *J. Amer. Chem. Soc.*, 1948, **70**, 4268.

[125] I. E. Newnham, *ibid.*, 1951, **73**, 5899.

[126] B. A. J. Lister, *ibid.*, p. 3123.

[127] J. C. Hutcheon and B. A. J. Lister, *Research*, 1952, **5**, 291.

[128] *J. Amer. Chem. Soc.*, 1949, **71**, 3263.

[129] *Ibid.*, p. 4147 ; 1951, **73**, 2902.

[130] K. A. Kraus and G. E. Moore, *ibid.*, 1949, **71**, 3855 ; 1951, **73**, 9713, 2900.

of elution of the niobium and tantalum. Zirconium normally preceded protactinium in the series, but here also, by adjustment of acid concentrations, zirconium could be more strongly retained than niobium. The behaviour of the metals in this fashion on elution depends upon the anionic species of each element existing in solution. It appears likely that both protactinium and niobium in low HF concentrations exist as their univalent oxygenated complexes, $PaOCl_4^-$ and $NbOCl_4^-$ (or more generally $H_nMOCl_{(4+n)}^-$). Increase in HF concentration leads to complex formation by which the negative charge is increased. Thus the equilibrium for niobium becomes :

$$NbX_6^- + nHF + jH_2O \rightleftharpoons H_{n-j}NbX_{6-m}F_n^{-1-j+m} + mX^{-1} + jH_3O^+$$

For tantalum two complexes, TaX_5F^- and $HTaX_5F_3^{-2}$, have been identified. The practical separation of the metals depends upon the concentration of HF necessary to bring about formation of each more highly charged, and hence less adsorbed, complex. All four metals were separated from each other in one experiment. After adsorption from a solution of 9M-HCl + 0·05M-HF on to a column of Dowex 1, zirconium was eluted, followed by protactinium, with a mixture of 9M-HCl and 0·004M-HF. The HF concentration was increased to 0·18M to extract niobium, and finally the elutriant was changed to 4M-NH_4Cl + 1M-HF to remove tantalum.

Observations [131] on the behaviour of protactinium in concentrated hydrochloric acid solution have led to the development of a very useful complexing technique. Protactinium is strongly adsorbed from solutions of hydrochloric more concentrated than 4M, and its distribution coefficient rises rapidly to a maximum at 8M. It may be eluted in a sharp band with acid concentrations below 4M, suggesting that protactinium does not form anionic complexes in low acid concentrations. Similar results were obtained with iron.[132] While chromium, aluminium, and the rare earths were almost unadsorbed from strong hydrochloric acid solution, the distribution coefficient for iron increased rapidly in solutions from *ca.* 1M to a maximum at 9M. Zirconium, hafnium, niobium and tantalum also form anionic complexes in fairly concentrated ($>$ 6M) hydrochloric acid solution.[133] Advantage has already been taken of this, in the extraction of zirconium and hafnium adsorbed on a cation exchanger. The distribution coefficients of zirconium and hafnium increase sharply above 6N-HCl, while those for niobium and tantalum are high in concentrated and dilute solutions but have a minimum at 4N-HCl. A simple separation of cobalt and nickel has been demonstrated.[134] The elution coefficient for both metals adsorbed on Dowex 1, on elution with 3N-HCl, is 2·5. For cobalt this falls to 0·02 with 9N-HCl and then rises to 0·055 with 12N-HCl while E_{Ni} remains at 2·5 throughout the whole range of acid concentrations.

A serious disadvantage to the use of citrate buffer solutions for the elution of the rare earths is the large volume of solution required. A

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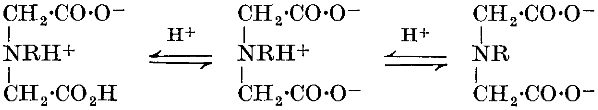
[131] K. A. Kraus and G. E. Moore, *J. Amer. Chem. Soc.*, 1950, **72**, 4293.

[132] *Idem*, *ibid.*, p. 5792.

[133] E. A. Huffman, G. M. Iddings, and R. C. Lilly, *ibid.*, 1951, **73**, 4474.

[134] K. A. Kraus and G. E. Moore, *ibid.*, 1952, **74**, 843.

number of other complexes have been studied with the hope of reducing this volume. The ammonium salts of the iminodiacetic acids form complexes with the rare earths which show increasing stability with increase of atomic number. The possible ionic forms of these acids are represented by the equilibrium



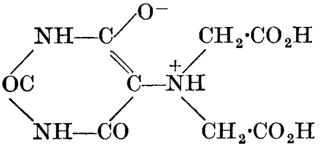
$$\begin{matrix} CH_2{\cdot}CO{\cdot}O^- \\ | \\ NRH^+ \\ | \\ CH_2{\cdot}CO_2H \end{matrix} \underset{}{\overset{H^+}{\rightleftharpoons}} \begin{matrix} CH_2{\cdot}CO{\cdot}O^- \\ | \\ NRH^+ \\ | \\ CH_2{\cdot}CO{\cdot}O^- \end{matrix} \overset{H^+}{\rightleftharpoons} \begin{matrix} CH_2{\cdot}CO{\cdot}O^- \\ | \\ NR \\ | \\ CH_2{\cdot}CO{\cdot}O^- \end{matrix}$$

(1) (2) (3)

Between pH values of 5 and 7, the most suitable range for rare-earth separations, forms (1) and (2) are in major concentration and rare-earth complexes of the type MA^+ and MA_2^- are formed, where M is the tervalent cation. Use of this type of complex has been demonstrated [135] by the use of nitrilotriacetic acid solution buffered to pH5 with ammonia for the separation of the cerium group on Amberlite 120 (sulphonic acid cation exchanger). C. E. Higgins and W. A. Baldwin have shown that tracer quantities of yttrium [91] and europium [136] may be separated on Dowex 1 by elution with a solution of 0·16M-versene.

An interesting analytical application of complexing elution is that for the estimation of iron and titanium in ilmenite.[137] A solution of the mineral was adsorbed on a cation exchanger and eluted with 2N-potassium cyanide to remove the iron. Titanium was subsequently removed with 10% sulphuric acid.

Uramildiacetic acid has been studied [138] as a possible eluting agent for Li, K, and Na. Here again the object was to cut down the volume of solution required for elution. The alkali metals form complexes with uramildiacetic acid (I) which are strongly pH dependent and except for lithium are stable only in alkaline solution. The resin has therefore to be used in a neutral form, preferably containing an adsorbed cation, whose affinity for the resin is less than that of the alkali metals. In a successful experiment, the resin was used in the tetramethylammonium form, and the metals were eluted with a solution of the tetramethylammonium salt of uramildiacetic acid. Variation of the pH of the eluting solution between 7 and 11 enabled Li, Na, and K to be separated.



(I)

Organic solvents containing mineral acids have recently been used to elute complex metal ions from resin exchangers. Complex cyanides such as auro-, argento-, ferro-, cupro-, and nickelo-cyanides are readily adsorbed

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[135] F. T. Fitch and D. S. Russell, *Canadian J. Chem.*, 1951, **29**, 363.
[136] U.S.A.E.C. Rep. ORNL 894, N.S.A., 1951, **5**, 542.
[137] Y. Yoshino and M. Kajima, *Bull. Chem. Soc. Japan*, 1950, **23**, 46.
[138] W. Buser, *Helv. Chim. Acta*, 1951, **34**, 1635.

from dilute sodium cyanide solutions on to an anion-exchange resin. While nickel can be removed with dilute hydrochloric acid and cupro- and ferro-cyanides with 2N-sodium cyanide, it is extremely difficult to elute auro- and argento-cyanides from strong base resins of the Amberlite IRA-400 type with normal aqueous eluting agents. Both are readily removed with solvents such as acetone, alcohol, or ether containing hydrochloric or nitric acid. Although this is perhaps not true chromatographic elution, some selectivity by the solvents was noted. In view of the high water content of ion-exchange resins it might be possible to combine an ion-exchange adsorption from aqueous solution with a " partition elution " using an organic solvent.

Theoretical Considerations

A general theory of chromatographic separation was first developed by J. N. Wilson and has since been revised and expanded by D. de Vault, E. Glueckhauf, J. Weiss, L. G. Sillen, and others. The mathematics of the theory is complicated and the reader is referred to the original papers and to a recent review.[140] In general the theory permits the prediction of the chromatographic behaviour of a number of solutes in a mixture if the adsorption isotherm for each is known. The equations necessary to cover linear Freundlich and Langmuir isotherms have been derived. The theory was derived on the assumption that the separations were achieved under equilibrium conditions, but it has been possible to derive modified equations for use in non-ideal conditions.[141] This has permitted the calculation of adsorption equilibria data from the diffuse rear boundary of an elution curve for linear or non-linear isotherms, providing the conditions do not depart radically from ideality. Such variables as grain size, flow rate, concentration, pore space, and diffusion constants in the liquid and in the solid adsorbent are catered for by the theory. Glueckauf [25] has determined the effect of some of these variables on the separation of the isotopes of neon on charcoal at —196°. He found close agreement between the practical results and theoretical predictions.

A simpler but more empirical approach has been favoured by a number of workers, who have employed the " plate " theory. Initially derived by A. J. P. Martin and R. L. M. Synge [10] to give a quantitative explanation of partition chromatography, the theory is based upon the similarity between the chromatographic process and that of distillation. A column is considered to consist of a number of theoretical plates. Each plate is of such a thickness that the solution issuing from it is in equilibrium with the mean concentration of solute in the non-mobile phase throughout the layer. An expression was derived which enabled the position of a band in a column after the passage of a known volume of solvent to be predicted. Little use has so far been made of this equation in inorganic separations, but a second

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[139] F. H. Burstall, P. J. Forrest, N. F. Kember, and R. A. Wells, in the press.

[140] E. Glueckauf, *Nature*, 1951, **167**, 715 ; J. F. Duncan and E. Glueckauf, *ibid.*, p. 714 ; E. Ekedahl, E. Hogfeldt, and L. G. Sillen, *ibid.*, p. 714.

[141] E. Glueckauf, *J.*, 1949, 3280.

expression derived[33] from it for the special case of separations on a paper strip has received more attention. For separations on sheets of paper :

$$R_F = \frac{A_L}{A_L + \alpha A_S} \text{ where } R_F = \frac{\text{movement of band}}{\text{movement of solvent front}}$$

from which $\alpha = A_L(1/R_F - 1)/A_S$, where α = partition coefficient of solute between water and solvent phases and A_L/A_S = ratio of volume of solvent and water phase in the chromatogram. The theory holds only for linear isotherms, but it appears likely that these apply in a large number of cases for separations on paper strips. If the partition coefficient is constant, the R_F values will also be constant, and this has been found to be so for a large number of inorganic separations. S. W. Mayer and E. R. Tompkins[106] have also derived a " plate " theory for ion exchange based upon the analogy of ion-exchange column procedures with fractional distillation. They derived the expression :

$$L_{\text{max.}} = [2\pi pC(1 + C)]^{-\frac{1}{2}}$$

where $L_{\text{max.}}$ = the maximum fraction of a solute in any volume v of solution (v = volume of solution in one theoretical plate), p = number of theoretical plates in column, and C = distribution ratio of solute in any plate.

As with the equation derived by Martin and Synge, this relation holds only for those cases where the amount of a solute adsorbed is proportional to its concentration in solution. For most ion-exchange work this is true, or nearly so, for dilute solutions. The theory has to some extent been used to predict the degree of separation attainable in several cases, but there is still a great tendency to produce the optimum separations by trial and error methods and then to use the practical data to test the theory.

In addition to attempts to produce a general theory of chromatography, much work has been directed towards the determination of the physical and chemical processes and their kinetics, which operate with various adsorbents. Recent suggestions for the mechanism of alumina columns have already been mentioned. The mechanism of adsorption in paper-partition separations appears to be fairly straightforward but several factors have received little consideration. A number of workers have noticed that, on allowing an organic solvent containing water to diffuse down a sheet of paper, two solvent fronts are formed. The paper behind the first of these fronts appears to contain both water and solvent, whereas the area between the front appears to contain only dry solvent. It has been shown[142] that the " wet " solvent front is in fact an indication of a water concentration gradient which extends from the solvent container to the solvent front. Moreover, if acid is present in the solvent an acidity gradient extends down the strip analogous to the distribution curve for water. What part these extreme non-equilibrium conditions play in producing separations is not known.

For a detailed study of the kinetics and theory of ion exchange the reader is referred to a number of text books[8, 94, 95] and a review,[143] in which

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[142] R. A. Wells, unpublished.

[143] E. R. Tompkins, *Analyst*, 1952, **77**, 970.

these matters have been fully discussed. Recent publications [144–146] have described methods for carrying out continuous ion-exchange separations in conditions of low concentration. In these cases separations do not necessarily occur under equilibrium conditions, and the authors have made substantial headway in correlating the kinetic theories of ion exchange with the plate theory in order to predict the course of separations carried out under non-ideal conditions.

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[144] N. K. Hiester, Tech. Rep. No. 6, U.S.A.E.C., COO-41, 1951.

[145] T. Vermeulen and N. K. Hiester, *Ind. Eng. Chem.*, 1952, **44**, 637.

[146] N. K. Hiester, R. C. Phillips, and E. T. Fields, Tech. Rep. II, U.S.A.E.C., COO-59, 1952.