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Inorganic Ion Exchange in Organic and Aqueous-Organic Solvents

A Review*

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SUMMARY OF CONTENTS

ION-EXCHANGE investigations in aqueous systems have established broad fundamental characteristics as well as many interesting details and applications. In attempts to widen the scope, as well as to confirm the influence of physical variables on the exchange process, ion-exchange studies and applications have, during the last decade, been extended to both organic and mixed aqueous - organic solvent systems.

Systematic investigations, initiated by Korkisch,[1] and Fritz and Rettig,[2] demonstrated the versatility of aqueous - organic solvent mixtures for metal separations. Interest in inter-lanthanide and inter-actinide separations has given particular impetus to these studies, although additionally, circumstances such as the difficulties produced by insolubility of organic materials in water,[3] the inability of alkaline earth metals to form complexes in the absence of a high proportion of organic solvent and mere curiosity have led to the use of mixtures of partly, or wholly, organic solvents.

The stability of ion-exchange resins in the presence of certain organic solvents was claimed in 1948,[4] but, in such media, recognition must be made of factors causing the breakdown of resins, for example, the de-amination of highly basic anion exchangers with consequent decrease in sorptive capacity. Fortunately, however, these changes take place mainly when the resins are subjected to high temperatures, regardless of whether they are in contact with aqueous or non-aqueous solvents such as methanol or ethanol.[5,6,7,8]

A few general principles of ion exchange in mixed solvents had been established twenty years ago.[4] For example, Na^+, K^+, Ba^{2+}, and Ca^{2+} ions were claimed to exhibit greater affinity for a cation exchanger in aqueous solutions of increasing ethanol or acetone content.[4] These enhanced selectivity trends were soon confirmed[9] in that the preference of the cation exchanger, Dowex 50, for sodium ions over hydrogen ions is greater in pure methanol (selectivity coefficient $K_{H}^{Na} = 3{\cdot}2$) than in pure water ($K_{H}^{Na} = 1{\cdot}52$), and even greater in 50 to 95 mole per cent. methanol solutions, than either of the pure solvents, with a peak selectivity coefficient of 17·2 in 75 mole per cent. methanol.

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* Reprints of this paper will be available shortly. For details see Summaries in advertisement pages.

Selectivity variation with organic solvents was shown to be supplemented in the presence of a mineral acid.[10,11] This is because the dissociation of the resin - cation complex is facilitated by formation of other complexes, including anionic complexes. Such complex formation is frequently enhanced by the dehydrating action of the organic solvent.

In 1959, Korkisch and co-workers[12,13] started an intensive study[1,14,15] of anion-exchange patterns with complexing eluants involving aqueous - organic solvents. Adding ethanol to thorium(IV) nitrate and uranium(VI) chloride complex systems procured the preferential sorption of the thorium and uranium, respectively, on the anion exchanger, Dowex 1. The general increase in sorption frequently observed with increased alcohol content in the solvent mixture soon became an accepted characteristic phenomenon.[14]

Rigorous theoretical treatment of ion-exchange equilibria in mixed solvent systems is difficult. Nevertheless, experiment has established useful general features for this purpose. Thus, in addition to the general increase in selectivity coefficients noted above, there is a linear relation between log selectivity coefficient and the reciprocal of the solvent dielectric constant.[16,17] Explanations of these phenomena range from the hypothetical de-solvation energy involved in ion exchange[18,19] to ion-pair formation,[20,21] and to changes in the solution and resin-phase activity coefficients.[22,23] Allowance must also be made for other factors, such as the dependence of separation factors on differences in the solvent composition of the resin phase and the external solution. This, it is claimed, causes a kind of partition chromatography to be superimposed on the ion-exchange chromatography.[24,25] Related to this is the view that the distribution of an uncharged species between two phases without further interaction is the main reaction and not simple ion exchange.[26]

In recent years, considerable effort has been given to extending the above studies[1,14,15,27,28,29,30,31] and in the present review the ion exchange of inorganic materials is considered on the separate premises of cation and anion exchange. As a preface to such a discussion, some of the basic principles of ion-exchange selectivities, thermodynamics and kinetics, and the behaviour of ion-exchange resins, are outlined.

ION-EXCHANGE SELECTIVITIES

Regardless of solvent, the exchange of univalent ions may be represented by the equation

$$A^+_R + B^+_S \rightleftharpoons B^+_R + A^+_S \quad \ldots \quad (1)$$

where A^+ and B^+ represent the ions being exchanged and R and S represent the resin and "external" solution phase, respectively,[32] and the equilibrium constant, K^B_A, may be written as

$$K^B_A = \frac{[B^+_R]\,[A^+_S]}{[A^+_R]\,[B^+_S]} \quad \ldots \quad (2)$$

where the square-brackets terms refer to ion activities. By neglecting activity coefficients of the ions in each phase, the expression for the equilibrium quotient or selectivity coefficient[9,27,32] will be

$$K^B_A = \frac{N_{B^+_R}\; C_{A^+_S}}{N_{A^+_R}\; C_{B^+_S}} \quad \ldots \quad (3)$$

where N represents the mole fractions of the ions in the resin phase and C the molar ion concentrations in the solution phase.

The selectivity coefficient, K^B_A, varies with the resin loading, that is, the proportion of each ion associated with the resin (Table I). For a given pair of ions, it also varies with the extent of resin cross-linking (divinylbenzene content) chosen.[27,32] Furthermore, selectivity coefficients may be combined into a selectivity scale. Such a scale compiled by Bonner and Smith[33] is referred to the lithium ion (Table II).

TABLE I

SELECTIVITY COEFFICIENTS (K^B_A) ON DOWEX 50 IN WATER FOR VARIOUS RESIN LOADINGS[27]

Resin loading, $N_{B^+_R}$	K^{Na}_H	$K^{NH_4}_H$	K^{Ag}_{Na}
0·1	1·6	2·2	3·0
0·3	1·5	2·0	2·9
0·5	1·5	1·8	2·9
0·7	1·5	1·6	3·0
0·9	1·3	1·3	3·7

TABLE II

SELECTIVITY SCALE FOR REMOVING UNIVALENT IONS FROM AQUEOUS SOLUTION BY DOWEX 50 RESINS[33]

	Divinylbenzene, 4 per cent.	Divinylbenzene, 8 per cent.	Divinylbenzene, 16 per cent.
Li^+	1·00	1·00	1·00
H^+	1·32	1·27	1·47
Na^+	1·58	1·98	2·37
NH_4^+	1·90	2·55	3·34
K^+	2·27	2·90	4·50
Rb^+	2·46	3·16	4·62
Cs^+	2·67	3·25	4·66
Ag^+	4·73	8·51	22·9
Tl^+	6·71	12·4	28·5

Selectivity coefficients for the exchange of bivalent ions from solution for univalent ions on the resin can also be similarly obtained, and the resultant relationships show that the effective resin selectivity is inversely proportional to the concentration of the solution, that is, the relative sorption of the bivalent ions will be greater in dilute solution.

Apart from selectivity coefficients, distribution coefficients are also widely used for comparing the selectivity of ions for resins. In such instances, the distribution coefficient, K_d, is normally defined by the relation

$$K_d = \frac{\text{mass of ion per gram of resin}}{\text{mass of ion per ml of solution}} \quad \ldots \quad \ldots \quad \ldots \quad (4).$$

When two species are to be separated, the separation factor, α, can be obtained from the ratio of the distribution coefficients. This ratio is a most important parameter in elution ion-exchange chromatography. Complexing eluants, organic solvents and extent of resin cross-linking each exert considerable influence on it. Indeed, the object of most investigations into separations by ion exchange, particularly of lanthanides and actinides, is the evaluation of such variables on separation.

Knowing the separation factor, the primary problem then is to select conditions of particle size, flow-rate and length of column that will yield the required separation. A general approach to the problem discussed by Cornish[34] depends on a knowledge of the distribution coefficients and equivalent quantities of the solute species to be separated for calculating the number of theoretical plates required to yield the desired purity. The length of column, L, appropriate to the required number of plates, N, may be derived from the relation

$$L = N \times \text{(height equivalent to a theoretical plate)} \quad \ldots \quad \ldots \quad \ldots \quad (5).$$

The height equivalent to a theoretical plate is obtained from its connection, in a graphical relationship, with resin particle size and eluant flow-rate.

This approach, being based on set conditions, does not allow for changes that may occur with gradient-elution techniques. Towards this end, Massart and Bossaert[35] have recently developed a method that enables the calculation of the effect of proposed gradients of a complexing eluant on ion-exchange separation to be made. This depends on a knowledge of distribution coefficients as a function of the complexing eluant concentration. Independently, similar methods for predicting the position of elution peaks in gradient-elution analysis have been described.[36,37] For example, experimental peak locations of lanthanides in nitric acid - ammonium nitrate systems in aqueous methanol compare favourably with those calculated by the equation[37]

$$V_m = V_i + V_o \ln\left(\frac{aC_o m}{V_o} + 1\right) \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6),$$

where V_m is the effluent volume corresponding to the peak maximum, V_i the free volume of the resin bed, V_o the volume of the mixing chamber, C_o the concentration in the mixing chamber and m the weight of resin in the column. The constant, a, is characteristic of individual lanthanides, dependent on both the distribution coefficient, K_d, and the complexing species (nitrate ion) concentration

$$K_d = a[NO_3^-] \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7).$$

Apart from predicting the positions of elution peaks, equation (6) can also be used for determining K_d.[37]

ION-EXCHANGE EQUILIBRIA

The fundamental characteristics of ion-exchange equilibria in aqueous solutions have been extensively studied, and the various theoretical features are now fairly well understood.[38 to 45] However, initially, experimental data on ion-exchange equilibria could not be adequately explained by the conventional Donnan theory or the mass-action law. Three important refinements were proposed to solve the problem.[43]

The first was to add a pressure - volume energy term to the Donnan equation[46,47,48,49]; the second, to use the Gibbs-Duhem equation for calculating the equilibrium constant[38,39,40,50,51,52,53,54]; and the third to consider water uptake by the resin. The relationships among these refinements have been discussed by Kakihana, Ohtaki and Nomura[43] on the basis of a classical thermodynamic treatment, certain assumptions being made, such as those imposed by lack of definite hydration numbers, even for ordinary aqueous solutions.

In treating non-aqueous systems, a comparison with aqueous systems is beset with many difficulties; the principal one arises from the differences in the standard states of the two systems. However, some progress has been made and fundamental equations derived for the ion-exchange equilibrium in mixed solvents.[16,55] Gupta's[16] approach is interesting, and it may be helpful to look first at the uni - univalent exchange system in water, equation (1), for which the following equation has been derived[38,39] by applying the law of mass action and the Gibbs-Duhem equation

$$\ln K = \int_0^1 \ln K_a \, d\, N_{B_R^+} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (8)$$

where

$$K = \frac{a_{B_R^+}\, a_{A_S^+}}{a_{B_S^+}\, a_{A_R^+}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

and K_a is the selectivity coefficient, K_A^B, for reaction (1) [see equation (3)] corrected for the solution-phase activity coefficients.

For the purposes of equation (8), the ion exchanger is considered as a solid solution (neglecting solvent uptake) of the components A_R^+ and B_R^+. The standard state of the solid exchanger phase is defined as its mono-ionic form in equilibrium with an infinitely dilute solution of the corresponding salt while that of the outside solution is the hypothetical one molal solution.

Equation (8) considers the dependence of selectivity coefficients on resin composition. It does not allow for variations in the water sorption by the ion exchanger, for which three additional integrals were proposed by Gaines and Thomas[40] to give

$$\begin{aligned} \ln K = & \int_0^1 \ln K_a \, d\, N_{B_R^+} + \int_{a_w\,(N_{B_R^+}=1)}^{a_w\,(N_{A_R^+}=1)} n_w \, d \ln a_w \\ & + \int_{a_w = 1(N_{B_R^+}=1)}^{a_w\,(N_{B_R^+}=1)} (V_B/\tau - n_w)\, d \ln a_w \\ & - \int_{a_w = 1(N_{A_R^+}=1)}^{a_w\,(N_{A_R^+}=1)} (V_A/\tau - n_w)\, d \ln a_w \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (10) \end{aligned}$$

where V_B and V_A are the equivalent volumes of pure B^+ and A^+ of the exchanger; τ, the molar volume of the water vapour; a_w, the water activity; and n_w, the number of moles of water associated with one equivalent of the exchanger.

The second integral in equation (10) implies the integration of the equivalent moisture, n_w, of the ion exchanger over the two extremes of resin composition, at a constant ionic strength, m. The third and fourth integrals rationalise the standard state of the ion exchanger from that of the mono-ionic form in equilibrium with an m molar solution of the corresponding salt to that of the mono-ionic form in equilibrium with pure water (an infinitely dilute solution of the corresponding salt).

The consideration of ion exchange in mixed solvents on the above basis introduces difficulties. For example, the addition of a second solvent introduces another term in the Gibbs-Duhem equation with consequent complication in integrations. Nevertheless, equation (10) forms the basis of Gupta's[16] semi-empirical approach.

Because in mixed solvents, ion exchangers show a preference for one of the solvents, and because interest centres round mixed solvents involving water, Gupta[16] adopted identical standard states with those noted above for aqueous systems. This implies that the effect of added solvent is determined completely by its influence on the activities of exchanger phase, electrolytes and water and, as such, the added solvent can be considered as a diluent for the water present in the system.

On representing the selectivity coefficient in mixed solvent systems, as corrected for solution-phase activity coefficients, by K'_a, the first integral term of equation (10) becomes

$$\int_0^1 \ln K'_a \, d\, N_{B^+_R} \quad \ldots \quad (11).$$

In mixed solvent applications, with n_w representing the actual number of moles of water per equivalent of exchanger under specified conditions, the processes concerned with the second, third and fourth integrals of equation (10) are dealt with in three steps.

In the first step, the variations in equivalent moisture over the whole range of ion-exchanger compositions at a particular ionic strength and solvent compositions are determined from the integral

$$\int_{a_w(N_{H_2O})\,(N_{B^+_R}=1)}^{a_w(N_{H_2O})\,(N_{A^+_R}=1)} n_w \, d \ln a_w \quad \ldots \quad (12)$$

where $a_w(N_{H_2O})$ refers to the water activity in the solvent mixture having N_{H_2O} mole fraction of water. The lower limit $a_w(N_{H_2O})$ $(N_{B^+_R} = 1)$ then implies water activity of an m molar solution of B^+ ions in the mixed solvent of N_{H_2O} mole fraction of water, the upper limit being similarly defined.

The second step concerns the correction for the effect of the ionic strength on equivalent moisture of the mono-ionic forms of the exchanger, referring them to the state of infinite dilution in mixed solvent and involves the integrals

$$\int_{a^\circ_w(N_{H_2O})\,(N_{B^+_R}=1)}^{a_w(N_{H_2O})\,(N_{B^+_R}=1)} (V_B/\tau - n_w)\, d \ln a_w \quad - \quad \int_{a^\circ_w(N_{H_2O})\,(N_{A^+_R}=1)}^{a_w(N_{H_2O})\,(N_{A^+_R}=1)} (V_A/\tau - n_w)\, d \ln a_w \quad \ldots \quad (13).$$

The first term in (13) takes into consideration the variations in equivalent moisture when the outside solution changes from m molar solution of B^+ ions in mixed solvent to an infinitely dilute solution of B^+ ions in the same solvent. The lower limit $a^\circ_w(N_{H_2O})$ $(N_{B^+_R} = 1)$ then means water activity in an infinitely dilute solution of B^+ ions in a solvent having N_{H_2O} mole fraction of water. The second term can be similarly explained.

The third and final step is to correct the equivalent moisture of pure exchangers at infinite dilution in the mixed solvent to that of infinite dilution in water and involves the integrals

$$\int_{a_w = 1(N_{B^+_R}=1)}^{a^\circ_w(N_{H_2O})\,(N_{B^+_R}=1)} (V_B/\tau - n_w)\, d \ln a_w \quad - \quad \int_{a_w = 1(N_{A^+_R}=1)}^{a^\circ_w(N_{H_2O})\,(N_{A^+_R}=1)} (V_A/\tau - n_w)\, d \ln a_w \quad \ldots \quad (14)$$

where the limits of the first integral are from an infinitely dilute solution of B^+ ions in the mixed solvent (with N_{H_2O} water mole fraction) to that of an infinitely dilute solution of B^+ ions in water. The limits of the second integral can be similarly explained.

Compared with the n_w terms, the V/τ terms of equations (13) and (14) are small for a moderately cross-linked exchanger[40,54] and can be neglected in combining expressions (11) to (14) to give ln K for a uni - univalent exchange in a mixed solvent (water $= N_{\mathrm{H_2O}}$).[16]

$$\begin{aligned}\ln K = &\int_0^1 \ln K'_\mathrm{a}\, d\, N_{\mathrm{R}}^{+} &&+ \int_{a_\mathrm{w}(N_{\mathrm{H_2O}})\,(N_{\mathrm{B}_\mathrm{R}^+} = 1)}^{a_\mathrm{w}(N_{\mathrm{H_2O}})\,(N_{\mathrm{A}_\mathrm{R}^+} = 1)} n_\mathrm{w}\, d \ln a_\mathrm{w} \\ &- \int_{a^\circ_\mathrm{w}(N_{\mathrm{H_2O}})\,(N_{\mathrm{B}_\mathrm{R}^+} = 1)}^{a_\mathrm{w}(N_{\mathrm{H_2O}})\,(N_{\mathrm{B}_\mathrm{R}^+} = 1)} n_\mathrm{w}\, d \ln a_\mathrm{w} &&+ \int_{a^\circ_\mathrm{w}(N_{\mathrm{H_2O}})\,(N_{\mathrm{A}_\mathrm{R}^+} = 1)}^{a_\mathrm{w}(N_{\mathrm{H_2O}})\,(N_{\mathrm{A}_\mathrm{R}^+} = 1)} n_\mathrm{w}\, d \ln a_\mathrm{w} \\ &- \int_{a_\mathrm{w} = 1(N_{\mathrm{B}_\mathrm{R}^+} = 1)}^{a^\circ_\mathrm{w}(N_{\mathrm{H_2O}})\,(N_{\mathrm{B}_\mathrm{R}^+} = 1)} n_\mathrm{w}\, d \ln a_\mathrm{w} &&+ \int_{a_\mathrm{w} = 1(N_{\mathrm{A}_\mathrm{R}^+} = 1)}^{a^\circ_\mathrm{w}(N_{\mathrm{H_2O}})\,(N_{\mathrm{A}_\mathrm{R}^+} = 1)} n_\mathrm{w}\, d \ln a_\mathrm{w} \quad \ldots \quad \ldots \quad (15).\end{aligned}$$

Experiment is the ultimate test of any theory, but insufficient experimental results are available to evaluate the integrals in equation (15) individually.[17] However, through the negligible contribution of certain terms, equation (15) reduces to the form[16]

$$\begin{aligned}\ln K \simeq &\int_0^1 \ln K_\mathrm{A}^\mathrm{B}\, d\, N_{\mathrm{B}_\mathrm{R}^+} &&+ 2 \ln \frac{\gamma^\circ_{\pm AX}}{\gamma^\circ_{\pm BX}} \\ &- \int_{a_\mathrm{w} = 1(N_{\mathrm{B}_\mathrm{R}^+} = 1)}^{a^\circ_\mathrm{w}(N_{\mathrm{H_2O}})\,(N_{\mathrm{B}_\mathrm{R}^+} = 1)} n_\mathrm{w}\, d \ln a_\mathrm{w} &&+ \int_{a_\mathrm{w} = 1(N_{\mathrm{A}_\mathrm{R}^+} = 1)}^{a^\circ_\mathrm{w}(N_{\mathrm{H_2O}})\,(N_{\mathrm{A}_\mathrm{R}^+} = 1)} n_\mathrm{w}\, d \ln a_\mathrm{w} \quad \ldots \quad \ldots \quad (16)\end{aligned}$$

as

$$\begin{aligned}K'_\mathrm{a} &= \frac{N_{\mathrm{B}_\mathrm{R}^+}\, m_{\mathrm{A}_\mathrm{S}^+}}{N_{\mathrm{A}_\mathrm{R}^+}\, m_{\mathrm{B}_\mathrm{S}^+}} \times \frac{\gamma'^2_{\pm AX}}{\gamma'^2_{\pm BX}} \times \frac{\gamma^{\circ 2}_{\pm AX}}{\gamma^{\circ 2}_{\pm BX}} \\ &= K_\mathrm{A}^{B} \times \frac{\gamma'^2_{\pm AX}}{\gamma'^2_{\pm BX}} \times \frac{\gamma^{\circ 2}_{\pm AX}}{\gamma^{\circ 2}_{\pm BX}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (17),\end{aligned}$$

that is, K'_a is the selectivity coefficient, $K_{\mathrm{A}'}^{\mathrm{B}'}$, for the mixed solvent corrected for the solution-phase activity coefficients of the electrolytes AX and BX (providing cations A^+ and B^+), γ' represents the activity coefficients of the ions in the mixed solvent referred to the standard state of infinite dilution, and the term involving them is close to unity as evidenced by some uni - univalent electrolytes in alcohol - water mixtures,[16,23,56] γ° corrects the standard state at infinite dilution in water and the term involved is insignificant.[16]

The form of equation (15) tested involves the collection of integrals 2 to 6 within a single term ln Q[17]

$$\begin{aligned}\ln K = &\int_0^1 \ln K_{\mathrm{A}'}^{\mathrm{B}'}\, d\, N_{\mathrm{B}_\mathrm{R}^+} + 2 \ln \frac{\gamma'_{\pm AX}}{\gamma'_{\pm BX}} \\ &+ 2 \ln \frac{\gamma^\circ_{\pm AX}}{\gamma^\circ_{\pm BX}} + \ln Q \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (18).\end{aligned}$$

The value of the integral in equation (18) can be obtained by graphical integrations from the plots of ln $K_{\mathrm{A}'}^{\mathrm{B}'}$ *versus* $N_{\mathrm{B}_\mathrm{R}^+}$ and has been determined for alkali metal (lithium, sodium and potassium) - hydrogen exchanges on Amberlite IR-120 and Dowex 50WX4 for a series of methanol - water mixtures.[17] The activity-coefficient terms for the various ions at the specified solvent composition were obtained by interpolating Åkerlöf's data[56] for methanol - water systems.

For aqueous systems, equation (10), the contribution of the solvent-activity terms to the equilibrium constants in solutions of total ionic strength of 0·1M, or less, is negligible. However, in mixed solvents, some of these are important, that is, ln Q in equation (18) is significant [*cf.* equation (16)], particularly in solutions of high organic solvent content.[9,17]

Variations in Q are explicable in terms of resin cross-linkage and its effects on swelling, and also in terms of the ionic form, suggesting that equation (13) can account for ion-exchange equilibria in mixed solvents.[17]

ION-EXCHANGE KINETICS

A few studies have been made of ion-exchange kinetics in non-aqueous and mixed solvents.[57 to 62] Exchange rates in organic solvents are generally slower than in aqueous systems,[57] while intermediate values are often observed in mixed solvents. However, sodium and potassium exchange rates with hydrogen on the resin KU 2 in 60 per cent. aqueous methanol exceed those in aqueous solution.[62]

Rates are also dependent on salts under examination as illustrated by the more rapid exchange of lithium, as sulphate, for hydrogen compared with lithium chloride.[62]

The ion-exchange reaction of equation (1) is known to operate by inter-diffusion of ions,[63] that is, by "particle diffusion" and "film diffusion," the slower of the two determining the exchange rate.

The "particle diffusion" controlled mechanism may be covered[63,64] by

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 Bt}}{n^2} \quad \dots \quad (19)$$

where F is the fractional attainment of equilibrium at time t, n is the number of resin particles, and

$$B = \frac{\pi^2 D_1}{r^2} \quad \dots \quad (20)$$

where r is the radius of the resin particle (assumed to be spherical) and D_i the effective diffusion coefficient of the ions in the resin phase.

For the "film diffusion" controlled mechanism, the following equation[63,64] applies

$$\frac{d\phi}{dt} = \frac{3D_{B^+}}{r\Delta r} [B^+] - [B^+]_S \quad \dots \quad (21),$$

where ϕ is the amount exchanged in milli-equivalents ml^{-1} of swollen resin at time t, $[B^+]$ the concentration of the bulk solution and $[B^+]_S$ the concentration in the solution immediately in contact with the resin phase. Again r is the radius of the resin particle, while Δr is the film thickness and D_{B^+} the diffusion coefficient of B^+ ions (assumed to be constant).

Assuming $[B^+]_S = 0$ at $t = 0$, equation (21) reduces to a form that can be used for calculating film thickness[64]

$$\left(\frac{d\phi}{dt}\right)_{t=0} = \frac{3\ D_{B^+}}{r\Delta r} [B^+] \quad \dots \quad (22).$$

The values of $(d\phi/dt)_{t=0}$ can be calculated from $\phi - t$ plots.

Film-thickness values, Δr, obtained by Shankar and Ghate[58] for the exchange of lithium for hydrogen on Amberlite IR-120, are constant over lithium chloride concentration ranges of 0·001 to 0·01 M at a given methanol content. Its value is about double for 0·05 M lithium chloride implying that for low lithium chloride concentrations, "film diffusion" is rate controlling and, at higher concentrations, "particle diffusion" can influence the rate in addition to film diffusion.[58]

With rising methanol content, Δr increases at all lithium chloride concentrations, from about 3·5μ for the purely aqueous systems to about 6μ for 80 per cent. methanol. These deviations from the ideal[58] are attributed to changes in the diffusion coefficient, D_{B^+}, through variations in dielectric constant, viscosity and degree of ionic hydration, as well as to changes in the particle size caused by resin shrinkage.

Analysis of the kinetic data by Shankar and Ghate[58] for the "particle diffusion" controlled mechanism shows linear Bt *versus* t plots for lithium chloride concentrations between 0·05 and 0·1 M, with slope B, and passing through the origin, as was similarly found by Gorshkov, Panchenkov and Ivanova[62] for lithium, sodium and potassium chlorides with resin KU 2 in

60 per cent. methanol. The deviations at 0·01 and 0·001 M lithium chloride concentrations led Shankar and Ghate[58] to suggest that "particle diffusion" is the major rate-controlling factor above 0·05 M.

The kinetics of calcium - hydrogen exchange on Amberlite IR-120 in anhydrous and aqueous ethanol is, over-all, of reversible second order, favouring an equal dependence on the particle and film diffusion steps.[57] However, the calcium concentration studies were restricted to 0·05 and 0·025 M.

SOLVENT SORPTION BY ION-EXCHANGE RESINS

Ion-exchange resins are osmotic systems wherein the cross-linked matrix, which restricts the fixed ions to the resin phase, functions analogously to the membrane in a refined Donnan system. This means that, subject to certain limitations, osmosis will occur, drawing solvent into the resin and so cause swelling, a property depending on several conditions, including the ionic state of the resin,[9,22,65] temperature[66] and the liquid in contact with the resin.[66,67]

Where mixed solvent systems are used, the possibility of preferential osmosis arises and, in this connection, several independent studies with aqueous - organic solvent mixtures show polystyrenesulphonic acid,[9,20,22,25,68,69,70,71] and quaternary-base[20] resin phases to be predominantly aqueous with the ambient solution predominantly organic. This applies generally to water mixtures with the organic solvents methanol, ethanol, isopropyl alcohol, acetone and dioxan. Thus, acetone containing 30 per cent. water, equilibrated with a 10 per cent. divinylbenzene cross-linked polystyrene resin in the hydrogen form, gave liquid in the resin phase of composition 72 per cent. water - 28 per cent. acetone, leaving the outer liquid with an elevated 75 per cent. acetone content and 25 per cent. water.[71] This effect increases as the dielectric constant of the organic solvent decreases.[20] It is to be noted that for the quaternary-base resins preferential water sorption occurs to a lesser extent than for the sulphonic resins.[20]

Parkhomenko and Kurilenko[65,72] examined the selectivity of solvent sorption by cation exchangers from aqueous methanol[65] and aqueous ethanol[72] over the full range of solvent composition. The results agree with the above for certain solvent mixtures, but over the full composition range plots of excess sorption of alcohol constituent by the resin against original volume per cent. of alcohol are S-shaped, that is, they rise to a maximum, descend to a negative minimum and rise again.[65,72] For ethanol,[72] the S-shaped curve was found to pass through zero excess sorption when the original percentage v/v of ethanol was 30 to 33 for the strongly acidic polystyrene resin, KU 2; 53 to 57 for the bi-functional phenol - formaldehyde resin, KU 1; and 77 for the weakly acidic polystyrene resin, KB 4-P2. The exact percentage v/v of ethanol was dictated by the resin cationic form (H^+, Na^+, Ca^{2+} or Fe^{2+}).

An interesting consequence of selective sorption is that conditions for partition chromatography arise, thereby enhancing the normal ion-exchange separation factors.[25]

While sorption of the more polar solvent from a mixed solvent system often appears to be the rule, the cationic (or anionic) state of the resin influences the extent of selective sorption to a marked degree.[20,65,72,73] The extent of swelling in a single solvent system is also governed by the ionic state of the resin as well as the solvent (Table III).

TABLE III

DOWEX 50X8 RESIN SWELLING PATTERNS IN SINGLE SOLVENTS

Resin form	Cation radius* (crystallographic), Å	Ratio $\frac{\text{swollen volume}}{\text{dry volume}}$ for resin				
		Water			Methanol	Ethanol
		25°C†	25°C‡	30°C§	30°C§	30°C§
HR	—	2·19	2·4	2·5	2·3	2·4
LiR	0·60	—	2·3	2·4	2·3	1·12
NaR	0·95	1·94	2·06	1·94	1·58	1·03
KR	1·32	—	1·84	1·95	1·51	—
CsR	1·69	—	1·75	2·07	1·53	—
AgR	1·26	1·76	—	1·70‖	1·05‖	—
NH_4R	(1·48)	1·73	1·75	1·83	1·51	—

* Reference 74; † Reference 75; ‡ Reference 76; § Reference 22; ‖ Reference 9.
(The values ‖ may be low, see reference 20.)

In transferring a strong electrolyte from a medium of high to one of low dielectric constant, for example, from water to methanol to ethanol, it is to be expected that the solvation of ions should decrease progressively with consequent increase in inter-ionic electrostatic interactions. Even in solutions of high dielectric constant, larger ions should be less highly solvated than smaller ones. Indeed, the resinates of larger cations show a lesser degree of swelling in all three solvents (Table III), suggesting some basic degree of swelling resulting from osmotic activity.[9,22] The larger swollen volumes of the hydrogen and lithium resinates in water, and methanol, appear to reflect both the greater solvation of these cations and considerable osmotic activity.[22] In ethanol, only the hydrogen resinate appears fully dissociated and swollen, a behaviour that has been linked to the possible formation of $CH_3CH_2OH_2^+$ ions.[22] Caution must therefore be exercised when discussing ion-exchange behaviour in mixed solvent systems, for in many exchanges a metal - hydrogen resinate is present.[22]

Oleophilic ion-exchange resins experience appreciable swelling in most organic solvents, including hexane and benzene,[77,78] and hence possess functional ion-exchange properties in such solvents. The appropriate hydrophobic or oleophilic groups can be introduced into the resin polymer structure by the copolymerisation of methacrylic acid and dodecyl methacrylate; the copolymerisation of styrene and isobutylene, followed by sulphonation; the formation of a cage polymer of polystyrene about a linear, oil-soluble polymer of isobutylene or butyl rubber, followed by cross-linking and sulphonation; or the chloromethylation of polystyrene, followed by treatment with a long-chain tertiary amine.[77,78] A feature of these ion-exchange polymers is that exchange rates are often comparable with those of conventional ion-exchange resins in aqueous solution.[77]

The neutralisation of oleophilic resins in the hydrogen form by organic bases is regarded as an association - dissociation equilibrium, whose value is a measure of the base strength towards the resin sulphonate groups.[79] Different selectivities result, suggesting separation possibilities in non-polar media, for example, aniline from pyridine, nicotine from aniline, and renoxidine from reserpine.[79]

SORPTION OF UNCHARGED SPECIES

The organic solvents used in non-aqueous and aqueous - organic mixed solvents are principally oxo-compounds of the alcohol, ketone, and carboxylic acid types, generally having dielectric constants below 40. Cations and anions should, therefore, pair more strongly, through purely electrostatic forces, than in water ($\epsilon_{25^\circ} = 78$). For both cation and anion exchange, this factor may in itself be expected to alter selectivities for the resin. Hence, organic and mixed aqueous - organic solvent systems are attractive to achieve desired ion-exchange processes as well as to observe both the influence of the dielectric constant of the medium and the rôle of the solvent in the ion-exchange process.

At this stage, it is pertinent to note that high sorbabilities sometimes encountered can be explained by neutral sorption.[14,15,26,80 to 86] Thus, rapid sorption of several salts takes place from acetone on the chloride form of the strongly basic Dowex A-1.[86] That cations, as well as anions, are simultaneously sorbed is dramatically illustrated by the decrease in colour observed in the solution phase when coloured salts are used, accompanied by a progressive colouring of the solid resin with which it is in contact.[86] Separation of sodium halides with a cation exchanger by using aqueous acetone,[87] and silver nitrate sorption by the strongly acidic cation exchanger, Permutit RS in acetonitrile,[67] both support this idea.

Distribution measurements of zinc, cadmium and mercury tracers between Dowex 1X8 anion exchangers and anhydrous ethanolic solutions of lithium chloride and hydrogen chloride[26] also support a neutral sorption mechanism. Results for resin invasion by electrolyte are explicable in terms of uncharged complexes, for example, MCl_2 predominating in the resin phase, and ion pairs between lithium and hydrogen cations and complex anions, for example, $H^+MCl_3^-$ and $H_2^{2+}\ MCl_4^{2-}$ in the solution phase.[26] The concept of increased ion-pair formation in the resin phase to explain the increased selectivity coefficients in mixed solvents does not invalidate equation (15), the resin-phase activity coefficients incorporate all such effects.[16]

An alternative explanation is based on the observation that water is necessary before sorption can proceed, suggesting sorption under these conditions to be caused by preferential solution of the salts in the aqueous phase associated with the resin.[68,88] The presence of water is regarded as a limiting factor in possible applications of this kind of sorption for removing salts as a means of purifying organic solvents.[88] With this in view, the weakly basic tertiary amine resin, De-Acidite H, has been examined for its sorbability of lithium, copper(II) and cobalt(II) chlorides and of nickel(II) nitrate from solutions of acetone and dimethylformamide.[88] The results indicated that sorption on the dry resin occurred because of amine complexes formed between the resin functional groups and the salt:

$$n\ \mathrm{RN(CH_3)_2} + \mathrm{MX_m} \rightleftharpoons [\mathrm{RN(CH_3)_2}]_n\ \mathrm{MX_m}$$

where $\mathrm{RN(CH_3)_2}$ is the repeating polymer unit. No sorption of lithium chloride occurred on dry De-Acidite FF.[88]

A similar study concerned a Dowex A-1 iminodiacetic acid type of chelating resin for following the ion-exchange behaviour of lithium, sodium and potassium in the presence of the water-miscible solvents, methanol, ethanol, propyl and isopropyl alcohols and acetone.[89] The aqueous selectivity order, *viz.*, $Li^+ > Na^+ > K^+$ (the reverse of that observed on sulphonic acid exchangers), was found to reverse in various ways with increasing amount of organic solvent in the aqueous phase.

A reversal in the normal resin rôle is also noticed with anion exchangers (EDTA form) for selective cation sorptions.[24,90] Separation factors can be increased by working with aqueous ethanol solutions rather than with aqueous systems. The metal chelates, such as calcium or magnesium, are thought to be more stable in the mixed solvent, thus permitting a cleaner separation from alkali metal ions.[24,90]

CATION EXCHANGE

Twenty years ago no information relating to equilibria between resinous ion exchangers and salt solutions in non-aqueous solvents had been published. However, some earlier experiments, involving a synthetic calcium zeolite equilibrated with sodium, potassium or caesium chlorides in aqueous ethanol, indicated the preferential sorption of the alkali-metal ions by the solid phase with rising ethanol content.[91,92] Similar observations were subsequently made with the calcium form of a phenol sulphonate resin,[93] although the tendency for equality in the extent of exchange of all ions was not observed as with the zeolite. Certain ions, for example, NH_4^+, showed a reduced resin affinity as the ethanol component increased.[93]

Straightforward cation-exchange studies in non-aqueous, and mixed, solvent systems have been motivated by the desire to learn more about ion-exchange processes, and useful additional data on ion selectivities for cation exchangers have been accumulated. In these respects, reference has already been made to the frequent increase in selectivity coefficients for the exchange of given pairs of ions accompanying a decrease in dielectric constant of the solvent medium, and to the greater magnitude of the coefficients when mixed solvents are used. Variations in these trends can lead to changes of order in selectivities, *e.g.*, on Dowex 50X8 the aqueous selectivity order of $Cs^+ > K^+ > CH_3NH_3^+ > NH_4^+ > Na^+ > Li^+$ is twice reversed in methanol where $K^+ > Cs^+$ and $Na^+ > CH_3NH_3^+ > NH_4^+$.[22]

The dominance of potassium over caesium in methanol has also been found in aqueous ethanol comprising 50 per cent., or more, of ethanol with a zirconium phosphate exchanger,[94] and on Dowex 50X1 in aqueous dimethylformamide greater than 25 per cent.[95] With the basic monoethanolamine as solvent, the aqueous selectivity order $HO.CH_2.CH_2.NH_3^+ > K^+ > Na^+ > Li^+$ has been observed only for low solvent levels in water with the sulphonic acid resins Amberlite IR-120 and Zeo-Karb 225. A complete reversal of the sequence characterises the mixed solvent media containing higher levels of monoethanolamine.[73] Similar reversal trends were observed for the carboxylic acid resin, Amberlite IRC-50, throughout the full range of solvent composition.[73]

Additional examples of individual variation in selectivities are the increasing affinity of sodium ions for Dowex 50 of various degrees of cross-linking,[96] and caesium ions for Dowex 50X8[97] with increasing acetone and ethanol content, respectively. On Dowex 50, $K_{\mathrm{H}}^{\mathrm{Hg_2^{2+}}}$ is of greater magnitude in ethanol and dioxan[69] and $K_{\mathrm{Na}}^{\mathrm{Ag}}$ greater in methanol[9] than water, while on the cation exchanger, Wofatit C, the Ba^{2+} exchange rate increases greatly in alcoholic solution.[98]

Selectivity boosts vary with resin loading as illustrated by the cross-over observed in the comparison of $K_{\mathrm{H}}^{\mathrm{NH_4}}$ in methanol and water for various loadings.[9,27,97]

The decreasing order, $K^+ > Na^+ > Li^+$, characterises alkali metal ion affinities on cation-exchange resins in various media,[22,95,99] but in comparing different media it should be noted that the affinities change in magnitude even though the selectivity order may prevail.

Thus, these affinities are greater in aqueous ethanol than in aqueous methanol of comparable concentrations,[99,100] a finding supplemented by the ion exchange of $^{134}Cs^+$ ions on KU 1, KU 2 and KB 4P2 resins.[101] In the Ca^{2+} — Cs^+ system, the equilibrium favoured sorption of calcium on changing from aqueous to non-aqueous (methanol, ethanol and acetone) conditions. The association of Ca^{2+} ions with the resin was so great in acetone solution that practically no desorption with Cs^+ ions occurred.[101]

The distribution of alkali[102] and alkaline earth[18] metal ions between different resins and solutions containing methanol, ethanol or acetone, and the cation exchange of alkali metal ions from ethylenediamine have been reported.[103] Exchange rates tend to be slower than in water.

Bafna[104] has found that the selectivity coefficients of lithium, sodium, potassium and ammonium chlorides increase with increasing acetone content of an acetone - water mixed solvent solution. The linear relationship of the log selectivity coefficient with the reciprocal of dielectric constant noted in several independent studies[18,21,22,69,105] extends to a variety of cross-linked resins Dowex 50-X1, X2, X4, X8, and X16 for sodium - hydrogen exchange in acetone - water mixtures.[96] However, for intermediate solvent compositions, there is frequently a curvature leading to a maximum, usually at a weight concentration of 80 to 90 per cent. organic solvent,[22,104] which approximates to a mole percentage of 60 to 70 per cent. for methanol - water, ethanol - water and acetone - water.

The dielectric constant alone cannot be responsible for these effects. Others, possibly solvation of ions and hydrogen bonding, are involved as illustrated by greater cationic sorption of Ca^{2+} ions in acetone than in ethanol despite their dielectric parity.[101]

While the relation between the metal ion selectivity coefficient and organic solvent content follows the same pattern from one study to another, it should be noted that the maximum values of selectivity coefficients quoted for similar systems show wide variations. The maximum value of $K_{\mathrm{H}}^{\mathrm{Na}}$ in methanol - water mixtures is variously reported as 25 on Amberlite IR 120,[100] 17·2 on Dowex 50,[9] and 21·5—also on Dowex 50.[22] These variations doubtless arise from the different resins and also different ionic strengths used, although it is claimed that for a given set of conditions, selectivity coefficients are reproducible to within ±5 per cent.[22]

The greater range of selectivity coefficients with changing solvent, when compared with pure water (Table IV), is of potential analytical interest. Ion dehydration and resin swelling have been proposed to explain exchange equilibria of lithium, sodium, potassium, silver and thallium ions in aqueous ethanol (0 to 60 per cent.) on Amberlite IR-112 and of the first three ions on Amberlite IRC-50.[106]

TABLE IV

COMPARISON OF SELECTIVITY COEFFICIENTS ($K_{\mathrm{H}}^{\mathrm{M}}$) ON DOWEX 50 IN ALCOHOL - WATER MIXTURES AND WATER[22]

	87·7 per cent. methanol - 12·3 per cent. water*						91·1 per cent. ethanol - 8·93 per cent. water*
Exchanging species (M – H)	Li – H	Na – H	K – H	Cs – H	NH_4 – H	CH_3NH_3 – H	Na – H
$K_{\mathrm{H}}^{\mathrm{M}}$ in alcohol - water mixed solvent ..	1·85	20·7	93	63	8·9	9·3	102
$K_{\mathrm{H}}^{\mathrm{M}}$ in water ..	0·83	1·54	2·25	2·31	1·80	1·82	1·54
$K_{\mathrm{H}}^{\mathrm{M}}$ Enhancement $\left(\frac{\text{line 2}}{\text{line 3}}\right)$ ..	2·2	13	41	27	4·9	5·1	66

* These values correspond to 80 mole per cent. alcohol - 20 mole per cent. water.

An interesting application of non-aqueous ion exchange is the removal of iodine cations from ethanolic solutions of compounds such as iodine(I) nitrate and sulphate which are easily decomposed by water. This has been achieved with Amberlite resin (H-form), the exchange being followed by observing either the increase in hydrogen-ion content or decreasing iodine content of the solution.[107]

CATION EXCHANGE WITH COMPLEXING ELUANTS

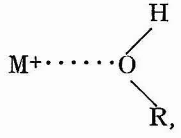
The selective sorption and elution of different cations based solely on a difference in resin affinity for each component are of limited application. As a result, eluting agents capable of forming complexes with some, or all, of the sorbed cations have received wide attention. For example, in purely aqueous solutions the use of buffered ammonium citrate solutions for separating lanthanides is well known, and there has been a wide and systematic study of cation-exchange behaviour in aqueous hydrochloric acid solutions. Consequently, organic solvents containing mineral acids, particularly hydrochloric, and other complexing species have been explored for their effective eluting potential for removing cations from ion exchangers.

Cation-exchange research in hydrochloric acid - organic solvent media has frequently been expressly concerned with separation problems. Thus, the resolution of lanthanide(III) ions in acetone-containing solution is claimed to be simpler in that the problems of rigorous temperature and pH control, characteristic of other methods, are avoided.[108] The separated species are generally obtained as simple chlorides after removing the organic solvent by distillation.

Compared with the single study of the alkali and alkaline earth metal exchange behaviour in methanol - hydrochloric acid on zirconium phosphate cation exchanger, the more familiar organic resinous exchangers have received wide attention.[99,105,109 to 132] The separation of lithium from other alkali metals with 90 per cent. methanol - 10 per cent. 12 M hydrochloric acid eluant for the lithium, is a typical example.[122] Complete separation of each alkali metal from lithium through to caesium is possible on Duolite C3 with two columns to complete the separation in the minimum time.[109] Thus, with 80 per cent. methanol - 20 per cent. of 2·4 M hydrochloric acid eluant, lithium and sodium are eluted individually followed by a mixed potassium and rubidium fraction eluted with 1·5 M hydrochloric acid and, finally, caesium eluted with 4 M hydrochloric acid. A second, longer column is used to separate the constituents from the previously concentrated potassium - rubidium fraction, when the potassium is eluted with 1·5 M hydrochloric acid and the rubidium with 6 M acid.

Duolite columns (sulphonated phenol - formaldehyde resins) were used[109] because of small differences in sorbability of the heavier alkali metal ions (potassium, rubidium and caesium) on Dowex 50 over the entire hydrochloric acid concentration range. Methanol tended to diminish the ratio of sorbability of the heavier cations even further, but significantly enhanced the sorbability ratios of the lighter members.[109]

The greater selectivity of the bi-functional sulphonated phenol - formaldehyde exchangers for the heavier alkali metal ions, compared with the sulphonated polystyrene - divinylbenzene exchangers, is now well established.[109,112,129] The effect can be explained by a non-exchange interaction between the hydroxyl groups in the resin and the Cs^+ ions and, to a lesser extent, Rb^+ ions.[112] This is confirmed by the fact that when phenol is introduced into the solvent, the affinity of the mono-functional sulphonic acid (Dowex 50) for Cs^+ ions is not only greatly depressed but the selectivity is even reversed.[112] Chromatographic investigations follow this trend,[133] and it has been supposed[112] that the weaker degree of solvation of Rb^+ and Cs^+ cations causes bonding between the metal cation and the hydroxyl group,



such bonds being stronger the more complex the hydrocarbon radical, R.

The behaviour of alkali metals on the mono-functional Amberlite IR-120 appears to be contradictory.[100,111,126,127,131] Thus, the five alkali metal cations can be separated by a solution containing 54·8 g of phenol, 25·2 ml of methanol and 20·0 ml of concentrated hydrochloric acid, the elution order being lithium, sodium, potassium, rubidium and caesium.[110,111,127] However, elution of potassium, rubidium and caesium in the absence of the other alkali metal cations gives the normal elution order: caesium, rubidium and potassium.[111,131]

Ethanol - hydrochloric acid[124,134] or acetone - hydrochloric acid[25,68,113] permits the chromatographic ion-exchange separation of lithium, sodium and potassium.

Tanaka[125] claims that the methanol in methanol - hydrochloric acid mixtures has a retarding influence on the elution of the heavier alkaline earth metal ions, an effect similar to that noted previously for the alkali metal ions, but, in this case, apparently permits a sharper separation of magnesium, calcium, strontium and barium on Amberlite IR-120, Diaion SK 1 and Dowex 50 than is possible with hydrochloric acid alone.

The range of cation-exchange applications is extended by a mineral acid because with suitable cations it produces a dissociation of the resin - cation complex and supplements alternative complex formation. In organic - aqueous mixed solvents, this is enhanced by the dehydrating action of the organic solvent, thus facilitating complex formation by the cations released. Such features are better illustrated by mixtures containing an ion with a stronger tendency towards complex formation than either the alkali or alkaline earth metal ions already cited. The behaviour of caesium, barium and zinc on a cation exchanger (KU 2)[135] provides an apt illustration.

True to form, K_d for both Cs^+ and Ba^{2+} ions increases with increasing organic solvent proportion of methanol, isopropyl alcohol or acetone. Alternatively, K_d decreases with increasing hydrochloric acid concentration. For zinc with hydrochloric acid, K_d falls with increasing organic solvent proportion for all three solvents. This can be attributed to the above dehydrating effect on the zinc ions, which can then form chloro-complexes.[135]

Quite apart from the alkali and alkaline earth metal ion studies cited, considerable attention has been directed to cation exchange of other ions with mixed solvent eluants of hydrochloric acid - organic solvents. These include hydrochloric acid - alcohol mixtures for the cationic sorption of indium(III),[136] gallium(III),[137,138] titanium(IV),[139] iron(III),[140] zirconium(IV),[141] niobium(V),[141] scandium(III),[142,143] praseodymium (III),[144] uranium(VI),[145] bismuth(III),[145] zinc,[146] cadmium[146,147] and mercury(II).[146]

Sorption of cations frequently increases on introducing an organic solvent into the hydrochloric acid system, although this is not universally so, particularly when anionic complex formation is appreciably stimulated.[135,140]

It is claimed[137] that a decisive factor affecting the distribution of gallium(III) between the cation-exchange resin, KU 2, and hydrochloric acid - alcohol solution is the change in electrostatic attraction between the ions, caused by a decrease in the dielectric constant of the solution. Branching of the alcohol chain possibly affects cation exchange, in that an increase of non-exchange sorption is observed in the presence of isopropyl alcohol compared with propyl alcohol.[138]

The distribution coefficient of uranyl ions on Dowex 50 is higher in isopropyl alcohol - 0·6 M hydrochloric acid than in any of a wide range of hydrochloric acid containing media.[145] It was found to be sufficiently high to retain uranium on a small resin column, contaminant bismuth passing unsorbed into the effluent as the anionic chloride complex. Other metal species, for example, vanadium, molybdenum, zinc, cadmium, indium and gallium, behave in a similar way to bismuth, thus facilitating their separation from uranium.[145] However, some earlier K_d data reported for aqueous isopropyl alcohol - 0·6 M hydrochloric acid[115] differ from those of a later more extensive study.[148]

The cation exchange behaviour of molybdenum(VI) on KU 2 is dependent on hydrochloric acid concentration within 0·01 and 4·0 M, and on ethanol concentration within 20 to 80 per cent. v/v, the figures quoted being the limits studied.[149]

Of the ketonic solvents, acetone has been an extremely popular choice for mixing with hydrochloric acid as it has been successfully applied in the separation of calcium from copper, zinc, mercury(II), cadmium and iron(III)[150]; copper from nickel[10]; iron(III), copper, zinc and lead from cobalt(II) and manganese(II)[151]; copper from zinc[152,153]; gold from nickel[154]; and scandium from manganese(II).[155] It has similarly been incorporated in the eluant for separating bismuth(III), cadmium, indium(III), zinc, iron(III), copper, uranium(VI), cobalt(III), gallium(III) and manganese(II).[2,156] Acetone - 0·6 M hydrochloric acid medium has been used for distribution-coefficient studies, on Dowex 50X8, of uranium(VI), thorium(IV), zirconium(IV), cerium(III), molybdenum(VI), vanadium(V), iron(III), aluminium, gallium(III), indium(III), bismuth(III), magnesium, calcium, lead, zinc, cadmium, copper, manganese(II), cobalt(II) and nickel[148]; and for examining the elution behaviour of copper, zinc, lanthanides(III), uranium(VI) and thorium(IV) from KU 2 and R 21 sulphonated phenolic resins.[108,144,157,158]

Korkisch and Ahluwalia[148] measured distribution coefficients in hydrochloric acid mixed with methanol, ethanol, propyl alcohol, 2-methoxyglycol, acetone, isopropyl alcohol, acetic acid or tetrahydrofuran. Their results provided a means of predicting a range of possible separations of metal ions, possibilities far greater in number and variety than exist in purely aqueous solutions, even with varying hydrochloric acid concentrations.[148]

Ethyl methyl ketone in admixture with hydrochloric acid has been shown to have some potential for the preferential elution of iron(III) over copper on Zeo-Karb 225.[10] The solvent has also been used to study sorption characteristics of scandium(III),[142] praseodymium(III)[144] and gallium(III).[138]

The analytical scheme devised by Van Erkelens[151] for biological ash samples includes a separation stage dividing constituents into groups, namely, molybdate, sulphate and phosphate; iron, copper, zinc and lead; cobalt and manganese; and the alkali and alkaline earth metals by using acetone - hydrochloric acid.

Effective separations of large amounts of iron(III) from cobalt(II) and nickel have been described for both tetrahydrofuran and acetone - hydrochloric acid eluants on Dowex 50.[159,160]

One interesting aspect of organic - hydrochloric acid eluants is "precipitation ion exchange."[161] This technique is based on initial sample sorption, followed by immobilisation of the matrix on the ion-exchange column by precipitation and non-selective elution of as many trace elements as possible before breakthrough of the matrix by its gradual dissolution. In this way it is possible to pre-concentrate from a cation-exchange column more than thirty trace (mainly transition) elements with greater than 90 per cent. recovery in a small volume from such matrix elements as sodium, potassium, strontium, barium and silver, by using concentrated hydrochloric acid as the precipitating eluant.[161]

The technique has been extended by using non-aqueous solvents. Thus, with 70 per cent. dioxan - 30 per cent. concentrated hydrochloric acid as precipitant - eluant, pre-concentration of more than forty elements is possible from an extended range of matrices comprising Group IA, IIA and IIIA elements.[162] Matrices of nickel, chromium, manganese, lead and aluminium may be worked with a precipitant - eluant of 81 per cent. dioxan - 10 per cent. ethanol - 9 per cent. concentrated hydrochloric acid.[162]

Possible applications of precipitation ion exchange are the ultra-purification of materials by exhaustive elution and the pre-concentration of trace elements from biological matrices containing large amounts of Group I and II elements.[162]

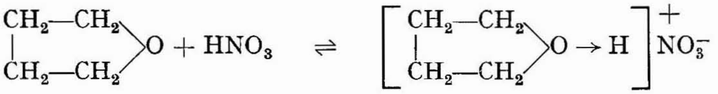
Cation-exchange separations on Dowex 50 have also been described, with organic - hydrochloric acid eluants containing amines and other complexing agents.[132]

Even although aqueous hydrobromic acid eluant permits separation of mercury(II), bismuth(III) and cadmium,[163] no comparable study has been made with mixed aqueous - organic solvent systems. To match the extensive study of distribution coefficients of a wide cation selection between Dowex 50 and organic solvent - hydrochloric acid mixtures,[148] Korkisch and his co-workers have carried out a similar study with hydrofluoric[164] and nitric acids.[165] Neglecting associated solubility problems, sorption and elution trends for hydrofluoric acid parallel the hydrochloric acid systems,[164] and there is little advantage with this more hazardous chemical.

Other instances of cation-exchange studies with organic solvent - nitric acid solutions include scandium(III) on KU 2,[143] the quantitative separation of uranium(VI) from thorium(IV) on Dowex 50,[166] and separations in the presence of amines and complexing agents.[132] This acid has also been included with tetrahydrofuran in "combined ion exchange - solvent extractions" of uranium(VI) on Dowex 50.[167,168,169]

The sorption behaviour of uranium(VI) with varying organic solvent content from 0 to 90 per cent., all containing 10 per cent. of 6 M nitric acid and water up to 100 per cent., showed that for both tetrahydrofuran and acetone, there were sorption maxima instead of the normal steady rise pattern of the distribution coefficient from 0 to 90 per cent.[168,169] This process, which seems to militate against cationic sorption and is unaccountable only in terms of anionic nitrate complex formation by the uranyl ion, is termed combined ion exchange - solvent extraction.

The following explanation in terms of a concurrent solvent extraction process with that of ion exchange has been proposed,[169] and is based on an analogy to uranyl nitrate extraction with diethyl ether:



$$\begin{matrix}CH_2{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix}\!\!>O + HNO_3 \rightleftharpoons \left[\begin{matrix}CH_2{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix}\!\!>O \rightarrow H\right]^+ NO_3^- \quad \ldots \quad \ldots \quad (23)$$

THF(ether) acting as Lewis base

Liquid anion exchanger in the nitrate form ($THFH^+NO_3^-$)

$$2[THFH]^+NO_3^- + [UO_2(NO_3)_4]^{2-} \rightleftharpoons [THFH]_2^+[UO_2(NO_3)_4]^{2-} + 2NO_3^- \quad \ldots \quad (24).$$

At high tetrahydrofuran concentrations, the liquid anion exchanger, $[THFH]^+NO_3^-$, is formed to a much greater extent, thus competing effectively with the solid cation exchanger, Dowex 50, for the uranyl ions, some of which are present as the anionic nitrate complex.

To date, of the many cations investigated, the combined ion exchange - solvent extraction behaviour is shown only by uranium(VI), bismuth(III) and thorium(IV); this phenomenon is advantageous in that after removing the extractable species (uranium in the example cited), a further fractionation of the sorbed metal ions can be achieved by appropriate elution.[169]

Aqueous thiocyanate - organic solvent mixtures have been examined for their effect in promoting anionic complex formation to bring about selective elution from the cation exchanger, Dowex 50X8.[170] Generally, it was found that the distribution coefficients are lower in solvents of low dielectric constant, although exceptions are known.[170]

Because of the enhanced anionic complex formation, decreasing the water ratio lowers the distribution coefficient, a feature that is of interest in the normally difficult quantitative recovery of thorium(IV) from a cation resin. For example K_d for thorium(IV) is only 0·7 in methanol - 1·6M ammonium thiocyanate, compared with 164 in the 1·6M aqueous salt solution and 67 in aqueous 4 M hydrochloric acid.[170] Several separations have been based on these distribution results.[170]

α-Hydroxyisobutyric acid as complexing agent has been investigated on Dowex 50X8,[171] when it was found that the europium - promethium separation improved by dissolving the reagent in non-aqueous solvents, the performance order being pyridine $>$ acetone $>$ dioxan $>$ methanol $>$ water.

The separation on Dowex 50X8 of magnesium, calcium, strontium, barium, aluminium and iron(III) has been successfully accomplished with formate buffers containing up to 10 per cent. methanol,[172] the rôle of the methanol being to retard alkaline earth elution rates, thus effecting sharper separations.

In a scheme for determining caesium-137 and strontium-90,[173] methanol - 0·2 M ammonium acetate (1 + 1) will elute sodium, potassium, magnesium and calcium from Amberlite CG-120, the retained caesium and strontium being subsequently removed with 2 M ammonium acetate.

Related to cation exchange with complexing eluants is the interesting concept of "distribution chromatography" described by Moskvin, Preobrajenski and Rjanuţina,[174] whereby combined dithizone extracts of zinc, cadmium and mercury in chloroform were placed on KU 2 containing aqueous hydrobromic acid. The metals were not eluted with chloroform, but successive elutions with ether, ether saturated with thiocyanic acid and M aqueous hydrobromic acid released mercury, zinc and cadmium, respectively.

ANION EXCHANGE

Applications and behaviour of anion exchange from solutions containing water-miscible organic solvents have been more intensively studied than cation exchange.

Selective cation sorption by an anion-exchange mechanism in the presence of suitable complexing eluants has solved many traditionally difficult separation problems, particularly with actinides and lanthanides, when mixed solvent systems based on water-miscible organic solvents have been freely used.[14,15,29,30]

Separation factors are again affected by the difference in resin phase and liquid solvent composition, that is, by conditions causing superposition of a kind of partition chromatography on the ion-exchange chromatography. That variations in separation factors are effected is illustrated by limited studies of straight anion exchange in mixed solvents.[175,176,177,178]

In the anion-exchange separation of sulphate, sulphite, thiosulphate, sulphide, selenite and tellurite, Iguchi[177,178] found that ethanol, added to the eluting agent, increased the sorbabilities of all but selenite and tellurite. Other studies, in ethanol - water mixtures, cover halide ions on the strongly basic anion exchanger, Amberlite IRA-400 (hydroxyl form),[175] and nitrate exchange for chloride ions attached to a weakly basic "N" anion-exchange resin.[176]

Conflicting interpretations have been proposed for the anionic molybdate[179] and tungstate[180] sorption on the strong anion resin, EDE-10 (chloride form). In each instance, the equilibrium

$$MO_4^{2-} + 4H^+ \rightleftharpoons MO_2^{2+} + 2H_2O \quad .. \quad .. \quad .. \quad .. \quad (25)$$

(where M is molybdenum or tungsten)

is proposed to account for the observations,[179,180] and for molybdate is tenable in accounting for the decrease in molybdenum sorption with increasing 0·1 to 2 M hydrochloric acid in ethanolic solution.[179] At acid concentrations greater than 2 M, heteropolyacids are formed, leading, it is claimed, to the observed increased anionic sorption,[179] whereas increasing ethanol content diminishes heteropolyacid production.[179]

The existence of such equilibria would appear to contradict the observed increase[180] in the anion-exchange affinity for tungstate. Indeed, cationic-sorption trends on the cation exchanger, KU 2, similarly contradict the fact that both molybdate[149] and tungstate[180] sorption actually fall for acidities between 0·01 and 0·5 M in aqueous and ethanolic media, but increase in the acidity range 0·5 to 4 M.

The chromatographic behaviour of boric acid in diethyl ether on Dowex IX 8 (chloride form) enables a rapid, quantitative separation from larger samples of uranyl nitrate.[177] The high solubility in ether of the uranyl salt, the adequate solubility of boric acid of 7·8 mg per 100 ml, non-retention of uranium by the resin and the ability to denude the column of uranium with ether are facilitating factors. Neither the volume nor the uranyl nitrate content of the solution affects the quantitative boric acid retention by the resin. Aqueous hydrochloric acid (5M) quantitatively elutes the boric acid, with the added advantage that any residual uranium is retained as an anionic chloride complex.[177]

ANION EXCHANGE OF CATIONS WITH COMPLEXING ELUANTS

HYDROCHLORIC ACID AND CHLORIDE SYSTEMS—

Hydrochloric acid is one of the most frequently investigated mineral acids in the aqueous anion-exchange field. The anionic chloride complexes formed show varying sorption behaviour under different pH conditions, thus enabling numerous metal separations. Regardless of mechanism, that is, whether it is by anion exchange of anionic chloride complexes or distribution of uncharged species between two phases,[26,81] many similar separations are possible in mixed aqueous - organic solvents although, in contrast with aqueous systems, the number of investigations is smaller. Lower alcohols and acetone are favoured solvents because of the relatively high solubility of many metal chlorides, as well as low cost availability. Metal species studied include members of the representative transition and inner transition series, particularly uranium and thorium.[14,181,182]

Many methods proposed for separating uranium(VI) from thorium(IV) and several other elements are based on the principle that anionic sorption of uranium(VI) occurs from aqueous hydrochloric acid.[183] Thorium(IV), which appears to form only a cationic complex, $[ThCl]^{3+}$,[184] shows negligible sorption under such aqueous conditions.[183] Simultaneous uranium(VI) and thorium(IV) sorption from hydrochloric acid in mixed aqueous - organic solvent media[14] is, therefore, a noteworthy feature.

This simultaneous sorption is facilitated by high alcohol content[14,185,186,187] of the hydrochloric acid and by the longer chain alcohols of lower dielectric constant.[14] Under comparable conditions, uranium(VI) sorption always considerably exceeds that of thorium(IV).[14] Even so, the distribution coefficient of thorium(IV) at high longer-chain alcohol levels is sufficient to ensure quantitative sorption of both elements.

The normal effect of hydrochloric acid concentration on their respective sorptions with anion exchangers is to raise the distribution coefficients with increasing acid - alcohol ratios for a wide variety of alcohols.[14,15,181,187] Increasing the alcohol content of solutions of fixed pH also raises the distribution coefficients.[14,15] For uranium(VI), any increase at a given alcohol concentration is practically linear with over-all solution acidity,[14] but with thorium(IV), results are more variable, deviating from linearity in 74 per cent. isopropyl alcohol, but showing no such variation in 96 per cent. propyl alcohol.[181]

The organic solvent sorption effect is possibly caused by the repression of UO_2Cl_2 dissociation, thereby permitting direct sorption on the resin.[187] The anionic sorption of uranium(VI) from aqueous methanol, even without hydrochloric acid, as well as the suppression of UO_2Cl_2 dissociation by hydrochloric acid, both support this concept. Enhanced sorption in acid is accountable in terms of negatively charged complexes, a theoretical capacity of the anion $[UO_2Cl_4]^{2-}$ at 404·6 mg of uranium per g of dry Dowex 1X 8 (chloride form), being in good agreement with the experimental value of 412·5 mg per g.[181]

Korkisch[15] attributes the divergence of thorium(IV) K_d values, found by Fritz and Pietrzyk[181] and Korkisch and Tera[188] in ethanol - hydrochloric acid, to the large amounts of thorium used by the former authors[181] in their equilibrium experiments. The steep descent in the distribution coefficients of both uranium(VI) and thorium(IV) with increasing metal ion concentration supports this view. For example, K_d for uranium(VI) in 90 per cent. ethanol - 10 per cent. of 6 M hydrochloric acid, while remaining constant at 7×10^3 up to a concentration of 100 mg per 100 ml of uranium(VI), falls sharply at higher concentrations, reaching 35 when 2000 mg per 100 ml of uranium(VI) is present.[14] The maximum exchange capacity of 412·5 mg of uranium(VI) per g of dry Dowex 1X 8 resin is exceeded for 1600 mg per 100 ml, or more, of uranium(VI) in the solution.[14]

For thorium(IV) in 96 per cent. isopropyl alcohol - 4 per cent. 12 M hydrochloric acid, the distribution coefficient remains constant at just over 10^3 up to 40 mg per 100 ml again falling rather rapidly at higher concentrations down to a value of 10 when 800 mg per 100 ml of thorium is present.[14] The capacity of the Amberlite IRA-400 used was 58 mg of thorium(IV) per g of dry resin.[14]

Detailed examination of these data suggests that uranium(VI) and thorium(IV) separation can most easily be effected in alcohol - hydrochloric acid mixture when methanol or ethanol is used. For higher alcohols, simultaneous sorption of both radio-elements occurs, but, even so, the appreciable differences in K_d values permits their chromatographic separations. Indeed, several methods for isolating the elements have been developed. For example, the metal ions sorbed on Dowex 1X 8 (chloride form) from 90 per cent. butyl alcohol - 10 per cent. 6 M hydrochloric acid can be separately eluted, the thorium with 90 per cent. methanol - 10 per cent. of 6 M hydrochloric acid and the uranium with M hydrochloric acid.[186] The procedure can be used for separating microgram or milligram amounts and one suggested application is the continuous milking of daughter thorium isotopes from natural uranium.[186]

Apart from uranium - thorium separation in media containing lower alcohols, uranium can simultaneously be isolated from a host of other species that may, or may not, form anionic chloro-complexes under the prevailing conditions. This is illustrated by a separation procedure for uranium(VI) from many cations and fluoride, sulphate and nitrate anions.[13,189] Sorption from 80 per cent. ethanol - 20 per cent. 4 M hydrochloric acid takes place on Dowex 1X 8 (chloride form) from which all ions, except uranium(VI) and co-sorbed tungsten(VI), molybdenum(VI), bismuth(III) and lead, are released with the 80 per cent. ethanol - 20 per cent. 4 M hydrochloric acid. Addition of ascorbic acid prevents iron(III) sorption. Subsequent elution with 0·1 M hydrochloric acid saturated with diethyl ether releases the uranium(VI) leaving the other co-sorbed ions on the resin. The method has been suggested for the microgram assay of uranium in natural silicate rocks and marine sediments.[13,189]

Anionic uranium(VI) and thorium(IV) sorption in 2-methoxy- and 2-ethoxyglycol systems[182] is similar to that in methanolic and ethanolic solution, that is, with lower, rather than higher, sorption observed for higher alcohols. It has been suggested that the ether grouping counteracts the effect of increased chain length,[182] and a mechanism analogous to that represented in equations (23) and (24) could well be responsible.

By using ether alcohols the separation of uranium(VI) from other species is greatly improved.[190,191,192] Lead is not separated, but a special feature is that iron(III), even in larger amounts can, because of its minimal K_d in these ether alcohols compared with other solvents,[190] easily be separated from uranium(VI). The method is thus recommended for uranium assay in ferrous alloy and steel samples, consisting predominantly of iron, as well as in sea water, marine sediments, monazites and granites.[191,192] The low iron(III) K_d values in ether alcohols are attributed to stable complexes formed with 2-methoxy or 2-ethoxyglycol,[15] a process analogous to that governing the ready extraction of iron(III) ions from hydrochloric acid into ethers and ketones, and to the solvent extraction part of the combined ion-exchange - solvent-extraction process.[167,168]

In ketone - hydrochloric acid mixtures, K_d for uranium(VI) first decreases with increasing ketone concentration, only attaining the same value as thorium(IV) for acetone.[193] The thorium(IV) pattern is a steady K_d increase up to the 95 per cent. solvent level in mixtures of the water-soluble acetone, ethyl methyl and methyl propyl ketones.[193] Of analytical significance is the fact that both uranium(VI) and thorium(IV) are strongly sorbed (K_d 800 and 1100, respectively) from 90 per cent. acetone - 10 per cent. M hydrochloric acid on to Dowex IX 8 (chloride form). Thorium(IV) and uranium(VI) are eluted with 6 M and M aqueous hydrochloric acid, respectively.[193]

Uranium is much more strongly sorbed than thorium on Dowex 1X 8 from hydrochloric acid containing dioxan, diethyl ether or di-isopropyl ether. In 50 per cent. dioxan - 50 per cent. 6 M hydrochloric acid, the K_d values for uranium (VI) and thorium(IV) are 560 and 14, respectively.[194] Because of immiscibility problems the K_d variation of uranium(VI) and thorium(IV) with ether concentration has only been investigated for dioxan.[194] The best conditions for preferential uranium(VI) sorption on Dowex 1 exist with 90 per cent. dioxan, when thorium(IV) shows minimal sorption. A similar solvent ratio with nitric acid instead of hydrochloric acid provides, on the other hand, the more nearly ideal conditions for preferential sorption of thorium(IV).[194]

Acidity of the ether, between 0·005 and 0·06 M, has negligible effect on the uranium(VI) distribution coefficient, the effect for thorium(IV) not having been studied.[194] However, low chloride solubility in ethers limits analytical applications.

In contrast to the practically non-existent sorption of both uranium(VI) and thorium(IV) from formic acid solution, their separation can easily be effected in acetic acid solution; K_d for uranium(VI) being 10^5 and for thorium(IV) being 20 in solutions containing 90 and 95 per cent. acetic acid and 10 and 5 per cent. 6 M and 12 M hydrochloric acid, respectively.[182]

A comparison of the sorption characteristics of uranium and thorium with the lanthanides shows that only uranium can be effectively separated.[15] The procedure, more successful in a solution containing methanol, ethanol or acetic acid, is important in separating uranium from its fission products. However, recently, Cummings and Korkisch[195] have described a separation of thorium(IV) from the lanthanides in acetone - hydrochloric acid. Methanol admixed with hydrochloric rather than nitric acid is more effective for separating lanthanides from actinide(III) ions,[196] and has also been used for inter-actinide separations, for example, californium and einsteinium from americium and curium.[196]

An organic solvent is required before lanthanides show any appreciable sorptive properties from hydrochloric acid solution.[197,198,199] Even then, resolution is difficult because of similar distribution results under various conditions of solvent type and hydrochloric acid concentration.[181,182,199]

Lanthanide sorption increases with alcohol chain length, so much so that simultaneous sorption with uranium(VI) and thorium(IV) is possible from a s-butyl alcohol medium.[182] Increasing the ethanol and hydrochloric acid compositions increases the sorption of yttrium, lanthanum and neodymium.[199]

Much information on the anionic sorption of normal transition elements has been obtained in the course of uranium and thorium research,[182,190] but, additionally, several systematic investigations have been specifically directed at the transition metals themselves.

Anionic sorption of palladium as $[PdCl_4]^{2-}$, and platinum as $[PtCl_6]^{2-}$, gives distribution coefficients dependent on the nature of the organic solvent, relative proportion of water, resin and acid concentration.[200] In alcoholic systems, Korkisch and Hazan[182] included several transition metal ions and found that cobalt(II) sorbs more strongly than iron(III) or nickel, and copper more strongly than chromium(III) or manganese(II). The general trend towards higher distribution coefficients for the higher branched alcohols is maintained.[182]

Anionic sorption of titanium(IV),[139] iron(III),[140] zirconium(IV) and niobium(V)[141] on Dowex 1 is enhanced by increasing the organic solvent content of hydrochloric acid.

The iron(III) complexes formed in ethers, ether alcohols or ketones leads to lower K_d values and permits effective separation of iron from other elements.[182] A further illustration is that Dowex 1X 8 (chloride form) retains nickel, cobalt(II), copper, manganese(II) and aluminium from 90 per cent. acetone - 10 per cent. 6 M hydrochloric acid, leaving the iron(III) to pass into the effluent. Elution with 70 per cent. acetone - 30 per cent. 2 M hydrochloric acid permits an ion-exchange - chromatographic separation of cobalt(II) from nickel.[201] Nickel, if present, partners manganese(II), aluminium and chromium(III), while cobalt(II) is eluted with copper. These actual separations are predictable from published results as shown in Table V.

TABLE V

DISTRIBUTION COEFFICIENTS IN HYDROCHLORIC ACID - ACETONE ON DOWEX 1X 8 (CHLORIDE FORM)[15,201]

	Elements					
Eluting mixture	Iron(III)	Nickel	Cobalt(II)	Copper	Manganese(II)	Aluminium
90 per cent. acetone - 10 per cent. 6M hydrochloric acid	<1	40	170	70	230	38
70 per cent. acetone - 30 per cent 6M hydrochloric acid	<1	2	20	23	3	8

An earlier, similar separation of cobalt(II) from nickel was achieved with 75 per cent. acetone - 25 per cent. 1·5 M hydrochloric acid on Amberlite IRA-400; the acetone eluant was selected because of the high distribution coefficient of the more strongly held cobalt(II) with acetone systems (see Table V).[202] The results of a study of three organic solvents by Subrahmanyam and Sastri[202] showed that both cobalt and nickel exhibited their highest distribution coefficients with acetone, followed by ethanol and methanol.

Cobalt(II) and iron(III), which are both strongly sorbed, can be separated from nickel in acetic acid solution and, by a chromatographic procedure, from one another.[182] Successful chromatographic procedures described for selective elution of these three metals, as well as copper and zinc, from methanol - hydrochloric acid solutions[203] depend on the change in K_d with variation in methanol - hydrochloric acid ratios. A typical separation and solvent-elution pattern is recorded in Table VI. Similar separations based on these principles have been devised for ethanol[181,185] and isopropyl alcohol[181] solutions. Ethanol - hydrochloric acid solutions have been used for separating copper and aluminium from diecast zinc alloys prior to individual titrimetric determination,[204] and for manganese(II) separation from nickel and calcium,[205] while almost absolute ethanol elutes scandium to leave yttrium on Dowex 1X 8 (chloride form).[205]

TABLE VI

SEPARATION OF TRANSITION METALS AND ZINC IN METHANOL - HYDROCHLORIC ACID ON DOWEX 1X 8 (CHLORIDE FORM)[203]

Elution order	Metal eluted	Eluant
1	Nickel	60 per cent. methanol - 40 per cent. 3·5M hydrochloric acid
2	Cobalt	60 per cent. methanol - 40 per cent. 2·5M hydrochloric acid
3	Copper	30 per cent. methanol - 70 per cent. 3M hydrochloric acid
4	Iron	M Hydrochloric acid
5	Zinc	Water

Sorption of copper, chromium(III) and manganese(II) shows the normal general increase from methanol through butyl alcohol and acetone to s-butyl alcohol solutions.[14] Similarly, vanadium(V) sorption is highest in a s-butyl alcohol solution and lowest in a methanol solution.[206,207] Copper and iron(III) have appreciable distribution coefficients in methanol solutions although those of nickel and vanadium(V) are negligible, and separations in pairs is possible. Nickel and vanadium(V) can be eluted from Dowex 1X 8 (chloride form) with 90 per cent. methanol - 10 per cent. 6 M hydrochloric acid, followed by elution of copper and iron(III) with M hydrochloric acid.[206,207] The method is suggested as suitable for the separation, and assay, of microgram levels of nickel and vanadium(V) in crude oils and petroleum products.[206,207]

Gold(III) sorbed on anion-exchange resins as cyanide or chloro-complexes can be completely eluted with acetone, ethanol or ethyl acetate containing 5 per cent. concentrated hydrochloric acid and 5 per cent. water.[208]

Formic acid, which has no methyl group, is an unique solvent. Korkisch and Hazan[182] found few instances of anionic-exchange behaviour from hydrochloric acid - formic acid media. Of the twenty-three ions examined, only manganese(II), zinc, cadmium, mercury(II), gallium(III) and indium(III) showed any sorption inclination, an additional six being sorbed from acetic acid systems.[182]

The distribution coefficients of zinc, cadmium and mercury on Dowex 1X 8 (chloride form) are in the range 10^2 to 10^3 for the 90 or 95 per cent. organic solvent - 10 or 5 per cent. 6 or 12 M hydrochloric acid solutions examined by Korkisch and Hazan,[182] those of zinc being greatest and mercury least. Observations made on Amberlite IRA-400 in aqueous ethanol, isopropyl alcohol, butyl alcohol or t-butyl alcohol - hydrochloric acid mixtures are in accordance with this,[146] the order of K_d values being $Cd^{2+} < Zn^{2+} < Hg^{2+}$,[146] compatible with the fact that in anhydrous ethanol containing hydrogen chloride or lithium chloride, cadmium has the lowest distribution coefficient.[26] Fritz and Pietrzyk[181] also studied the sorption behaviour of zinc and cadmium in hydrochloric acid containing methanol, ethanol and isopropyl alcohol, particularly regarding pH influence and non-aqueous volume ratio. Their results show that, following an initial rise, the sorption of both zinc and cadmium decreases when the hydrochloric acid concentration is increased, and the zinc sorption is less than cadmium at the lower acid concentrations. This order explains the preferential elution of zinc with 0·01 M hydrochloric acid containing 10 to 25 per cent. methanol in Berg and Truemper's separation scheme.[209] It is difficult to explain in terms of the evidence presented by Yoshino and Kurimura.[210] This indicates that the organic solvent favours the dehydration of hydrated zinc ions, $[Zn(H_2O)_4]^{2+}$, culminating with the complex, $[ZnCl_4]^{2-}$. Kraus and co-workers previously suggested the chloro-complex to be responsible for increasing anionic sorbability in aqueous solutions.[197,211,212]

Gallium(III) and indium(III) have been mentioned above in connection with their weak sorbability from formic acid solution. However, other solvents are essential for adequate sorbability levels, permitting a separation from aluminium which, except for acetone, gives lower K_d values.[182] Separations are possible in methanol, ethanol, propyl and isopropyl alcohols with decreasing efficiency in that order. Separations are more difficult in butyl alcohol and s-butyl alcohol solutions because of marginal distribution coefficient differences. In these, and other alcohol media, chromatographic procedures must be used.[213] A gallium - indium separation is difficult, but in acetone - hydrochloric acid medium the exceptional behaviour of aluminium and indium permits separation of indium from gallium.[182,213] Thus, on Dowex 1X 8 (chloride form) the sequential elution order, gallium, indium, aluminium, follows the successive use of 80 per cent. acetone - 20 per cent. 3 M hydrochloric acid, 90 per cent. acetone - 10 per cent. 6 M hydrochloric acid and 70 per cent. acetone - 30 per cent. 2 M hydrochloric acid, respectively, when each eluant has the same over-all acid concentration (0·6 M).

Magnesium, calcium and strontium in alcohol solutions show the same characteristic sorption increase with increase in alcohol chain length, strontium having the highest and magnesium the lowest K_d value, but with sufficient difference only for chromatographic separation of the elements.[15,182]

Beryllium can be separated from the alkaline earth metals, aluminium and practically all other elements, but not from the alkali metals, ammonium ions and phosphoric acid, by passing a solution in 90 per cent. propyl alcohol - 10 per cent. 6 M hydrochloric acid through Dowex 1X 8 (chloride form). On elution with the same solvent, beryllium, alkali metals, ammonium ions and phosphoric acid appear in the effluent.[214] The sorbed constituents can be released with M hydrochloric acid.

Finally, Ruch, Tera and Morrison[215] have examined the anion-exchange behaviour of most Group I and II metals at various dioxan - hydrochloric acid ratios. The extent of alkali and alkaline earth metal sorption increases with increasing dioxan concentration and decreases with increasing hydrochloric acid concentration at high dioxan levels. Rubidium, and other alkali metal ions are likely to be preferentially eluted, thereby offering separation possibilities from magnesium, calcium, strontium and barium on Dowex 1X 8 with 78 per cent. dioxan - 22 per cent. 0·49 M hydrochloric acid as eluant.

NITRIC ACID AND NITRATE SYSTEMS—

The anionic character of uranium(VI) and thorium(IV) in nitrate-containing solutions[216] facilitates anionic sorption on strongly basic resins from aqueous systems. However, sorption in many instances is poor, as with the lanthanides from pure nitric acid solutions on strongly basic anion exchangers of the quaternary amine type.[217,218,219,220,221] The poor sorbability can be remedied by replacing nitric acid with ammonium[183,219] or lithium nitrate.[222,223] However, as for chloride systems, sorbability is promoted by adding alcohols,[1,14,15,29,30,37,132,187,224 to 253] 2-methoxyglycol,[213,233,254] dioxan,[194,214,215,255] diethyl ether,[194,256] carboxylic acids,[192,233] tetrahydrofuran[214,251] or acetone[86,132,193,214,257,258,259,260] to the aqueous phase.

Many metals, particularly uranium(VI) and thorium(IV), have been examined in nitrate-containing solutions. Dowex 1X 8 has been commonly used, although Amberlite IRA-400[37,227,236] and Amberlyst XN-1002[243] have both been used for lanthanides.

An important vehicle for anionic sorption from organic solvent - nitric acid solutions is the formation of an anionic complex,[241,261,262] such as $[UO_2(NO_3)_6]^{4-}$.[241]

It has been found that uranyl nitrate complex sorption from nitric acid - alcohol solutions is favoured by increasing alcohol chain length, as well as by increasing alcohol concentration.[14] But the thorium(IV) nitrate complex, on the other hand, is most strongly sorbed from methanol.[14,252] These trends, coupled with the higher thorium(IV) distribution coefficients, generally of the order of 10^2 under most alcohol concentrations, permit separation of thorium(IV) from uranium(VI).[14] For example, by selecting a sorption solution of 80 per cent. ethanol - 20 per cent. 3·5 M nitric acid with Dowex 1X 8 (nitrate form), K_d is 700 for thorium(IV) but only 9 for uranium(VI), a condition favouring thorium sorption, leaving uranium in solution with titanium(IV), zirconium(IV), aluminium and the alkali metals.[12] Microgram assay of thorium in silicate rocks and marine sediments, with 0·1 M nitric acid saturated diethyl ether eluant, is based on these facts.[14] Other variations involving ethanol - nitric acid media,[228,229,230] and even higher alcohols,[14,82,83,84] have also been successful for thorium separations.

High separation factors are available for exploitation in the thorium - uranium systems cited, for example, 90 per cent. methanol - 10 per cent. 5 M nitric acid, with K_d values of 12,475 and 33 for thorium(IV) and uranium(VI), respectively, can be used for separating thorium from uranium and from a wide range of other elements, on elution with M nitric acid.[231]

Separate studies[186,187,232,252] have been concerned with the effect of nitric acid concentration. Thus, with thorium solutions in 96 per cent. methanol of varying nitric acid concentration, it was shown[252] that acidity did not influence the sorption of the negatively charged nitrate complex. Within the range 0·6 to 0·005 M nitric acid, no hydrolysis of the complex occurs, as indicated by 99·94 per cent. thorium sorption in each instance. For 0·0025 M nitric acid, however, the partial hydrolysis of the thorium nitrate[252] represents a much lower acidity level than the threshold 0·04 M hydrochloric acid concentration corresponding to the breakdown of the chloride complex.[188] In other instances, the distribution coefficient usually increases with increasing nitric acid concentration,[187,232] although with thorium(IV) in 60 and 80 per cent. ethanolic systems, the distribution coefficient attains a maximum value at 0·7 M acid and subsequently falls.[232] The uranium(VI) distribution coefficients in 40, 60, and 80 per cent. ethanolic solution on the other hand tend to have limiting values when nitric acid exceeds 1 M.[187]

As with hydrochloric acid systems, the effect of increasing uranium(VI), and thorium(IV), concentration is a decreased distribution coefficient.[14]

With hydrochloric acid it is possible to extend the above uranium - thorium separation scheme involving alcohol - nitric acid mixtures to include bismuth[234] because of poor thorium(IV), but strong bismuth(III), sorption from methanol - hydrochloric acid solutions.[187] The procedure evolved[234] depends on simultaneous sorption of the three metallic species on Dowex 1X 8 (nitrate form) from a solution in 96 per cent. propyl alcohol - 4 per cent. 5 M nitric acid. The uranium is eluted with 80 per cent. methanol - 20 per cent. 5 M nitric acid, followed by thorium with 80 per cent. methanol - 20 per cent. 6 M hydrochloric acid and, finally, bismuth with M nitric acid.

Uranium(VI) and thorium(IV) have been studied in non-alcoholic solvents,[192,194,257] but, unlike the pH-dependent alcohol - nitric acid systems, no such effect was found in diethyl ether, at least within the 0·01 to 0·1 M range studied.[194] Furthermore, the acidity dependence was not pronounced in 80 per cent. dioxan - 20 per cent. nitric acid even although the nitric acid concentration range reached 2 M.

Both aluminium and iron(III) show a decreasing affinity for Dowex 1X 8 in diethyl ether solutions of increasing nitric acid concentration, but at no stage within the concentration range studied is there any interference with the uranium separation from these elements or from thorium.[194]

As for alcoholic systems, increased resin affinity follows increasing acetic acid concentration.[192] While this increase was greatly magnified for an organic solvent content exceeding 90 per cent., log K_d increases linearly with acetic acid content. Because of solubility limitations, distribution coefficients adequate for quantitative sorption of microgram and milligram quantities of the elements are limited to 80 to 90 per cent. organic solvent.

Generally, propionic acid produces higher distribution coefficients than acetic acid but, as with chloride systems already mentioned, sorption from formic acid - nitric acid media is weak.[192]

Of the wide range of metal distribution coefficients in 90 per cent. acetic or propionic acid - 10 per cent. 5 M nitric acid on Dowex 1X 8, thorium(IV) has a high value, $1{\cdot}6 \times 10^5$, compared with about 10^3 for bismuth(III), lanthanum(III), praseodymium(III) and cerium(III). Coefficients for other lanthanide(III) species, lead(II) and uranium(VI) are lower, falling between 10^2 and 10^3, and 10 to 10^2 for transition metal ions. Values not far removed from unity hold for chromium(III), iron(III), magnesium and aluminium.

Regarding representative metal ions, there is some increase in distribution coefficient with atomic weight, which for chromium, gallium(III) and indium(III) are 0·1, 5·4 and 21, respectively, in 90 per cent. acetic - 10 per cent. 5 M nitric acids. Such a trend is of little analytical significance, as a K_d value of about 10^2 is considered an essential prerequisite to any strong metal - resin affinity.[192]

It is clear that there are many instances of sufficiently high, as well as varied, distribution coefficients in 90 per cent. organic acid - 10 per cent. 5 M nitric acid mixtures to allow many feasible separations. Large amounts of phosphate, sulphate and chloride do not interfere with separations, whereas quite small fluoride levels cause considerable interference.[192]

A separation procedure, based on the above data and tested on a marine sediment sample, is deemed to be well suited for the quantitative separation of uranium, thorium, the lanthanides, yttrium, cadmium, bismuth and lead as a group from other elements.[192]

Variation of nitric acid concentration up to 1·5 M in 90 per cent. acetic acid results in slightly increased distribution coefficients for ter- and quadrivalent ions and a slight decrease for bivalent ions.[192] Similar effects are observed with ammonium nitrate.[192]

Increasing the metal ion concentration results in even lower K_d values for poorly sorbed species, but the greater the K_d value the more likely it is to be unaffected by increasing metal concentration.[192]

With tetrahydrofuran as the organic solvent constituent there is the possibility of a competing liquid anion-exchange process (equations 23 and 24) and it is not surprising, therefore, that both uranium(VI) and thorium(IV) pass into the eluant.[263] This feature permits the separation of lead from a wide range of metals with Dowex 1X 8 and 90 per cent. tetrahydrofuran - 10 per cent. 5 M nitric acid eluant. In these circumstances only lead, lanthanum(III), cerium(IV) and praseodymium(III) are retained on the resin, the remainder, including the lanthanides from samarium(III) to lutetium(III), passing into the eluant.[263] The lead can be eluted with 80 per cent. tetrahydrofuran - 20 per cent. 2·5 M nitric acid. The separation can be applied to sediments, petroleum products, alloys and biological material.[263]

Appropriate use of nitric acid - acetone provides a further basis for separating and recovering thorium(IV) and uranium(VI).[193] In this way, thorium ($K_d = 1100$) is retained on Dowex 1X 8, and uranium(VI) ($K_d = 10$) passes into the effluent of 90 per cent. acetone - 10 per cent. 10 M nitric acid eluant. When the recovery of both metals is desirable, hydrochloric acid offers advantages in that 90 per cent. acetone - 10 per cent. M hydrochloric acid permits the sorption of both thorium(IV) ($K_d = 1100$) and uranium(VI) ($K_d = 800$) on Dowex 1X 8. Subsequent separation and recovery can be made by elution with 6 M hydrochloric acid for thorium ($K_d = 1$); uranium ($K_d = 900$) is held by the resin and may be released by elution with M hydrochloric acid.[193] Ethyl methyl, diethyl or methyl propyl ketones offer no special advantage over acetone.[193]

Anion exchange of other actinides from a variety of nitric acid - organic solvent media has been investigated.[226,251,253] Separation of americium(III) and curium(III) on Dowex 1X 8 and AV-17 are based on the increased Kd_{Am}-to-Kd_{Cm} ratio from 2·0 to 3·3 when the methanol component is increased from 80 to 95 per cent. with 0·2 M nitric acid content.[253] Within this range, Kd_{Cm} increases markedly from 9 to 550.[253]

Nitric acid - ketone solutions constitute an explosion hazard,[258] and Alstad and Brunfelt[259] found that 40 per cent. concentrated nitric acid - 60 per cent. acetone reacted violently after 1 day.

At low nitric acid content, the lanthanides are strongly sorbed with K_d ranging from 10^2 to 10^5 in 90 per cent. acetone - 10 per cent. concentrated nitric acid medium.[259] With increasing nitric acid distribution coefficients decrease, illustrating the general effect of K_d increase with increasing organic solvent. Indeed, in passing from 8 M aqueous nitric acid to 90 per cent. acetone - 10 per cent. concentrated nitric acid medium distribution coefficients rise by a factor[259] of 10^3 to 10^5.

The lesser drop in the dielectric constant for 90 per cent. methanol - 10 per cent. concentrated nitric acid increases the distribution coefficient to a smaller degree, an enhancement factor of about 10^2 being characteristic of lanthanides on Dowex 1X 4 for the medium cited when compared with water.[227]

K_d values for 85 per cent. propyl alcohol - 15 per cent. concentrated nitric acid[244] and 85 per cent. acetone - 15 per cent. concentrated nitric acid[259] are similar, matching the approximately equal dielectric constants, 18·3 and 20·7, respectively. Lanthanide separation appears sharper with the acetone, but different resins were used—Amberlyst XN-1002, with its dimethylethanolammonium radicals, for the propyl alcohol and Dowex 1, with its trimethylbenzylammonium radicals, for the acetone system.

There is little apparent difference between ethanolic and acetone systems,[259] but any differences found in systems of similar dielectric constants cannot easily be understood without adequate explanation of the nitric acid state in various mixed liquid phases and the activity coefficient dependence on ion association.

The decrease in K_d with increasing atomic number, and with increasing nitric acid content, has been used to design a lanthanide separation procedure.[259] Edge,[237,246] having studied the ion-exchange behaviour of many lanthanides in mixed alcohol - acetic acid solutions has adapted methanol - nitric acid solution for their group separation, as advocated by Ross and Romer[245] for separating gadolinium and europium.

Substitution of nitrates for nitric acid in aqueous methanol solution has shown, for example, that 65 per cent. methanol, 5 M with respect to ammonium nitrate, gives distribution coefficients from lanthanum to gadolinium on Amberlite IRA-400[37,235,236] that are a factor of 2 to 4 less than those observed by Alstad and Brunfelt[259] for a 5 M nitric acid solution in 65 per cent. acetone. In the light of previous statements concerning relative distribution coefficient data in methanol and acetone media, this seems to suggest that ammonium nitrate somewhat enhances the distribution coefficient.

In ammonium nitrate solution the $\log[NO_3^-] - \log K_d$ relation of near unit slope (*cf.* equation 7) permits separation factors to be determined for pairs of ions in a similar way to direct calculation from K_d, giving values between 1·3 and 1·7 for lanthanum to gadolinium.[37]

Compared with ammonium nitrate, lithium nitrate further enhances metal ion sorption from methanolic media. For example, metal distribution coefficients for 1·3 M lithium nitrate in 65 per cent. methanol[37] are similar to those for 5 M nitric acid in 65 per cent. acetone, suggesting that replacing nitric acid by nitrate now matches the dielectric constant enhancement provided by acetone. In addition to the linear $\log[NO_3^-] - \log K_d$ relationship, the lines from gadolinium to lanthanum are steeper, so that separation factors parallel increasing nitrate ion concentration. For M lithium nitrate in 65 per cent. methanol, the separation factors lie between 1·4 and 2·6.[37] Adjacent lanthanide pairs can be resolved fairly well for both ammonium and lithium nitrate solutions. With gradient elution, the whole cerium sub-group can be eluted in about 400 drops.[37]

The above survey clearly indicates that the metal ions forming strong anionic nitrate complexes are limited to lead, bismuth, gold, the lanthanides and certain actinides, especially thorium. This feature was of importance in choosing 90 per cent. methanol - 10 per cent.

6 M nitric acid eluant for the selective sorption, over molybdenum(VI), of rhenium(VII) on Dowex 1X 8 rather than the corresponding hydrochloric acid solution.[238] Of many organic solvents, with the exception of methanol, only s-butyl alcohol showed any promise where separation from molybdenum(VI) was concerned.[238]

In the absence of other strongly sorbed species, individual members can, of course, be separated from those weakly sorbed. Thus, both bismuth and lead can be collected on Dowex 1X 8 from 95 per cent. methanol - 5 per cent. 5 M nitric acid, separation of the two metals being accomplished by elution of lead with M hydrochloric acid, and bismuth with M nitric acid.[248] The method can be extended, and the determination of cerium in ferrous alloys is possible, cerium, bismuth and lead being collected from the methanol - nitric acid solution. The cerium is preferentially released with 90 per cent. methanol - 10 per cent. 6 M hydrochloric acid.[249]

A further example is separation of bismuth from copper-base alloys with 90 per cent. 2-methoxyglycol - 10 per cent. 5 M nitric acid.[254]

Even when there is less tendency to form anionic complexes, interesting separations can be performed with proper choice of organic solvent. In this respect, knowledge and experience of chromatographic solvents have provided useful clues, and for separating cadmium from zinc, isopropyl alcohol or acetic acid was considered suitable by Korkisch and Feik.[233] Their prediction proved correct and in a wider investigation of 90 per cent. organic solvent - 10 per cent. 5 M nitric acid solution other suitable organic solvents were discovered. Thus, for propionic acid both cadmium and zinc ($K_d = 173$ and 37, respectively) are sorbed by Dowex 1X 8, selective elution being possible with ethanol.[233] However, the most successful quantitative separation of cadmium from zinc, as well as aluminium, was achieved with a 90 per cent. ethanol - 10 per cent. 5 M nitric acid medium.[233]

For recovery purposes, preferential sorption of the required constituent followed by subsequent elution is the procedure generally discussed so far. It occasionally happens, however, that preferential elution is the most appropriate. In such an instance, it is necessary to establish conditions favouring sorption of any unwanted species. This has been adopted for anion-exchange conditions fitted for beryllium separations.[214] Many potentially useful circumstances were found whereby aluminium and magnesium were sorbed on Dowex 1 leaving beryllium in the effluent. However, because of more favourable separation factors, the parallel studies with hydrochloric acid already cited provided better conditions.[214] The method has also been applied to the preferential elution, with 95 per cent. methanol - 5 per cent. 5 M nitric acid, of small quantities of beryllium, vanadium(V), magnesium, calcium, aluminium, gallium(III) and indium(III), leaving gram amounts of sorbed uranium.[240]

Many doubts have been cast on the rôle of anionic complexes in anion exchange from mixed solvent media. Nitrate systems are not free from these, even though the trends observed and discussed above would seem to support an important rôle for anionic complexes. However, Waki[262] claims, on the basis of metal nitrate complex behaviour in solutions containing large amounts of isopropyl alcohol, that, in general, anionic complexes are absent, even in solutions of low dielectric constant. For the resin phase, however, the rôle of the anionic complex is supported by the presence of high nitrate complexes, such as $[Ca(NO_3)_6]^{4-}$, $[Mg(NO_3)_4]^{2-}$ and $[Ag(NO_3)_3]^{2-}$.[262]

Waki's results indicate some association between alkaline earth metal ions and the resin phase. Alkali and alkaline earth metal ions have been studied mainly in nitric acid - dioxan[215,255] and nitric acid - alcohol[215,239,243,247,264] systems. Favourable gradient-elution separation procedures have been established for the Group II elements.[239,243,255] Only a partial separation was possible for Group I elements.[255]

The increase in K_d from Group I to Group II or down either Group, together with the normal rise with increasing proportion of organic solvent, are general features of these elements.

With high dioxan ratios the distribution coefficients decreased with increasing nitric acid concentration, the reverse being true for lower amounts of organic solvent.[255] This might be attributed to the acid - resin competition with higher organic solvent contents because of the acid ion association. Insufficient association occurs at low solvent levels to prevent interference with its complexing rôle with the salt.[255]

Amberlyst XN-1002, which exhibits rapid sorptive rates from non-aqueous systems has been used for studying alkaline earth metal ions.[239,243] Higher alcohols possessed no particular advantage over lower alcohols,[239] and 95 per cent. methanol - 5 per cent. 0·25 M nitric acid gave good calcium - strontium separation.[243] Magnesium, if present, can be eluted with 95 per cent. ethanol - 5 per cent. 0·25 M nitric acid followed by calcium with 95 per cent. methanol - 5 per cent. 0·25 M nitric acid and, finally, strontium with 95 per cent. methanol.[243]

HYDROBROMIC ACID SYSTEMS—

Only one study of anion exchange from mixed aqueous - organic solvent solution containing hydrobromic acid has been reported,[265] possibly because the anion-exchange separation of copper, cobalt(II), zinc and gallium(III) in aqueous hydrobromic acid was no better than in hydrochloric acid under comparable conditions.[266]

In 90 per cent. methanol - 10 per cent. 4·5 M hydrobromic acid the sorption behaviour of some elements compared with sorption from hydrochloric acid is remarkably different. However, except for zinc, gallium and indium, there is little difference between the methanolic and the purely aqueous system.[265] Thus, uranium(VI) with high K_d in methanol - hydrochloric acid, is essentially non-sorbable from methanol - hydrobromic acid, while gallium(III) and indium(III), even though sorbable, have lower K_d values in hydrobromic than in hydrochloric acid.

Zinc, cadmium, gallium(III), indium(III), lead, copper and bismuth(III) are simultaneously sorbed on Dowex 1X 8 (bromide form) from 90 per cent. methanol - 10 per cent. 4·5 M hydrobromic acid medium, separation into sub-groups being achieved by elution with 0·45 M aqueous hydrobromic acid.[265] A practical application is gallium assay in bauxite, which requires a quantitative separation from a variety of other elements, including iron and aluminium.[265]

The general pattern in other organic solvent - hydrobromic acid mixtures is characterised by increasing sorption from methanol to s-butyl alcohol, but as such they are considered less suitable for analytical application than the above methanol solution, in which the distribution coefficients of poorly sorbed species are low enough to permit their rapid removal.[265]

Any tendency for iron(III) sorption can be checked by inclusion of ascorbic acid.[265]

SULPHURIC ACID SYSTEMS—

Sorption of uranium(VI) or thorium(IV) on Dowex 1X 8 from alcohol - sulphuric acid solutions follows increasing alcohol concentration, but is not influenced by dielectric constant or alcohol chain length.[14,187,232,267] The greatly increased sorption with decreasing sulphuric acid concentration is another effect quite opposite to that in hydrochloric and nitric acid solution.[14] Despite these different effects, sorption is, however, higher in the mixed solution than in purely aqueous systems,[14,187,232,267] even though the same neutral sorption mechanism is proposed for each type of medium.[15]

A mechanism involving sulphato complexes has also been suggested. The break in the K_d *versus* uranium(VI) plot is attributed to the formation on the resin of two sulphato dioxouranium(VI) complexes.[14] Thus, $[UO_2(SO_4)_4]^{6-}$ and $[UO_2(SO_4)_3]^{4-}$, once believed to be formed at low and high uranium concentrations, respectively,[15] have now been established,[80] the trisulphato complex facilitating increased uranium sorption.

The addition of 2-butoxyethanol or dibutylmethanol to 0·7M methanolic sulphuric acid causes a slightly increased distribution coefficient of uranium(VI),[15,268] but the reverse effect occurs with ethanol. The maximum sorption is found in isopropyl alcohol medium containing a little 2-butoxyethanol or dibutylmethanol.

The distribution of copper, magnesium, zinc, cadmium, aluminium, indium(III), manganese(II), iron(III), cobalt(II) and nickel between Dowex 1X 8 (sulphate form) and solutions of 80 or 90 per cent. methanol, ethanol, propyl and isopropyl alcohols, acetone, 2-methoxyethanol and tetrahydrofuran, each 0·05 M with respect to sulphuric acid, have been investigated.[269] In this respect, copper and indium can be separated in 80 per cent. methanol - 20 per cent. sulphuric acid solution,[269] although anionic sorption of iron(III), cobalt(II) and nickel from ethanol - sulphuric acid has also been reported.[270]

Titanium(IV) sorption behaviour on Dowex 1X 8 from 80 per cent. ethanolic sulphuric acid parallels thorium(IV),[232] while that of a given lanthanide (lanthanum, neodymium and praseodymium) on Amberlite IRA 400-X8 decreases with increasing sulphuric acid concentration.[271] The same pattern observed for yttrium[271] is reminiscent of its anion-exchange behaviour from dilute aqueous ammonium sulphate.[272]

Like thorium(IV), lanthanide sulphates are of limited solubility in alcohol - sulphuric acid and, as such, of limited potential for large scale separations.[15]

THIOCYANATE SYSTEMS—

Advantages gained by including organic solvents in a thiocyanate eluant for separations on cation exchangers[170] are also claimed for anion-exchange resins.[273]

Thorium(IV) in methanol, ethanol and acetone systems showed the highest sorption affinities in methanol and the lowest in acetone. More extensive studies with a range of metal ions show potential separations to be favoured by low thiocyanate concentration; successful separations include lanthanum(III) from thorium(IV), gadolinium(III) from thorium(IV), yttrium(III) from thorium(IV), gadolinium(III) from scandium(III) and erbium(III) from scandium(III), each on Dowex 1X 8 (thiocyanate form). Lanthanum was also separated from thorium on Amberlyst XN-1002.[273]

Predicted separations are, however, not always successful,[273] for example, scandium and thorium tailing on Dowex 1X 8 prevents their separation. Despite significant K_d differences for individual lanthanides, they are frequently inadequate for clean-cut separations.[273]

An interesting effect is reported for chromium(III) ($K_d > 36$).[273] Significant amounts passed through the column during attempted loading from 85 per cent. ethanol - 15 per cent. of 0·1 M ammonium thiocyanate, but the sorbed portion remained on the column even during attempted elution with aqueous hydrochloric acid. This peculiar effect has been attributed to the slow formation of a stable thiocyanatochromium(III) complex.[274]

ORGANIC ACID SYSTEMS—

Aliphatic mono- and dicarboxylic acids form negatively charged complexes with many metal ions and have been used for anion-exchange separations. Most effort has been directed towards new analytical procedures for separating uranium from other elements with monocarboxylic acids,[1,15,275,276,277,278] especially in alcohols, acetone and dioxan.

In pure formic acid, or with water, uranium(VI) sorption on Dowex 1X 8 is too low for practical purposes.[15] However, in 10 to 80 per cent. formic acid - 90 to 20 per cent. organic solvent, uranium(VI) forms relatively stable anionic formate complexes leading to strong sorption on anion exchangers.[15,276] Specifically, in 90 per cent. organic solvent - 10 per cent. formic acid, the uranium(VI) distribution coefficient on Dowex 1X 8 is frequently higher by several orders of magnitude than that of other elements. Separation schemes are therefore possible, for example, uranium(VI) from copper and lead by using formic acid - methanol,[276] uranium(VI) from copper, nickel, and lead with formic acid - ethanol solution, and the simultaneous sorption of uranium(VI) and gadolinium(III) from a variety of formic acid - organic solvent mixtures, except methanol.[15]

In contrast to the formic acid - organic solvent systems, uranium(VI) sorption in acetic acid mixtures is high, and even in pure acetic acid is sufficient to permit quantitative retention of milligram amounts on Dowex 1X 8.[276]

Separations in acetic acid systems include uranium(VI) from copper, cobalt(II), nickel, lanthanum(III) and gadolinium(III) by using aqueous acetic acid solution, and uranium(VI) from copper, nickel and cobalt(II) in acetic acid - butyl alcohol.[276]

It is not always feasible to exploit the potentialities offered by acetic acid mixtures, and it should be noted that lead, strontium and barium salts are practically insoluble in 10 per cent. acid - 90 per cent. organic solvent mixtures. Nevertheless, useful separations have been obtained. Others include uranium(VI) from lanthanides in many 95 per cent. organic solvent - 5 per cent. acetic acid mixtures examined by Hazan and Korkisch.[277,278]

In pure propionic acid, and in solutions containing a high percentage of the acid, K_d of uranium(VI) on Dowex 1X 8 is higher than in similar acetic acid mixtures, showing a maximum of over 10^5 in 100 per cent. acid. Again, distribution data for elements in many 90 per cent. organic solvent - 10 per cent. acid mixtures suggest several separations of uranium (VI) from a variety of elements.[15]

Neither strontium nor barium is sorbed on Dowex 1X 4 from α-hydroxyisobutyric acid in water - alcohol mixtures,[279] and separation from the lanthanides, themselves sorbed, is therefore possible. Lanthanide sorption, as might be expected, is sensitive to water content variation, a feature exploited in lanthanide fractionation. For example, traces of lanthanides [lanthanum(III) to terbium(III)] can be isolated from 100-mg erbium(III) samples by elution with a 60 per cent. aqueous methanol solution, 0·02 M with respect to α-hydroxyisobutyric acid.[279]

Studies on europium and yttrium with α-hydroxyisobutyric acid, present in a variety of mixed aqueous - alcohol solutions, indicate that the α-hydroxyisobutyric acid chelate stability constants, and the anion-exchange separation factors, increased with rising concentration of the non-aqueous component.[280]

The distribution coefficients of uranium(VI) with dichloroacetic acid are available over the full concentration range, but the mono- and trichloro acids being solids at room temperature, corresponding K_d values have only been measured in solutions containing up to 40 g per 100 ml of acid.[276]

The mono- and dichloroacetic acids are responsible for higher distribution coefficients for uranium(VI) in organic solvent than in aqueous solvents,[276] the order being 10^2 to 10^3 times greater for the former acid to give K_d values within the range 10^4 to 10^5 in organic solvent. For the latter acid, the order is greater by a smaller magnitude,[276] the over-all K_d values being lower and reaching a value of rather less than 10^3 for the pure acid.

Separation schemes involving mono- and dichloroacetic acids have been proposed[15,276] and apart from uranium(VI) preferential sorption on Dowex 1X 8 (monochloroacetate form) of copper and cobalt(II) from monochloroacetic acid - propyl alcohol (10 g per 100 ml) can be mentioned. Separation of sorbed elements is then effected by elution of the cobalt(II) with monochloroacetic acid - s-butyl alcohol.

Analytical application of trichloroacetic acid in solvents other than acetone is severely restricted by the generally weak sorptions.[276]

Complexing properties of picolinic acid have been exploited for metal separations in mixed solvents on the Lewatit MII and Amberlite IRA-401[281] anion exchangers. The complex formation order in ethanol or dioxan is $Co^{2+} \sim Ni^{2+} > Zn^{2+} > Fe^{2+} > Cd^{2+}$. Metals that do not form anionic complexes can be eluted from an anion-exchange column under conditions of maximal sorption of metals forming negatively charged complexes. Metals retained can be eluted with mineral acid. The principle is illustrated by the separation of nickel from a copper alloy,[281] when Amberlite IRA-401, previously washed with 0·05 M picolinic acid in 70 per cent. ethanol, is treated with a previously prepared solution of the alloy containing picolinic acid. The copper is eluted with 0·05 M picolinic acid in 30 per cent. dioxan, and the nickel subsequently released by 2 M hydrochloric acid.

Procedures involving picolinic acid have also been described for iron(III) and nickel, iron(III) and zinc, copper and zinc, copper and nickel, manganese(II) and nickel, and chromium(III) and nickel.[281]

Of the following di- and tricarboxylic acids, oxalic, malonic, succinic, glutaric, tartaric and citric acids, malonic acid in methanol is much the most effective complexing agent for uranium(VI), thorium(IV) and the lanthanides,[282] and presents possibilities for co-sorption of these elements on anion-exchange resins.

CONCLUSION

The use of organic solvents for ion exchange is effective as a further dimension for designing separation schemes, despite limitations imposed by solubility factors. Even although considerable research effort is still required for a complete understanding of the underlying theory and mechanism of the exchange process in mixed systems, continuing experimental trends certainly produce criteria useful for the design of workable separation schemes.

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Polarographic Determination of Caesium in the Presence of Other Alkali Metals Based on Interaction with the Cinnamaldehyde Radical Anion

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In this determination of caesium the wave i_M, corresponding to the reduction of a species formed by interaction of a cinnamaldehyde radical anion with alkali-metal ions, is measured. This wave appears in 0·1 M lithium hydroxide solutions between the first two one-electron reduction steps of cinnamaldehyde.

The height of this wave i_M increases with increasing alkali-metal concentration, and is most sensitive to caesium, which can be determined in the range 0·003 M to 0·1 M, in the presence of less than 0·03 M rubidium, 0·05 M potassium and 0·1 M sodium, to within an accuracy of 5 per cent. The only observed interference was from short-chain tetra-alkyl ammonium cations.

THE methods available for the determination of caesium in the presence of other alkali metals usually involve lengthy separation procedures or complex instrumentation.

The gravimetric[1] and spectrophotometric[2] methods proposed for the determination of caesium rely on the formation of heteropolyacids or other complex compounds, and are tedious, giving poor reproducibility. Other chemical methods rely on a preliminary chemical separation based on the differing solubilities of the chlorides,[3] heteropolyacids or chloroplatinates,[4] followed by a determination of the caesium, in which some less specific method is used. Separation by ion exchange may not always be quantitative. Paper chromatography[5] separates caesium, rubidium and potassium, but a determination on small samples is difficult. Flame photometry[6] can be applied, but interferences from other alkali metals make the choice of standards critical for an accurate determination. The caesium resonance line is at such a long wavelength that its sensitivity by flame photometry is low, and the response of most detectors is limited. The unsatisfactory nature of caesium hollow-cathode lamps also make its determination by atomic-absorption spectroscopy difficult. X-ray emission spectroscopy[7] and neutron-activation procedures[8] require expensive instrumentation and usually a preliminary separation.

The half-wave potentials of all alkali metals, except lithium, are so close together[9] that neither d.c. polarography nor any of the recent electroanalytical techniques can effect resolution of the waves of caesium from those of other alkali metals. Nevertheless, during a polarographic study of the reduction of cinnamaldehyde, the formation of a new wave was observed in the presence of low concentrations of caesium ions or at considerably higher concentration of other alkali metals. The height of this wave, i_M (Fig. 1, curve b), was used in the development of a simple, and reasonably selective, method for the determination of caesium.

As the formation of the wave i_M, of analytical importance, takes place only in alkaline media, only the polarographic behaviour of cinnamaldehyde[10,11] at higher pH values will be discussed here in some detail. Under these conditions the reduction of the unprotonated form of cinnamaldehyde takes place principally in two two-electron steps. In the first step the double bond is reduced, and this process is followed, at more negative potentials, by the

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* On leave of absence from J. Heyrovský Institute of Polarography, Czechoslovak Academy of Science, Prague.

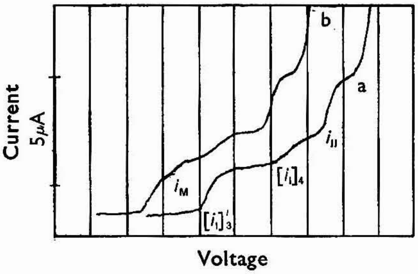

Fig. 1. Comparison of cinnamaldehyde wave in the presence and absence of a neutral salt. 2×10^{-4}M Cinnamaldehyde, in 2 per cent. ethanolic solution of 0·1M lithium hydroxide, containing (*a*) 0; (*b*) 0·4M lithium hydroxide. The 0·0001 per cent. gelatin curves start at −0·8V, 0·2V per abscissa, recorded 1 minute after mixing

reduction of the carbonyl groups. When the pH value is sufficiently high for the protonation of the product of the first electron uptake (radical anion $C_6H_5CHCHCHO^{(\dot{-})}$) to be negligibly slow, the hydrogenation of the double bond takes place in two one-electron steps, and the scheme (1) to (5) can be considered—

Wave*

$$C_6H_5CH{=}CHCHO + e \underset{E_1}{\rightleftharpoons} C_6H_5CHCHCHO^{(\dot{-})} \qquad (i_I)'_3 \;.. \quad (1)$$

$$C_6H_5CHCHCHO^{(\dot{-})} + e \xrightarrow[E_2]{} C_6H_5CHCHCHO^{(2-)} \qquad (i_I)_4 \;.. \quad (2)$$

$$C_6H_5CHCHCHO^{(2-)} + 2H_2O \overset{K_a}{\rightleftharpoons} C_6H_5CH_2CH_2CHO + 2\,OH^- \qquad .. \quad (3)$$

$$C_6H_5CH_2CH_2CHO + H_2O \underset{k_d}{\overset{k_r}{\rightleftharpoons}} C_6H_5CH_2CH_2CH(OH)_2 \qquad .. \quad .. \quad (4)$$

$$C_6H_5CH_2CH_2CHO + 2e + 2H_2O \xrightarrow[E_3]{} C_6H_5CH_2CH_2CH_2OH + 2\,OH^- \quad i_{II} \;.. \quad (5).$$

* This assignment of individual waves was used in the over-all reduction scheme.[11]

In the first step $(i_I)'_3$ at potential E_1 a radical anion is formed, which is further reduced in the step $(i_I)_4$ at potential E_2 to a biradical (Fig. 1, curve a). This biradical reacts with the solvent in a series of acid - base equilibria, summarised in (3) to give 3-phenylpropionaldehyde, which can be hydrated (4). Only the non-hydrated form of 3-phenylpropionaldehyde undergoes electro-reduction (5) giving the wave i_{II}, the height of which is limited by the rate of the dehydration reaction with constant k_d. This second two-electron process is unimportant in the present discussion, and only an over-all reaction is shown in equation (5).

In the presence of low concentrations of caesium or high concentrations of other alkali metals, the radical anion formed in the first step (1) reacts with the univalent cation (M^+) to give a ketyl radical, denoted here as $C_6H_5CHCHCHO^{(\dot{-})}M^+$. This is reduced as a wave i_M in a one-electron process—

$$C_6H_5CHCHCHO^{(\dot{-})} + M^+ \underset{k_{-M}}{\overset{k_M}{\rightleftharpoons}} C_6H_5CHCHCHO^{(\dot{-})}M^+ \quad .. \quad .. \quad .. \quad (6)$$

$$C_6H_5CHCHCHO^{(\dot{-})}M^+ + e \xrightarrow[E_M]{} C_6H_5CHCHCHO^{(2-)}M^+ \; i_M \quad .. \quad .. \quad (7)$$

$$C_6H_5CHCHCHO^{(2-)}M^+ + 2H_2O \rightleftharpoons C_6H_5CH_2CH_2CH_2CHO + M^+ + 2\,OH^- \;.. \quad (8)$$

where k_M and k_{-M} are rate constants of the forward and backward reactions.

Because the value of potential E_M is between E_1 and E_2, the wave i_M is observed between waves $(i_I)'_3$ and $(i_I)_4$ (Fig. 1, curve b). The height of the wave i_M for individual alkali-metal ions, M^+, depends both on the equilibrium constant $K_M = \frac{k_M}{k_{-M}}$ and on the value of the rate constant of the ketyl radical formation k_M. For a given alkali-metal cation the height of the wave i_M depends on the ion concentration and can be used for the determination of this cation.

EXPERIMENTAL

APPARATUS—

The polarographic curves were recorded on either a Cambridge pen recording polarograph or a Radiometer PO4 polarograph. A Kalousek vessel with a separated calomel electrode (S.C.E.) was used. The capillary had, at the potential of the S.C.E. in M potassium chloride, an outflow velocity of $m = 2{\cdot}96$ mg per second and a drop time of $t_1 = 3$ seconds for a mercury pressure of $h = 60$ cm.

SOLUTIONS—

The supporting electrolytes were prepared from analytical-reagent grade chemicals. A stock 0·01 M solution in spectroscopic ethanol was prepared from cinnamaldehyde redistilled at reduced pressure. Gelatin was prepared as a 0·01 per cent. aqueous stock solution.

TECHNIQUE—

A volume (9·8 ml) of the supporting electrolyte was de-aerated, 0·2 ml of the 0·01 M stock solution of cinnamaldehyde was added, a further brief de-aeration was carried out and the waves were recorded starting 1 minute after the addition of cinnamaldehyde, thus avoiding any errors caused by hydrolysis.

In solutions of high ionic strength 9·7 ml of supporting electrolyte and 0·1 ml of 0·01 per cent. gelatin were used, thus suppressing any streaming maxima of second kind.

RESULTS

The effect of alkali-metal cations on polarographic curves of cinnamaldehyde, in particular on the height of the wave i_M, was investigated in a solution containing 0·1 M hydroxyl ions. In these solutions the pH was neither too high to result in the hydrolysis of cinnamaldehyde, which is cleaved in alkaline solutions, but the reaction is not appreciable until pH 13·7, nor too low to cause an increase in the height of the first wave above the value corresponding to a one-electron diffusion-controlled process caused by protonation of the radical anion. This reaction, which corresponds to reactions (6) and (7) in which $M^+ = H^+$, results at lower pH values in an increase of the wave $(i_I)'_3$. In solution, 0·1 M in hydroxyl ions, the contribution of this process to the height of the wave $(i_I)'_3$ was sufficiently small not to interfere.

Lithium hydroxide (0·1 M) was used when investigating the effects of caesium, rubidium and lithium ions, added as chlorides, and of potassium-ion concentrations below 0·1 M. Potassium hydroxide was used for higher potassium concentrations, and sodium hydroxide was used to maintain the alkalinity for all sodium solutions.

The height of the wave i_M increases with increasing concentration of the univalent ion concentration (Figs. 2 and 3). The dependence of the ratio $\frac{i_M}{(i_I)_3}$ on log $[M^+]$ has the shape of a dissociation curve (Fig. 2), and the experimental points show a reasonable fit to the theoretical curves. For $\frac{i_M}{(i_I)_3} < 0{\cdot}4$ the wave i_M was proved to be kinetically controlled[3] by its independence of the mercury pressure, so that the height of the wave i_M depends for various cations both on the position of equilibrium (6) and on the rate of the ketyl formation with constant k_M. The value of the ratio $\frac{i_M}{(i_I)_3}$ at a given alkali-metal ion concentration would make it possible to calculate the value of the rate constant k_M for the rate of formation of the ketyl radical at the electrode surface, provided that the equilibrium constant of reaction (6) is known. Unfortunately, experimental results on the value of the ratio $K_M = \frac{k_M}{k_{-M}}$ are not yet available.

Although it is impossible to separate the constants k_M and k_{-M}, it is possible to compare qualitatively the effect of the type of cation on the product $k_M \cdot K_M$. The shift of the dissociation curves in Fig. 2 indicates that the equilibrium and rate-governed reactivity in reaction (6) towards the ketyl formation increases in the sequence Li^+, $Na^+ < K^+ < Rb^+ \ll Cs^+$. The same conclusion allows the comparison of wave heights at a given concentration. Fig. 2 indicates that solutions containing 0·1 M Cs^+ will give a high wave i_M and those containing 0·1 M Rb^+ or K^+ will give a considerably smaller wave. A concentration of only 0·01 M Cs^+ will still give an easily measurable wave i_M, but none of the other cations in 0·01 M solutions will affect the wave height at all. Fig. 2 also allows us to predict the ratio in which the cations can be determined; to obtain the same wave height as observed in 0·01 M Cs^+ it is necessary to use about 0·1 M solutions of Rb^+, 0·5 M K^+ or M Na^+ or Li^+ ions. Furthermore, it is possible to deduce from Fig. 2 in which concentration region (for a given concentration of cinnamaldehyde) the conditions will be most suitable for the determination of a given cation. The greatest sensitivity will be achieved in the concentration region in which the dissociation curve is steepest (Fig. 2). In this region the plot of $\frac{i_M}{(i_I)'_3}$ against log $[M^+]$ should be linear.

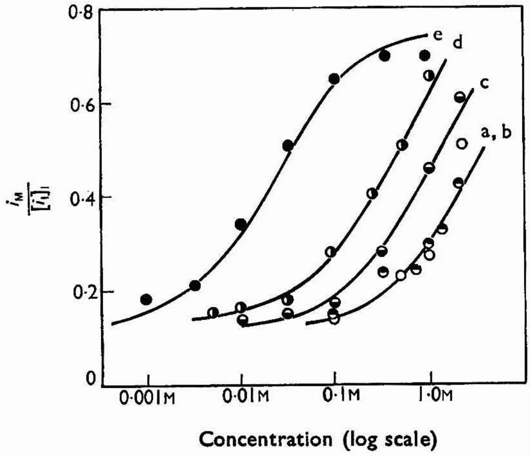

Fig. 2. Effect of concentration of cations on the height of wave i_M in the solutions of 2×10^{-4}M cinnamaldehyde in 0·1 M lithium hydroxide containing 2 per cent. of ethanol and 0·0001 per cent. of gelatin. (*a*) Open circles: lithium; (*b*) halved circles: sodium; (*c*) potassium; (*d*) rubidium; and (*e*) caesium, all added as chlorides

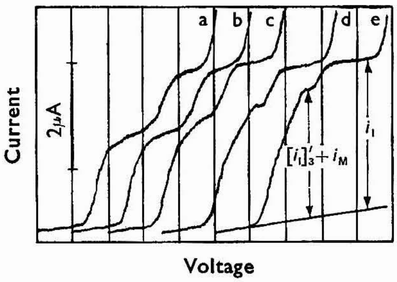

Fig. 3. Effect of caesium concentration on the height of the wave i_M in solutions of 2×10^{-4}M cinnamaldehyde in 0·1 M lithium hydroxide containing 2 per cent. of ethanol and 0·0001 per cent. of gelatin. Concentrations of caesium chloride: (*a*) 0·001 M; (*b*) 0·003 M; (*c*) 0·01 M; (*d*) 0·03 M; and (*e*) 0·1 M. Curves recorded 1 minute after mixing, starting at −0·8V, 0·2V per abscissa

The predictions based on Fig. 2 were tested with synthetically prepared mixed solutions containing caesium and other alkali-metal ions. It was confirmed that caesium can be determined in the range 0·003 M to 0·1 M, if the concentration of rubidium is less than 0·03 M, potassium less than 0·05 M and sodium less than 0·1 M. This was done by measuring the height of the wave i_M and plotting calibration graphs for caesium in the presence of 0·001 M to 0·1 M rubidium, 0·01 M to 0·3 M potassium and 0·01 M to M sodium. A typical calibration graph is shown in Fig. 4. For the construction of this graph the total height of $[(i_I)'_3 + i_M]$ was measured, as shown in Fig. 3. As the height of the wave $(i_I)'_3$ could not always be measured with a sufficient precision (Figs. 1 and 3) and, moreover, because its height can be increased above the value corresponding to a one-electron diffusion-governed process, even in 0·1 M lithium hydroxide, the total height of the first two-electron step corresponding to $[(i_I)'_3 + i_M + (i_I)_4] = i_I$ was measured. Value $\frac{i_I}{2}$ corresponds to the one-electron diffusion current. To find the increase caused by wave i_M above the one-electron diffusion current, the value $\frac{i_I}{2}$ was subtracted from the experimentally found $[(i_I)'_s + i_M]$. In Fig. 4 the graph of the ratio of $\frac{i_I}{2}$ against the increase caused by wave i_M., *i.e.*, $2\,\frac{[(i_I)'_s + i_M - i_I/2]}{i_I}$ was plotted against logarithm of caesium concentration.

The plots in Fig. 4 indicate that the condition of linearity over the studied concentration range is fulfilled. Because of the logarithmic scale it is indicated that the wave height will be most sensitive to changes in caesium concentration at lower caesium concentrations, and that hence the accuracy of the caesium concentration will be greatest between 0·01 M and 0·1 M caesium (at the given cinnamaldehyde concentration), but lower at higher or lower caesium concentrations.

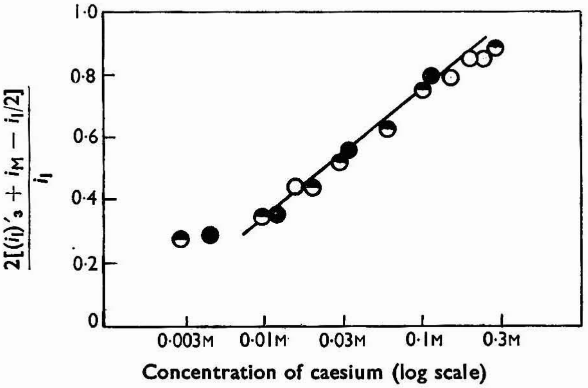

Fig. 4. Calibration curve for caesium in the presence of varying amounts of caesium chloride. The height of the wave i_M expressed as $A = 2[(i_I)'_s + i_M - i_I/2]/i_I$ as a function of caesium concentration. Waves recorded in a solution of 2×10^{-4} M cinnamaldehyde in 0·1 M lithium hydroxide containing 2 per cent. of ethanol and 0·0001 per cent. of gelatin in the presence of 2×10^{-3} M rubidium chloride (open circles), $2{\cdot}5 \times 10^{-2}$ M sodium chloride (halved circles) and 1×10^{-2} M potassium chloride (full points)

These established concentration limits can be lowered by changing the cinnamaldehyde concentration. The amount of the caesium salt needed for analysis can be lowered by using smaller volumes of the alkaline cinnamaldehyde. Also, an investigation of α,β-unsaturated carbonyl compounds of different structure could lead to an increase in sensitivity or selectivity of the method. The method described gives a detection limit of about 3 per cent. of caesium in a sodium salt, 0·1 M in solution. Caesium concentrations higher than about 5 per cent. can be determined with reasonable accuracy.

INTERFERENCES—

The presence of ammonium ions in the sample, as anticipated, had no effect on the height of the wave i_M, because in 0·1 M hydroxide solution they are quantitatively converted into free ammonia. Longer chain tetra-alkyl salts, *e.g.*, cetyltetramethylammonium, also do not affect the height of wave i_M and hence the caesium determination. This is probably because these substances are adsorbed at the surface of the dropping mercury electrode by their long aliphatic chain in such a way that an interaction with the radical anions of cinnamaldehyde in the vicinity of the electrode surface is prevented.

Short chain tetra-alkyl salts interfere, as they increase the height of the wave i_M even at low concentrations. A measurable increase can be observed in the presence of 8×10^{-4} M tetramethylammonium salt, and a detectable difference even in 8×10^{-5} M tetraethylammonium salt solutions. Fortunately, these cations rarely occur in samples in which caesium is to be determined. If the caesium is required to be determined in a mixture with short-chain tetra-alkylammonium compounds, preliminary decomposition of the latter in hot acidic solutions should be effective.

When alkaline earth metals are present they form, under the conditions used, precipitates of hydroxides and carbonates. The increase in current i_M caused by the alkaline-earth metal ions remaining in solution can be calculated by carrying out a determination with a solution containing the alkaline-earth metal alone. As anticipated, the increase in wave i_M is independent of the anion present. The same wave height (i_M) was observed for fluorides, chlorides, bromides, iodides, perchlorates and sulphates of the alkali metals.

Before the determination of caesium is carried out, it is suggested that the total amount of alkali-metal ions present in the sample be determined either by polarography[12] or by some other method. For a polarographic determination, 0·3 ml of 10 per cent. orthophosphoric acid is added to 6 ml of the sample to separate the alkaline earth metals. After the addition of 3 ml of 0·5 M tetramethylammonium hydroxide and de-aeration, polarographic curves are recorded. The wave at −2·0 volts gives the total amount of caesium, rubidium, potassium and sodium, and that at −2·2 volts is caused by lithium.

RECOMMENDED PROCEDURE—

Dissolve the sample in 0·1 M lithium hydroxide. Transfer a 9·7-ml aliquot into a polarographic cell, add 0·1 ml of 0·01 per cent. gelatin solution and de-aerate. Add 0·2 ml of 0·01 M cinnamaldehyde solution, de-aerate for a further 30 seconds and record a polarographic curve, starting at −0·8 volt, 1 minute after adding the cinnamaldehyde. Taking the wave height i_I at −1·6 volts (Fig. 3) as standard for a two-electron reduction, the wave i_M should be between 20 and 70 per cent. of a one-electron wave. If the ketyl wave is smaller or larger, either dissolve a larger amount of sample in lithium hydroxide or dilute the sample solution with 0·1 M lithium hydroxide containing cinnamaldehyde.

Height of the wave $[(i_I)'_3 + i_M]$ is measured at −1·35 volts and that of i_I at −1·62 volts as shown in Fig. 3. The ratio $\frac{2\,[(i_I)'_3 + i_M - i_I/2]}{i_I}$ is calculated and compared with the calibration graph constructed as in Fig. 4.

The method can be carried out with 0·017 g of caesium chloride dissolved in 10 ml of 0·1 M lithium hydroxide. The determination can be carried out with an accuracy of ±5 per cent., and about a 5-fold excess of rubidium or potassium and a 20-fold excess of sodium can be tolerated.

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Studies in the Analytical Chemistry of Selenium: Absorptiometric Determination with 2-Mercaptobenzoic Acid

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Selenium(IV) forms a 1:3 complex with 2-mercaptobenzoic acid that shows maximal absorption at 268 nm in the pH range 0·5 to 2·5. The formation of the complex provides the basis of a rapid and sensitive method for the determination of selenium in the presence of a wide range of elements. When the complex is extracted into ethyl acetate, 22 of 36 other ions investigated do not interfere, even at 200-fold excess. The interference of the others, including tellurium, is readily overcome by a simple technique of total-ion exchange, by masking or by solvent extraction. Of the ions examined only mercury(II) still interferes.

The molar absorptivity of the complex at 268 nm is 15,600 and the sensitivity index 5×10^{-3} μg per cm^2. The complex is formed instantaneously and maintains an unchanging absorbance for over 2 hours. The method is suitable for the determination of selenium in the range 0·008 to 1·5 p.p.m. in aqueous solution.

THE methods available for the spectrophotometric determination of selenium can be conveniently divided into three classes. The first class involves the formation of piazselenols, which are either coloured or fluorescent, and includes the well known 3,3′-diaminobenzidine methods[1,2] and the 2,3-diaminonaphthalene method.[3] *o*-Phenylenediamine,[4,5] 1,2-diaminonaphthalene,[5] 4-methylthio-1,2-phenylenediamine,[6,7] 4,5-diamino-6-thiopyrimidine,[8] and 4-methyl-, 4-chloro- and 4,5-dichloro-*o*-phenylenediamine[9] have also been investigated as reagents. Although this type of reaction is fairly sensitive, the reagents tend to be unstable in solution, even at 0° C, and the methods are susceptible to interference, even from mild oxidising agents. Moreover, the development times tend to be about 30 minutes or longer.

The second class, which involves the reduction of selenium(IV) to the elemental form, often with the simultaneous production of a coloured oxidation product, includes the well known selenium sol and iodine methods,[10] the oxidation of phenylhydrazine-*p*-sulphonic acid to the diazonium ion, followed by coupling with 1-naphthylamine,[11] the oxidation of *NN*-diphenylhydrazine,[12] a few catalytic reactions[13,14] and the oxidation of pyrrole.[15]

The third class involves the formation of complexes in which the selenium bonds either partially or completely to sulphur ligands. Typical reagents in this class, which includes 2-mercaptobenzoic acid, the reagent under investigation, are compared in Table I.

2-Mercaptobenzoic acid has been used for the absorptiometric determination of nickel[25] and fluoroacetates,[26] and as a precipitant for thorium.[27] The method described here for selenium is more sensitive than any other method in this class (*cf*. Table I), and the colour development is virtually instantaneous. The reagent solution can be used for up to 48 hours after preparation, without refrigeration. Selectivity is improved by total-ion exchange, masking and pre-extraction techniques.

TABLE I

COMPARISON OF THE SENSITIVITY OF SOME METHODS FOR THE DETERMINATION OF SELENIUM WITH SULPHUR LIGANDS

Reagent	Reference	Sensitivity, µg	Molar absorptivity	Interferences mentioned
2-Mercaptobenzoic acid	*	0·005	15,600	Hg, Te, Cu, Ni, Co, Ag, Li, Zr
2-Mercaptobenzothiazole	16	0·008	9480	Fe, Cu, Zn, Cd, Pb, W, Ti, Mo, Hg, As, Sb, Pd, U, Te
2-Mercaptobenzimidazole	17, 18	0·007	10,500	Te, Cu, Bi, IO_3^-, BrO_3^-, Mo
1-Phenylthiosemicarbazide	19	0·014†	5200	Fe, Cu, V
N-Mercaptoacetyl-*p*-anisidine	17	0·063†	1200	Te, Cu, Bi, Mo
N-Mercaptoacetyl-*p*-toluidine	17	0·063†	1200	Te, Cu, Bi, Mo
Thioglycollic acid	20	0·045†	1660	Ag, Cr, Cu, Fe, Ge, Hg, V, As, Bi, Mo, Sb
Diethyldithiocarbamate	21	0·041†	1800†	Ag, As, Bi, Cd, In, Pb, Sb, Te, Tl, V, Zn
1-Amidino-2-thiourea	22	0·033	2400†	—
Bismuthiol II	23, 24	0·007†	10,580	Te, Cu, Fe, Bi, As, V, Hg, Pd

* Present paper

† Estimated values.

EXPERIMENTAL

APPARATUS—

A spectrophotometer with 1-cm silica cells and a pH meter were used.

REAGENTS—

Mercaptobenzoic acid solution, 10^{-3} F—Treat 0·1542 g of reagent (British Drug Houses Ltd.) with 2-fold excess (about 1 ml) of 2 F sodium hydroxide solution and dilute to 1 litre. The solution should be discarded after 2 days.

Selenium(IV) solution, 10^{-3} F—Dissolve 0·07896 g of pure selenium shot (Johnson Matthey Chemicals Ltd.) in 10 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid, with warming to aid dissolution and expel brown fumes; dilute to 1 litre.

1 ml of solution ≡ 78·96 µg of selenium.

Sodium acetate buffer solution, pH 2·3—Dissolve 136·1 g of sodium acetate trihydrate in water, add 400 ml of 2 F hydrochloric acid and dilute to 1 litre.

Tribenzylamine, 5 per cent. in chloroform—British Drug Houses Ltd.

Ethyl acetate—General-purpose reagent grade.

Chloroform—General-purpose reagent grade.

Diverse ions—Prepare 10^{-1} F solutions of various cations, usually as nitrates or chlorides, and of various anions, usually as sodium or potassium salts. Analytical-grade reagents were used whenever possible.

PREPARATION OF CALIBRATION GRAPH—

Transfer, by pipette, 0·01 to 1·00 ml of 10^{-3} F selenium(IV) solution (0·79 to 79 µg of selenium) and 20 ml of reagent solution into a 50-ml calibrated flask. Add 10 ml of sodium acetate buffer solution (pH 2·3) and dilute to volume. Extract the contents of the flask with 20 ml of ethyl acetate by shaking them for about 30 seconds in a separating funnel. Allow the layers to separate, discard the aqueous phase, and run the ethyl acetate layer into a 1-cm silica cuvette. Prepare a blank by taking all of the reagents (except selenium) through the procedure. Measure the absorbance of the test solutions against the blank solution at 268 nm.

The calibration graph is a straight line passing through the origin, and is linear within the range used above. Extraction and colour measurements can be made immediately or within a total lapsed time of 2 hours.

DETERMINATION OF UNKNOWNS—

Proceed as above with an aliquot of the test solution containing less than 79 μg of selenium(IV) in less than 18 ml.

(*a*) If present in the original sample, ions such as Fe(II), Sn(II), SO_3^{2-}, I^- and CN^- should be oxidised with a mild oxidising agent, which can itself be readily removed (*e.g.*, bromine water), before proceeding with the method. The selenium(VI) that may be formed can be readily reduced to selenium(IV) by refluxing for 20 minutes with the minimum volume of concentrated hydrochloric acid necessary to effect dissolution.

(*b*) If ions such as Co(II), Cu(II), Li, Ni and Mn(II) are present, add about 1 g of a strong cation-exchange resin, *e.g.*, Zeo-Karb 225 (H^+), and shake or stir magnetically for 20 minutes. Decant and wash the resin with the minimum amount of water before proceeding as in (*a*).

The ion-exchange time can be reduced to 2 minutes for cobalt, copper, nickel and silver by adding an excess of ammonia solution before applying ion exchange.

(*c*) When zirconium is present, *e.g.*, 200 to 300-fold excess, add 10 ml of 10^{-1} F EDTA before proceeding as in (*a*).

(*d*) If tellurium(IV) is present, make the medium about 5 F in hydrochloric acid by adding concentrated hydrochloric acid. Shake with three successive 50-ml aliquots of 5 per cent. tribenzylamine in chloroform. Discard the organic phases and shake the raffinate with three 10-ml aliquots of chloroform. Finally, adjust the pH to about 2·3 with 4 F ammonia solution and proceed as usual. This procedure is capable of dealing with 5000-fold molar excess of tellurium(IV).

NOTE—In all instances the blank solution should be treated as the test solution with all of the reagents and extractions.

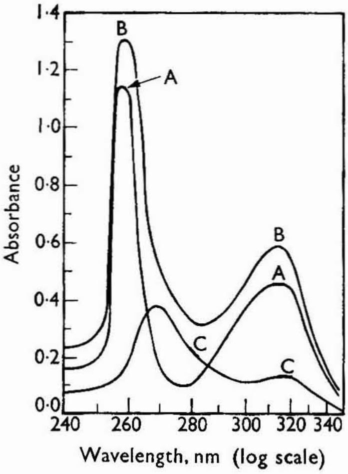

Fig. 1. Absorption spectra of: A, extract of reagent with 20 ml of ethyl acetate from 2·5 ml of 2-mercaptobenzoic acid stock solution and 5 ml of buffer solution diluted to 50 ml plotted against ethyl acetate blank; B, as A, but with 1 ml of selenium (IV) solution; and C, B plotted against A

DEVELOPMENT OF THE COMPLEX—

Fig. 1 shows the absorption spectra of A, the extracted reagent, and B, the extracted complex, together with the extracted excess of reagent necessary for complete colour development, plotted against an ethyl acetate blank. Both spectra show strong absorption maxima at 256 and 313 nm in the approximate intensity ratio 2:1. An examination of both the organic extract and the aqueous phase by measurement of the atomic fluorescence of selenium at 196·1 nm[28] in an air - propane flame indicated quantitative extraction of selenium, whereas no selenium was extracted in the absence of the reagent. This, taken together with the precipitation of a Se(IV)-2-mercaptobenzoic acid adduct in aqueous solution and the clear 1:3 stoicheiometry of the complex (see under Nature of the reaction product) is clear evidence of the existence of a complex, despite the apparent absence of bathochromic or hypsochromic effects on complexation when an ethyl acetate blank is used. When B is plotted against A, however, the complex is the predominant species, C, and the two absorption maxima occur at 268 and 315 nm, the former being considerably more sensitive.

pH RANGE—

Variation of the acidity of the aqueous solution revealed that the maximum sensitivity for the extraction occurred within the pH range 0·5 to 2·5. Over this range the extraction of the selenium (as determined by atomic fluorescence) was found to be quantitative. Above pH 7, the complex was either not formed or not extracted. Further studies were, therefore, conducted arbitrarily at pH 2·3.

EFFECT OF TIME ON COLOUR DEVELOPMENT—

The absorption of the selenium complex reached a maximum in the aqueous solution within 1 minute of the addition of the reagent. Both the original aqueous solution and the ethyl acetate phase showed no significant change in absorbance for at least 2 hours thereafter.

STABILITY AND EXCESS OF REAGENT—

The reagent solution can be used for 48 hours if kept at room temperature, provided at least a 20-fold excess of reagent is used. Only a 10-fold reagent excess is required for complete development if the reagent solution is prepared fresh daily. This is shown in Fig. 2, which indicates that a large excess of reagent has no deleterious effect on the system.

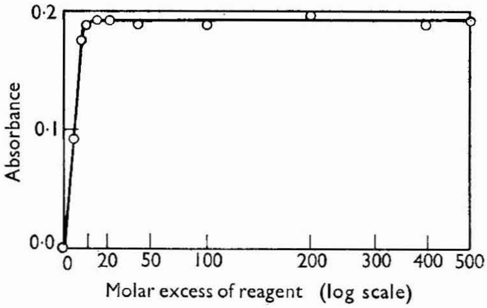

Fig. 2. Effect of excess of reagent on absorption of selenium (IV) complex

EFFECT OF TEMPERATURE—

Temperatures between 0° and 70° C had no significant effect on the system provided that a 100-fold excess of reagent was used, and that the blank was prepared under conditions identical with those of the test solution. The solutions must, however, be cooled before the extraction because of the volatility of the ethyl acetate.

NATURE OF THE REACTION PRODUCT—

Both the continuous variation method and the molar ratio method clearly indicated the formation of a 3:1 reagent:selenium(IV) complex at pH 2·3. This result was confirmed in a preliminary investigation of the application of the reagent to the gravimetric determination of small amounts of selenium(IV) at pH 1·80.

BEER'S LAW AND SENSITIVITY—

The system was used over the range 0·02 to 12 p.p.m. in the organic phase (0·008 to 4·8 p.p.m. in the aqueous phase). Beer's law was obeyed in the range 0·02 to 4 p.p.m., and the molar absorptivity over this range was found to be $\epsilon_{268\,\mathrm{nm}} = 15{,}600$. The variation in standard deviation taken from the calibration graph is shown in Table II.

TABLE II

PRECISION RESULTS WITH 2-MERCAPTOBENZOIC ACID PROCEDURE FOR SELENIUM(IV)

Concentration of selenium(IV), p.p.m.	Absorbance range	Average absorbance	Standard deviation	Relative standard deviation, per cent.
0·02	0·003 to 0·009	0·006	0·002	33·3
0·50	0·092 to 0·096	0·094	0·002	2·1
1·00	0·188 to 0·193	0·190	0·003	1·5
2·00	0·376 to 0·386	0·380	0·004	1·1
3·00	0·560 to 0·575	0·570	0·006	1·1
4·00	0·750 to 0·770	0·760	0·008	1·1

INTERFERENCES—

Two-hundred-fold excesses of the following ions caused less than 3 per cent. interference in the determination of a 1 p.p.m. (concentration in organic phase) selenium(IV) solution: Na^+; K^+; Al^{3+}; Ga^{3+}; Ca^{2+}; Sr^{2+}; Ba^{2+}; Cd^{2+}; Mg^{2+}; Be^{2+}; Zn^{2+}; Fe^{3+}; SeO_4^{2-}; SO_4^{2-}; TeO_4^{2-}; PO_4^{3-}; NO_3^-; F^-; Cl^- Br^-; $C_2O_4^{2-}$; and CH_3COO^-. Ions such as Fe^{2+}, Sn(II), SO_3^{2-} and I^- interfere by reducing selenium(IV) to the metal and must be removed by a preliminary oxidation. The tolerance limits (taken as the molar excess causing an interference of not more than ±3 per cent.) for the major interferences were as follows: Ni^{2+}, Co^{2+}, Ag^+, Li^+, Mn^{2+} and CN^- 10-fold; Zr(IV) 2-fold and Te(IV), one tenth. Mercury(II) must be absent.

The ions Li^+, Cu^{2+}, Ni^{2+} and Mn^{2+} can be removed quantitatively by total-ion exchange. A suitable amount of Zeo-Karb 225 cation-exchange resin, in the H^+ form, is added to the neutral sample solution, which is then shaken or stirred for 20 minutes. In the absence of elements that form insoluble hydroxides, Cu^{2+}, Co^{2+}, Ni^{2+} and Ag^+ can be removed as their ammine complexes in the presence of an excess of ammonia solution (sp.gr. 0·88) by shaking, as above, for only 2 minutes. Zirconium can be masked with EDTA and tellurium can be quantitatively[29] removed by extracting from 5 F hydrochloric acid with three aliquots of 5 per cent. tribenzylamine in chloroform. The sample must then be washed with three 10-ml aliquots of chloroform, and the pH is adjusted to about 2·3 with 4 F ammonia solution. Provided that a blank is made up under identical conditions, this procedure gives results within 3 per cent., even for large excesses of tellurium(IV). The results of the analyses of some synthetic samples containing interfering ions are shown in Table III. Although mercury(II) is partially removed by both the tribenzylamine procedure and the ion-exchange procedure, the reagent gives an extractable complex with mercury that absorbs very strongly at 268 nm; CN^- cannot be used as a masking agent because it interferes itself and must be removed in the preliminary treatment of the sample.

TABLE III

EFFECT OF FOREIGN IONS ON DETERMINATION OF SELENIUM(IV) BY THE RECOMMENDED 2-MERCAPTOBENZOIC ACID PROCEDURE

Concentration of selenium(IV), p.p.m.	Interfering ion	Molar excess	Selenium(IV) found, p.p.m.	Error, per cent.
0·80	Te(IV)	1000	0·81	+1·3
2·00	Te(IV)	5000	1·98	−1·3
0·80	Ag^+	1000	0·79	−1·3
0·80	Ni^{2+}	1000	0·78	−2·5
0·80	Mn^{2+}	1000	0·78	−2·5
0·80	Cu^{2+}	1000	0·79	−1·3
0·80	Li^+	1000	0·78	−2·5
0·80	Zr^{4+}	250	0·78	−2·5

CONCLUSION

2-Mercaptobenzoic acid is one of the most sensitive of the known complexing agents for the absorptiometric determination of selenium(IV). Interferences are few and all of those encountered, except that of mercury(II), have been overcome by simple and rapid separation, or masking procedures. The reagent is also more stable than most others.

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The Purification of Commercial Alizarin Red S for the Determination of Aluminium in Silicate Minerals

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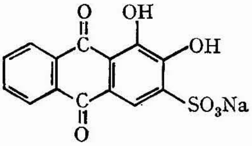
Sephadex G-10 has been used to isolate sodium alizarin sulphonate from commercial samples of Alizarin Red S that contained variable and large amounts of inorganic salts. Aluminium in silicate minerals can be reliably determined with the purified reagent, which gives a linear response up to 180 μg of aluminium.

SODIUM alizarin sulphonate, **I**, manufactured under the name Alizarin Red S, was first used by Atack[1] as a colorimetric reagent for the detection and determination of aluminium. When determining the aluminium content of silicate minerals we found considerable variations in the length of calibration graphs by using different commercial samples of the reagent at the same concentration. Qualitative tests showed that the samples we examined contained large amounts of sodium and potassium, as sulphates and chlorides. Thin-layer chromatography showed the amounts of organic impurities to be negligible. The chromatograms also showed that the main organic component reactive to aluminium was a mixture, which was later found to consist of sodium and potassium alizarin sulphonates and alizarin sulphonic acid.



I

Alizarin Red S samples were conveniently analysed by making use of the adsorptive chromatographic properties of the dextran gel, Sephadex G-10, which we have described earlier.[2] Aqueous solutions containing 20 to 30 mg of the samples were passed through small columns of the gel, and the components eluted with water. Inorganic salts appeared first, followed by the main Alizarin Red mixture. The small amount of organic impurity was immobile in water, but could be eluted with 50 per cent. aqueous ethanol. Sodium and potassium in the fractions were determined by flame photometry. The relative proportions of the inorganic and organic fractions were determined by withdrawing aliquots, evaporating them to dryness and weighing.

Because of the relatively weak adsorption of Alizarin Red S on Sephadex G-10, and its ease of elution with water, it is possible to isolate sodium alizarin sulphonate conveniently in sufficient amount for many determinations (10 ml of an 0·05 per cent. solution of the reagent is required for a single determination). The amount of the immobile organic impurity in the commercial reagent is usually so small that if large amounts of Sephadex G-10 are not available for large-scale separations, a single column can be used repeatedly without eluting it with 50 per cent. aqueous ethanol between runs.

The yield of active alizarin sulphonate from the Sephadex separation is almost quantitative, but the amounts that can be obtained by using a fixed amount of the gel depend not only on the salt content of the sample but also on its solubility in water, *i.e.*, there is a limit to the amount of some of the samples that can be applied to the column. We found that samples containing potassium alizarin sulphonate are much less soluble than those consisting only of sodium alizarin sulphonate. Thus, we have chosen for routine purification a sample free from potassium, which can be applied to the column at a concentration of 20 per cent. w/v.

Potentiometric titration of alizarin sulphonic acid against sodium hydroxide shows that the acidic group is neutralised at pH 4. Sodium alizarin sulphonate from the Sephadex column usually contains alizarin sulphonic acid in greater or lesser degree. By adding the amount of sodium hydroxide necessary to increase the pH to 4, any sulphonic acid is converted into the sodium sulphonate before the column effluent is distilled or evaporated to dryness.

EXPERIMENTAL

MATERIALS—

Four commercial samples, each labelled Alizarin Red S, from three manufacturers were used.

SPECTROPHOTOMETRY—

Absorption spectra were measured with a Hilger & Watts Spectrochem. Mk 2 spectrophotometer.

ANALYSIS OF ALIZARIN RED S SAMPLES—

Total sodium and potassium were determined by flame photometer (EEL) in aqueous solutions containing 25 mg of Alizarin Red S in 100 ml of water.

Inorganically bound sodium and potassium were determined by passing a solution of 20 to 30 mg of Alizarin Red S in 5 ml of water through a column (15 cm long and 2 cm in diameter) of Sephadex G-10 that had been allowed to swell in water alone. The column was eluted with water, giving a band of inorganic salts (band 1) between 20 and 40 ml of effluent. (In the samples containing no potassium, the anion in band 1 was sulphate; in the samples containing sodium and potassium, sulphate and chloride were identified.)

Further elution removed Alizarin Red as a single band (band 2) containing sodium and potassium alizarin sulphonates and alizarin sulphonic acid. Immobile organic impurities, negligible in amount, could be eluted with 50 per cent. aqueous ethanol. Bands 1 and 2 were diluted to 100 ml with water, and an aliquot removed for dry-weight determinations. Table I shows the compositions of bands 1 and 2.

TABLE I

COMPOSITION OF COMMERCIAL ALIZARIN RED S SAMPLES

	Sample			
	A	B	C	D
Total sodium, per cent.	14·79	15·48	5·36	6·04
Total potassium, per cent.	0	0	7·17	6·92
Sodium in band 1, per cent. of original material	12·38	13·20	3·01	3·21
Potassium in band 1, per cent. of original material	0	0	3·61	4·13
Sodium in band 2, per cent. of original material	2·69	2·33	2·32	2·76
Potassium in band 2, per cent. of original material	0	0	3·22	2·59
Salt content (band 1), per cent.	52·0	51·3	23·3	24·6
Alizarin Red content (band 2), per cent.	47·7	48·3	75·9	75·4
Sodium alizarin sulphonate,* per cent.	40·0	34·6	34·5	41·1
Potassium alizarin sulphonate,† per cent.	0	0	29·6	23·8
Alizarin sulphonic acid,‡ per cent.	7·7	13·7	11·8	10·5

* Sodium alizarin sulphonate contains 6·71 per cent. of sodium.
† Potassium alizarin sulphonate contains 10·90 per cent. of potassium.
‡ Alizarin sulphonic acid calculated by difference.

THIN-LAYER CHROMATOGRAPHY OF COMMERCIAL ALIZARIN RED S—

Samples at a concentration of 1 per cent. w/v in water were chromatographed on 250 μ thick layers of cellulose powder (Grade MN300, Macherey, Nagel & Co.). Chromatographic plates, 20 × 20 cm, and solvent butanol - acetic acid - water (6 + 1 + 2 v/v) were used.

The somewhat elongated yellow spot of the Alizarin Red S mixture had an average R_F value of 0·40 (centre). Small amounts of organic impurities showed as red - purple spots with R_F values 0·0 to 0·12 and 0·81 to 0·90. All of the spots became red when sprayed with an aqueous solution of equal parts of potassium aluminium sulphate (1 per cent. w/v) and calcium chloride (1 per cent. w/v).

With the above solvent system sodium and potassium alizarin sulphonates are not separated from alizarin sulphonic acid, but it is useful for first investigating the extent of contamination of the sample by the coloured organic impurities. However, alizarin sulphonic acid can be separated from the sulphonates with water-saturated butanol. The sulphonic acid appears as a comet-shaped spot, with its head towards the solvent front, R_F value 0·46 (tail) to 0·53 (head). Sodium and potassium alizarin sulphonates both appear as comet-shaped spots with identical R_F values 0·31 (head towards origin) to 0·39 (tail).

The monosodium and disodium phenates of sodium alizarin sulphonate are red - purple and purple compounds, respectively, and are immobile in water-saturated butanol.

POTENTIOMETRIC TITRATION OF ALIZARIN SULPHONIC ACID—

Sodium alizarin sulphonate, equivalent to 100 mg of alizarin sulphonic acid, was dissolved in 50 ml of water and the solution passed through a column of Amberlite CG120 cation-exchange resin (H^+ form). The column was washed with water until the effluent was colourless, and the total coloured effluent concentrated to 50 ml; the pH of the solution was 2·1. The solution was titrated potentiometrically against 0·028 N sodium hydroxide, one equivalent of which had been used to neutralise the sulphonic acid on reaching pH 4·0. A colour change from yellow to red began after the formation of the sodium sulphonate, indicating the start of neutralisation of the phenolic groups.

PREPARATION OF SODIUM ALIZARIN SULPHONATE—

Sephadex G-10 (75 g) was allowed to swell in water overnight and then poured into a glass column (32 cm long and 3·25 cm in diameter). One gram of Alizarin Red S (B.D.H. Ltd., sodium 15·5 per cent.; calibration 0 to 80 μg of aluminium) was dissolved in 5 ml of hot water; when cool, the solution was transferred, by pipette, on to the Sephadex and the column eluted with water. Sodium sulphate was present in the effluent at 85 ml, and had passed through the column by 125 ml. Sodium alizarin sulphonate, with alizarin sulphonic acid, ran as a very broad band, and first appeared in the effluent at 145 ml. Elution was continued until the effluent was colourless. The solution containing the sodium sulphonate and sulphonic acid was concentrated to 50 ml, and the pH adjusted to 4·0 with N sodium hydroxide. The resulting solution of sodium alizarin sulphonate was distilled or evaporated to dryness (yield, 48·3 per cent. of the weight of starting material).

Samples of commercial Alizarin Red S containing potassium alizarin sulphonate were difficultly soluble in water; the highest concentration at which one of the samples could be used was only 2 per cent. In such instances, the preparation of a sufficient amount of Alizarin Red for routine work requires the use of a proportionally larger amount of Sephadex G-10 than that given above.

The presence of potassium alizarin sulphonate in the separated product is not a disadvantage, because the salt is as effective as sodium alizarin sulphonate for determining aluminium.

DETERMINATION OF ALUMINIUM IN SILICATE MINERALS—

Solutions were prepared for analysis by the method of Shapiro and Brannock.[3] The weight of mineral taken was 50 mg, giving a volume of 1 litre of test solution.

REAGENTS—

Calcium chloride solution—Add 15 ml of concentrated hydrochloric acid to a suspension of 7 g of calcium carbonate in 100 ml of water; boil the solution for a few minutes, cool and dilute to 500 ml.

Hydroxylammonium chloride solution—Prepare a 10 per cent. w/v solution of hydroxylammonium chloride in water immediately before use.

Potassium ferricyanide solution—Dissolve 0·375 g of potassium ferricyanide in 50 ml of water immediately before use.

Thioglycollic acid solution—Dilute 2 ml of thioglycollic acid to 50 ml with water immediately before use.

Buffer solution, pH 4·8—Dissolve 100 g of crystalline sodium acetate in 250 ml of water, add 30 ml of glacial acetic acid and dilute to 500 ml with water.

Sodium alizarin sulphonate reagent—Prepare a 0·05 per cent. w/v solution of sodium alizarin sulphonate in water.

Standard aluminium solution—This was prepared from U.S. National Bureau of Standards sample No. 99 [soda felspar, containing 19·06 per cent. of aluminium oxide (Al_2O_3)] by Shapiro and Brannock's[3] method.

PROCEDURE—

From 1 litre of the prepared solutions, transfer, by pipette, 15-ml aliquots of the standard aluminium solution, samples and blank into 100-ml calibrated flasks. Then add, in the following order, calcium chloride solution (2 ml), hydroxylammonium chloride solution (1 ml), potassium ferricyanide solution (1 ml) and thioglycollic acid solution (2 ml). Mix the contents of the flasks and allow them to stand for 5 minutes. Add buffer solution (10 ml), allow to stand for 10 minutes, then add sodium alizarin sulphonate solution (10 ml), and dilute the solutions to 100 ml. After 45 to 75 minutes, measure the optical densities of the solutions against the reagent blank at 490 nm.

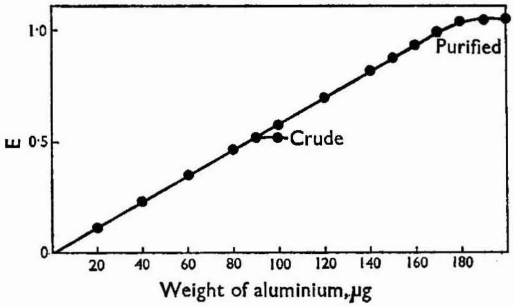


Fig. 1. Calibration graph for aluminium with sodium alizarin sulphonate

The aluminium contents of the samples can be read from a previously prepared calibration graph (Fig. 1), or the percentage of aluminium can be calculated from the formula—

$$\text{percentage of aluminium oxide in sample} = \frac{\text{percentage of aluminium oxide in standard} \times W_1 \times E_2}{W_2 \times E_1},$$

where W_1 and W_2 are the weights in milligrams of standard and sample, respectively, and E_1 and E_2 are their corresponding optical densities, the volumes of aliquots of the standard and the sample being equal.

DISCUSSION

In descriptions of methods in which Alizarin Red S is used for the determination of aluminium, the purity of the reagent has seldom been considered. Parker and Goddard[4] noted that "different batches of Alizarin have different characteristics." They also stated that recrystallised Alizarin Red S was used in some of their experiments, but gave no details of the solvent used for recrystallisation. The present experiments have shown that differences in the quality of the commercial reagent are the result of admixed sulphates and chlorides of sodium and potassium. A reagent of consistently good quality for determining aluminium is obtained by removing the inorganic salts and converting the free sulphonic acid into the sodium sulphonate. It is immaterial whether or not the alizarin sulphonate is present as the potassium or the sodium salt.

Various authors have discussed the conditions under which aluminium is determined, the main differences in the methods being in the pH, the wavelength at which the optical density of the aluminium - alizarin complex is measured and concentration of reagent. Atack[1] gave no specific values for pH, or wavelength of measurement, and used the reagent at a concentration of 0·1 per cent. w/v. Mussakin[5] measured the colour at pH 3·6 with a Duboscq colorimeter. Barton[6] claimed that interference from iron was eliminated by measuring the colour at 370 nm, and used the reagent at a concentration of 0·1 per cent. w/v. The most detailed study of the reaction between aluminium and Alizarin Red S was made by Parker and Goddard,[4] who made the important discovery that the addition of calcium ions to the test solution doubles the sensitivity of the reaction. They ascribe the effect to the formation of a calcium - aluminium complex. In their method a 0·04 per cent. w/v solution of the reagent buffered to pH 4·55 is used, and the colour measured at 485 nm. Shapiro and Brannock[3] measure the colour at 475 nm, but we have modified this part of their method. We find that, with purified Alizarin Red S at a pH of 4·8, the wavelength of maximum absorption by the complex is 490 nm (Fig. 2); at this wavelength the interference from titanium is negligible, and interference from iron is eliminated with potassium ferricyanide and thioglycollic acid before developing the aluminium - alizarin complex.

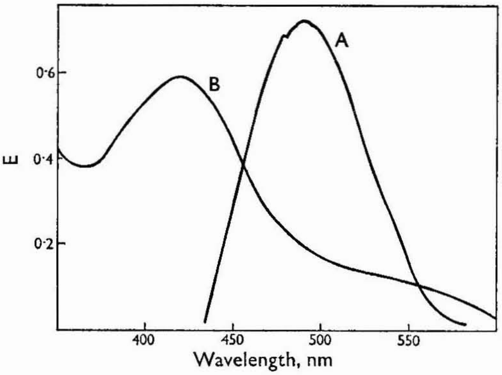


Fig. 2. Absorption spectra: A, aluminium - alizarin complex against reagent blank; and B, sodium alizarin sulphonate against water blank

The reaction between aluminium and sodium alizarin sulphonate requires two molecules of reagent to one atom of aluminium for complex formation. In our method we use 10 ml of reagent solution containing 5 mg of sodium alizarin sulphonate which, theoretically, will form a complex with 197 µg of aluminium. Of the commercial samples of Alizarin Red S examined the shortest straight-line calibration was found to be 0 to 80 µg of aluminium. Separation of the sodium alizarin sulphonate on Sephadex G-10 improved the calibration to 0 to 180 µg of aluminium. The use of such an extended calibration, with our method of determination, enables 45 per cent. of aluminium oxide to be determined in a silicate mineral. The upper limit of determination, stated by Shapiro and Brannock,[3] with the same volume of test solution (15 ml), is 24 per cent. of aluminium oxide.

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The Extraction of Iron with Di-(2-ethylhexyl)-orthophosphoric Acid, and its Direct Determination with Bathophenanthroline

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A simple, direct determination of iron(III) extracted from chloride solutions with di-(2-ethylhexyl)orthophosphoric acid is described. Iron in the organic phase is first reduced with ascorbic acid, bathophenanthroline and pyridine are then added and the colour developed measured at 533 nm. With this procedure, which involves extraction of the iron with a phase-volume ratio of 1 : 1, an improvement on the already appreciable selectivity of other bathophenanthroline procedures is obtained.

Extremely small amounts of iron can be determined with satisfactory precision when extraction is carried out with an inorganic-to-organic phase-volume ratio of 100 : 1. Results for the determination of iron in high-pressure boiler water are reported.

MANY investigations have been made into simple methods for determining small amounts of iron, an important requirement in corrosion control in thermal and nuclear power plants. The most popular technique is spectrophotometry. Chromogenic groups containing the ferroin group form coloured complexes with iron(II) that have high molar extinction coefficients; these reagents are selective, and the complexes can readily be extracted into small volumes of organic solvents, thus permitting the removal of interferences and increasing the sensitivity.

Bathophenanthroline, first used in 1952,[1] has been widely applied and is still the most popular reagent; it is readily available and its iron complex has a high molar extinction coefficient. Its sensitivity has been recorded by Wilson,[2] who stated that 2·1 μg of iron per litre could be determined with a standard deviation of ±0·19 "within batches." He developed the complex in aqueous solution and extracted it into isopentyl alcohol, the ratio of original inorganic sample to final organic solution used for measurement being 8 to 1; reproducibility of extraction was satisfactory. Concentration by reduction in volume accounted for the high sensitivity. Higher volume ratios appear not to have been used, and our own experiments with these showed that reproducibility of extraction then became poor.

An alternative method of concentration involves the extraction of iron into an organic solvent before complexation. Iron in inorganic combination, *e.g.*, as chloride, can be extracted in this way, and ethers, ketones, amines and ammonium compounds, and neutral and acidic organophosphorus derivatives have been used. Their immiscibility with water and effective extraction of iron permits high inorganic-to-organic ratios to be used. After extraction, the iron can be returned to an aqueous phase for determination, but it is preferable to make the determination directly in the organic phase, thus avoiding errors during extraction and making the method simpler.

The extraction of iron into various organic phases for spectrophotometric determination has been reported, the iron being subsequently determined with 1,10-phenanthroline,[3,4] dibenzoylmethane[5] or thiocyanate.[6,7] The stated purpose of these workers was to eliminate interfering ions, and they paid no attention to the volume ratios or sensitivity.

The use of bathophenanthroline to enhance sensitivity has been suggested[3,8]; coupling its high molar extinction coefficient with a reproducible extraction step giving a high inorganic-to-organic volume ratio would produce a very sensitive method for the determination of iron. Di-(2-ethylhexyl)orthophosphoric acid (HDEHP) appeared to be a promising extractant for this purpose; as, however, only iron(III) passes into the organic phase, a procedure was required that enables the iron(II) - bathophenanthroline complex to be developed after reduction of iron(III).

A method involving extraction of iron(III) with HDEHP from chloride solutions, and its subsequent reduction with ascorbic acid and determination with bathophenanthroline, after addition of pyridine, has, therefore, been developed; the spectrophotometric procedure was optimised with respect to the various parameters involved. The extraction step was carried out initially with a phase-volume ratio of 1 : 1 and the same experimental conditions used to investigate interference effects. The method was then extended to include the extraction of iron with higher inorganic-to-organic phase-volume ratios, which resulted in a very sensitive procedure for the determination of iron.

The procedure for extraction with a phase-volume ratio of 1 : 1, with its significant features, and its extension by extraction with a 100 : 1 volume ratio are given below.

The standardisation of the procedure, the effect of foreign substances and the extension of the colorimetric procedure to other extraction systems are dealt with in greater detail elsewhere.[9]

Experimental

Apparatus and reagents—

The spectrophotometric determinations were carried out with a Uvispek spectrophotometer (Hilger & Watts Ltd.), with glass optics and 1-cm glass cuvettes.

Di(2-ethylhexyl)orthophosphoric acid—Obtainable from Virginia-Carolina Chemical Co., Richmond, U.S.A.

All other reagents used were of RP or RS quality, obtainable from C. Erba, Milan.

The preparation of iron-free HDEHP and stock solutions of iron were carried out as described previously,[7] where details of the extraction equipment used are also given.

Extractions were carried out with solutions of HDEHP (0·5 M) in cyclohexane equilibrated with twice their volume of 0·1 M hydrochloric acid.

Extraction procedure—

A phase-volume ratio of 1 : 1 is used in the extraction step for amounts of iron in the aqueous phase ranging from 0·04 to 6 μg per ml, the solution being previously made 0·1 M with respect to hydrochloric acid. If the original acid concentration is higher than 0·1 M, the solution can be neutralised to phenolphthalein with sodium hydroxide, and the requisite amount of acid then added, care being taken to ensure that the final chloride concentration is below 3·8 M. If iron(II) is to be determined, small amounts of hydrogen peroxide (less than 3×10^{-3} per cent.) are added to the aqueous solution.

Shake 10 ml of the iron-containing solution for 10 minutes in a separating funnel with an equal volume of an equilibrated 0·5 M HDEHP solution in cyclohexane. To avoid turbidity in the final solutions care must be taken to keep the greased surface of the funnel in contact with cyclohexane to a minimum.

Spectrophotometric procedure—

Transfer, by pipette, 5 ml of the organic layer from the funnel into a 10-ml calibrated flask. Add 1 ml of a freshly prepared 0·05 M ascorbic acid solution in 95 per cent. ethanol and mix. Add 1 ml of a mixture of absolute ethanol and pyridine (45 + 55) and 2 ml of 0·002 M bathophenanthroline in 95 per cent. ethanol. Make up to volume with 95 per cent. ethanol, mix and allow the solution to stand. After 30 minutes, measure the colour at 533 nm against the reagent blank.

The iron value is obtained from the following equation—

$$\text{Optical density} = 3{\cdot}94 \times 10^{-2}.c$$

where c is the total amount of iron in micrograms in the final 10 ml of solution, *i.e.*, in 5 ml of the original 0·1 M hydrochloric acid solution.

OBSERVATIONS ON THE METHOD—

The visible and ultraviolet spectra of the colour produced in the organic phase are similar to those obtained with it in aqueous solutions (Sturla, A., private communication). The resulting molar extinction coefficients are also similar, being $2{\cdot}20 \times 10^4$. Beer's law is obeyed for amounts of total iron up to 30 µg; for higher iron concentrations the calibration graph is unusual as it rapidly smoothens out to constant optical density values, and then decreases appreciably as the iron content increases. Other experimental results reported elsewhere[9] suggest that this behaviour is caused by the formation of a colourless iron - bathophenanthroline complex, which absorbs in the ultraviolet region, when iron is present in large excess.

The precision of the method was determined at the 0·2 and 1·4 µg per ml iron levels in the initial solution, and average optical densities were 0·039 and 0·268; the standard deviations, as calculated from 16 independent results, were 0·0012 and 0·0014, respectively. Similar standard deviations were obtained when calculated from 6 independent development steps with the same organic solution containing iron at both of these levels.

EFFECT OF FOREIGN SUBSTANCES—

As mentioned, iron(II) - bathophenanthroline procedures involving complex formation in the original aqueous phase suffer from few interferences. According to Penner and Inman,[10] Wilson[2,11] and Bell, Stanwix and Boase,[12] only cobalt, nickel, cadmium, manganese, zinc and copper, among the many elements tested, give rise to some unfavourable effects, which can be overcome (partially in some instances) only by the use of suitable masking agents, or by the addition of excess of reagent.[10,13]

On the other hand, under the extraction conditions adopted in this work, cobalt, nickel and cadmium ions remain completely in the aqueous phase, while relatively small amounts of manganese, zinc and copper are extracted with the iron by HDEHP; the method is, therefore, satisfactorily selective.

The effect of 57 foreign cations on the determination of 1·105 µg of iron per ml was investigated; the cations were added to the original aqueous solution in amounts ranging from 1 to 170 micro-equivalents per ml (10 micro-equivalents per ml in most instances). Few interferences were noted. Effects occurring with scandium, thorium, niobium(V), molybdenum, manganese(II), zinc, indium and tin(II) were easily overcome by use of a more concentrated (0·01 M) bathophenanthroline solution. As expected, no interference was given by 0·3-mg amounts of cobalt, nickel or cadmium per ml. Relatively large (5 to 10 micro-equivalents per ml) amounts of manganese(II) and zinc were also tolerated, provided that the more concentrated bathophenanthroline solution was used. The interference of copper was only partially overcome, the amount tolerated being, in any event, enhanced (1 micro-equivalent per ml) compared with traditional methods.

On the other hand, serious interference was encountered with vanadium(III), gallium, yttrium and the heaviest rare earths in the extraction step, and only a few micrograms of these ions can be tolerated. With traditional procedures, vanadium is reported not to interfere,[13] but no information is available regarding the other elements. The interference of anionic species was also investigated; results showed that, with up to 3·8 M chloride levels, neither the iron extraction nor the subsequent colorimetric determination was affected. Other common anions, such as nitrate, perchlorate, sulphate and fluoride, even at molar concentrations, do not interfere. Phosphate ion (added as disodium hydrogen phosphate) at 0·05 M concentration did not interfere.

Because of the application of the extended method to high-pressure boiler waters (see below), the interference from other foreign substances normally present in such waters was investigated; no interference was caused by the presence of 10 µg per ml of hydrazine, cyclohexylamine or morpholine, or of 100 µg per ml of detergents.* These latter compounds were found to interfere in the traditional method[2,11] unless present in concentrations below 1·2 µg per ml. Hydrogen peroxide can be tolerated in concentrations below 1×10^{-2} volumes: 1×10^{-3} volumes of hydrogen peroxide are sufficient to oxidise the small amounts of iron(II) involved in the method.

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* Olà, Dixan, Omo, Teepol and Unilever (20 µg per ml of each) were used.

EXTENSION OF THE METHOD TO THE DETERMINATION OF IRON AT VERY LOW CONCENTRATIONS—

Experiments with inorganic-to-organic phase ratios higher than unity showed that, even with a phase ratio as high as 200 to 1, the extraction step was still satisfactory, both for iron recovery and reproducibility, provided that the shaking time was long enough (1 hour).

In an investigation, iron was extracted from 1 litre of 0·1 M hydrochloric acid by shaking it for 1 hour with 10 ml of equilibrated 0·5 M HDEHP solution in cyclohexane. The calibration graph obtained as described under Spectrophotometric procedure was similar to that given by 1 : 1 volume-ratio extractions, being only slightly lower (2 per cent.).

In these experiments, care was taken to avoid contamination by iron; glassware was previously treated with 6 M hydrochloric acid, HDEHP solution in cyclohexane, acetone and 0·01 M hydrochloric acid purified by HDEHP extraction, in that order. Water was deionised and distilled twice in quartz apparatus. Water made 0·01 M with respect to hydrochloric acid and purified by extraction with HDEHP was used to obtain the lower portion of the calibration graph (the identical behaviour in the extraction at suitable iron levels from fresh and saturated water had been checked).

Reagent blanks were obtained by applying the whole procedure to iron-free water. However, a suitable blank could be obtained by developing the colour in the equilibrated HDEHP solution, thus avoiding the previous extraction step; this was true only when the amount of iron brought into solution by the addition of hydrochloric acid was below the sensitivity of the method itself, as it was in most instances; this amount can be checked by the results obtained when applying the procedure to 0·2 M acidic solutions.

The precision of the extended method was determined at the 0·7 and 7·8 µg per litre iron levels; average optical densities were 0·013 and 0·142, and standard deviations 0·0020 and 0·0022, respectively, as calculated from 11 and 10 independent results. Therefore, as little as 0·7 µg of iron per litre can be determined, with a standard deviation of ±0·11.

APPLICATION OF THE EXTENDED METHOD—

The method involving extraction with a phase ratio of 100 : 1 was applied to the determination of the total iron content in the blowdown and condensate of two power stations, and the results obtained were checked with the conventional bathophenanthroline method used at these stations, which was derived from Wilson's procedure and involved the dissolution of "non-reactive"[2,11] iron with thioglycollic acid and extraction of the iron - bathophenanthroline colour with carbon tetrachloride.

As thioglycollic acid impairs the HDEHP extraction step, another dissolution method was used,[14] in which chlorine, produced by reacting hydrochloric acid and hydrogen peroxide, was bubbled for 10 minutes into the samples, and the excess then removed by boiling.

TABLE I

DETERMINATION OF IRON IN HIGH-PRESSURE BOILER WATER

	Organic-phase determination		Conventional bathophenanthroline determination
Run	Phase volume ratio used for extraction	Iron found, µg per litre	Iron found, µg per litre
A	50 : 1	28·0, 28·0	25·0, 28·0
B	100 : 1	6·8, 6·4, 7·0 6·2, 6·3	8·5, 8·7, 6·2 7·5
C	100 : 1	1·8, 1·8 0·9, 1·2	1 to 1·5, 1 to 1·5 0 to 1, 0 to 1
	200 : 1	1·75	
D	100 : 1	2·0, 2·2	2·3, 2·5
E	100 : 1	3·2, 3·0	3·2, 3·2
	200 : 1	3·25	
F	100 : 1	1·1, 1·1	1·7, 1·7
	200 : 1	1·1	

Several runs of analyses were performed, each run being made on several water samples, collected independently and consecutively, directly from the sampling valves. The results obtained are presented in Table I. The agreement between the two methods is satisfactory, considering the unavoidable uncertainty in the collection of the samples. The good reproducibility of the HDEHP method is also evident, even at the lowest iron concentrations when the conventional method can give only an approximate result.

CONCLUSION

The extraction of iron from chloride solutions with HDEHP, and its subsequent determination in the organic phase with bathophenanthroline, gives promising results. Fewer interferences occur than with traditional bathophenanthroline procedures. Moreover, it seems probable that the selectivity of the method can be further improved as the spectrophotometric procedure can be successfully applied to iron extracted either with HDEHP from inorganic media other than chloride, or with other well known iron extractants, such as tributyl phosphate, tri-octylphosphine oxide or tri-octylamine.[9]

In this work, the method was extended to the extraction of iron with an inorganic-to-organic phase-volume ratio of 100 : 1 to include the iron levels present in high-pressure boiler waters. It is likely that the use of higher ratios will enable an extremely high sensitivity to be achieved.

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The Chemical Analysis of Copper, Chromium and Arsenic Preservative-treated Wood

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Methods are described for the rapid determination of copper, chromium and arsenic in preserved timber. These preserving compounds are leached from thin sections of wood with hydrochloric acid, sodium hydroxide and dilute sulphuric acid, respectively. Copper, chromium and arsenic are reacted with zinc dibenzyldithiocarbamate, diphenylcarbazide and ammonium molybdate - hydrazine reagent, respectively, and the determinations completed by spectrophotometric measurement of the coloured complexes formed.

The procedure is particularly useful for the study of the distribution, over small areas, of copper, chromium and arsenic-containing preservatives in wood.

Investigation into the preservation of timber with aqueous solutions of formulations containing copper, chromium and arsenic has resulted in the need for simple, rapid and accurate methods of analysis for these elements in the range 0·005 per cent. upwards. Chemical methods[1,2,3,4,5] are available for the determination of copper, chromium and arsenic in preserved timber, but involve lengthy ashing or acid-digestion procedures. The time taken for analysis, together with the manipulative operations involved, renders them slow and creates a bottleneck in research projects or treating practice when a large number of analyses may be required. Chemical analysis is needed for the determination of preservative distribution, permanence and loading and, because of the variable behaviour of wood, research projects often need to be planned on a statistical basis requiring a large number of separate determinations to ensure significant results. For these reasons chemical techniques were sought that should, if possible, have the following attributes: simplicity of sample preparation, no ashing or acid digestion, a minimum number of stages in the procedure, the greatest possible speed and accuracy of results.

The usual form of treatment with a copper, chromium and arsenic formulation is carried out by impregnating seasoned timber with an aqueous solution of preservative containing copper sulphate, potassium or sodium dichromate and arsenic pentoxide, by the full-cell, vacuum and pressure-impregnation process[1] or the Lowry empty-cell, pressure-impregnation process.[1] After impregnation, the chemical components of the preserving solution react with each other, and with the wood, and become fixed, *i.e.* copper, chromium and arsenic compounds are formed that are insoluble in water.

Past work in this laboratory has shown that unfixed preservation chemicals can be quantitatively leached from thin sections of wood up to 300 μ thick.[6] To apply leaching techniques it is, therefore, necessary to render the fixed copper, chromium and arsenic compounds soluble so that they can be leached from the wood and reacted with colorimetric complexing reagents to allow a fast spectrophotometric finish to the determinations. It was found that the fixed copper, chromium and arsenic compounds could be rapidly leached from thin sections of wood with concentrated hydrochloric acid, 2 N sodium hydroxide solution containing 50 vol hydrogen peroxide, and 0·5 N sulphuric acid, respectively. Scots pine, *Pinus sylvestris*, and lime, *Tilia vulgaris*, were used for the experimental work. Neither species caused any apparent difficulties during the leaching out stages of the procedures when sections up to 300 μ thick were used.

The determinations of copper with zinc dibenzyldithiocarbamate,[7] chromium with diphenylcarbazide[8] and arsenic by the molybdenum-blue method[9] are well known procedures. Therefore, it was decided to evolve methods of analysis in which these techniques were used.

EXPERIMENTAL

To examine techniques for determining copper, chromium and arsenic in timber it was necessary either to prepare standard samples containing a known amount of preservative evenly distributed throughout the specimen, *e.g.*, by freeze-drying,[10] or to compare the results given by the proposed procedure with those obtained with established methods, by using adjacent samples from the same piece of treated wood. Because little is known about the mechanism by which the salts are fixed in wood and possible interference to the process by freeze-drying, it was decided to use the comparison of results technique.

Preserved wood from another project, which had been treated as follows, was used for the experimental work. Thin sections, 100 μ thick, were cut with a microtome from the radial face of blocks, 140 mm long and 10 mm wide, of Scots pine and lime. The thin sections were bound together in packages of 20, which were submerged in 3 per cent. w/v solutions of various formulations of copper sulphate, potassium dichromate and arsenic pentoxide and subjected to a vacuum of 710 mm of mercury for 60 minutes to evacuate air from the cells. The vacuum was released, and a pressure of 7 kg per cm^2 applied for 30 minutes to the solution containing the specimens. The pressure was released, and the specimens were removed from the solution, the surfaces of the packages being superficially dried on filter-paper, and wrapped in polythene bags for 10 to 12 days to allow the preservative to become fixed. After fixing, the specimens were removed from the polythene wrappings and dried to about 7 per cent. moisture content.

COPPER—

Fixed copper, chromium and arsenic preservatives are soluble in solutions of mineral acids, and copper reacts with zinc dibenzyldithiocarbamate in N hydrochloric acid solution to form a yellow complex that is soluble in carbon tetrachloride. Therefore, by making use of these properties the preservative was dissolved and leached from wood with concentrated hydrochloric acid, the solution diluted with water, zinc dibenzyldithiocarbamate in carbon tetrachloride added and the solution shaken to form the complex, which was extracted into the organic phase. The organic phase was then separated for spectrophotometric measurement of the optical density of the yellow copper complex.

Measurements of optical densities of test solutions were made at wavelength 435 nm with a Unicam SP 600 spectrophotometer, with 10-mm cells. The spectrophotometric calibration graph was constructed in the range 0 to 40 μg of copper and a straight-line relationship was obtained.

The time required to leach out the copper was determined by leaching 10-mm lengths of the treated wood strips for various periods. The results showed that copper was completely leached out within 5 minutes.

Leaching time, minutes	2	3	5	30	60
Copper content in wood, per cent.	1·23	1·26	1·31	1·32	1·31

The effect of the presence of chromium and arsenic on the recovery of copper was investigated by applying the procedure to solutions containing known amounts of copper, chromium (as dichromate) and arsenic (as arsenate). No interference with the copper recovery was experienced.

Added chromium and arsenic	Copper added, μg	Copper recovered, μg
100 μg of each	31·7	31·7
200 μg of each	31·7	31·7

The recovery of copper by the proposed method was compared with that from an acid-digestion procedure. Alternate 10-mm lengths of a treated thin strip of wood were decomposed with 100 vol hydrogen peroxide and concentrated nitric acid. The solutions were evaporated to dryness, the residues taken up in 10 ml of hydrochloric acid and the determinations finished colorimetrically with zinc dibenzyldithiocarbamate, as described in the proposed method. The copper in each of the remaining strips of treated wood was determined by the leaching procedure. The results given by the two methods were in good agreement (Table I).

CHROMIUM—

One of the best colorimetric reagents for sexavalent chromium is diphenylcarbazide, but the dichromate in the preservative is normally partially reduced in treated wood to a lower valency state and, therefore, needs to be oxidised to form the complex. The procedures for oxidising chromium in acidic solution to the sexavalent state are relatively slow compared with oxidation with hydrogen peroxide in sodium hydroxide solution.[11]

It was decided to examine the possibility of leaching the chromium from the wood with sodium hydroxide solution containing hydrogen peroxide. Pieces of the strips of treated wood, 10 mm long, were placed in 25-ml beakers, 2 ml of 2 N sodium hydroxide and 1 drop of hydrogen peroxide added to each, and the solutions heated at about 120° C for 5 minutes to decompose the hydrogen peroxide. The solutions were acidified with dilute sulphuric acid, diluted and 1,5-diphenylcarbazide solution was added. The resulting solutions were diluted to standard volumes and the optical density of the violet - red coloured complex was measured on a spectrophotometer at wavelength 540 nm, with 1-cm cells. The spectrophotometric calibration graph was constructed in the range 0 to 130 μg of chromium, and a straight-line relationship was obtained.

Similar pieces of treated wood were dissolved in a mixture of concentrated nitric acid and 100 vol hydrogen peroxide. The chromium was oxidised to the sexavalent state and determined spectrophotometrically with 1,5-diphenylcarbazide. The results given by the two procedures were in good agreement (Table I), which showed that the chromium compound present in the preserved wood was soluble and leachable in sodium hydroxide solution containing hydrogen peroxide.

To ensure that the presence of copper and arsenic had no effect on the recovery of chromium, the procedure was applied to solutions containing known amounts of chromium, copper and arsenic. No interference with the chromium recovery was experienced.

Added copper and arsenic	Chromium added, μg	Chromium recovered, μg
100 μg of each	40·2	40·2
200 μg of each	40·2	40·1

ARSENIC—

At first, it was thought necessary to decompose the wood and oxidise the arsenic in the solution to the quinquivalent state, but during examination of the arsenic leached from wood with dilute sulphuric acid it was generally found that all of the arsenic was present as arsenate, and it was, therefore, possible to use a simple leaching procedure. Direct application of the proposed method will give rise to inaccurate results if a significant amount of arsenic is present as arsenite. In the absence of arsenite, the weighed sample was warmed with ammonium molybdate - hydrazine sulphate reagent in 0·5 N sulphuric acid solution until formation of the blue molybdoarsenate reduction complex was complete. The solution was diluted to a standard volume and the optical density of the blue complex measured with a Unicam SP 600 spectrophotometer.

Measurements of the optical densities of the test solutions were made at wavelength 840 nm, with 10-mm cells. The spectrophotometric calibration graph was constructed in the range 0 to 80 μg of arsenic, and a straight-line relationship was obtained.

The effect of the presence of copper and chromium on the recovery of arsenic was investigated by applying the procedure to solutions containing known amounts of arsenic, chromium (as dichromate) and copper (as copper sulphate). No interference with the arsenic recovery was experienced. Also, complete recovery of arsenic was obtained in the presence of 200 μg of chromium in the tervalent state.

Added copper and chromium	Arsenic added, μg	Arsenic recovered, μg
100 μg of each	40·7	40·6
200 μg of each	40·7	40·7

Recovery of arsenic by the proposed procedure was compared with that by an acid-digestion method. Alternate 10-mm lengths of a thin strip of treated wood were decomposed with concentrated nitric acid and 100 vol hydrogen peroxide. The solution was evaporated to dryness and the residue heated at a temperature not higher than 130° C for half an hour to expel nitric acid. Ammonium molybdate - hydrazine sulphate in 0·5 N sulphuric acid was added and the determination completed colorimetrically, as described in the proposed procedure. The arsenic in each of the remaining strips was determined by the leaching procedure. The results given by the two procedures were in good agreement (Table I).

SAMPLING—

The structure of wood is variable, even over small areas. In copper, chromium and arsenic-treated timber, concentration gradients of preservatives can occur across the growth rings. Therefore, only radial or cross-sections cut across several growth rings, which are more representative of the preservative in the bulk of the wood, were taken for analysis.

After the methods with samples 100 μ thick had been developed, the maximum thickness of wood from which the total preservative content could be recovered was investigated by using commercially treated Scots pine. Adjacent radial or cross-sections, with 100 mm^2 area and increasing thickness up to a maximum of 300 μ, were cut on a microtome and analysed by the proposed procedures. The results showed that complete recovery of the preservative was obtained with radial sections up to 200 μ and cross-sections up to 300 μ thick.

It is possible, by altering the final stages in the proposed procedures, *i.e.*, by increasing, when necessary, the volume of the standard solutions for spectrophotometric measurement, to take for analysis at least ten thin sections of 50 mm^2 area and 50 μ thick from various parts of the specimen to make up a representative sample for one determination. In this way a good average sample is obtained for the determination of the loading of preservative in bulk wood.

RESULTS

The proposed procedures and acid-digestion methods were applied to the thin strips of copper, chromium and arsenic-treated wood. Adjacent samples were analysed by the different techniques to reduce the effect of any variations in the wood. The results given in Table I are in good agreement, and show that the proposed procedures are quantitative and possess the required speed and precision. Similar results were obtained with either Scots pine or lime. The standard deviations, each based on eleven determinations at the 0·5 per cent. level, were ±0·020 per cent. for copper, ±0·016 per cent. for chromium and ±0·014 per cent for arsenic.

TABLE I

RESULTS OBTAINED BY LEACHING AND ACID DIGESTION

	Content, per cent., by—		
Element	Leaching	Acid digestion	Strip No.
	0·35	0·36	1
	0·37	0·36	
Copper	1·18	1·18	
	1·14	1·08	2
	1·10	1·10	
Chromium ..	0·58	0·60	3
	0·60	0·59	
	0·80	0·81	4
	0·80	0·81	
	0·49	0·50	
	0·51	0·50	5
	0·49	0·53	
	0·50	0·49	
Arsenic	0·65	0·65	
	0·64	0·63	6
	0·69	0·69	
	0·89	0·87	
	0·93	0·93	7
	0·86	0·86	

To demonstrate the usefulness of the proposed methods, the distribution of copper, chromium and arsenic through a 35 mm thick piece of commercially treated Scots pine was investigated. Radial sections were taken for analysis at intervals of 2·5 mm. The curves obtained by plotting the copper, chromium and arsenic contents against thickness are shown in Fig. 1. The 45 determinations, including sample cutting, carried out to construct the distribution curves for copper, chromium and arsenic were completed within 9 hours.

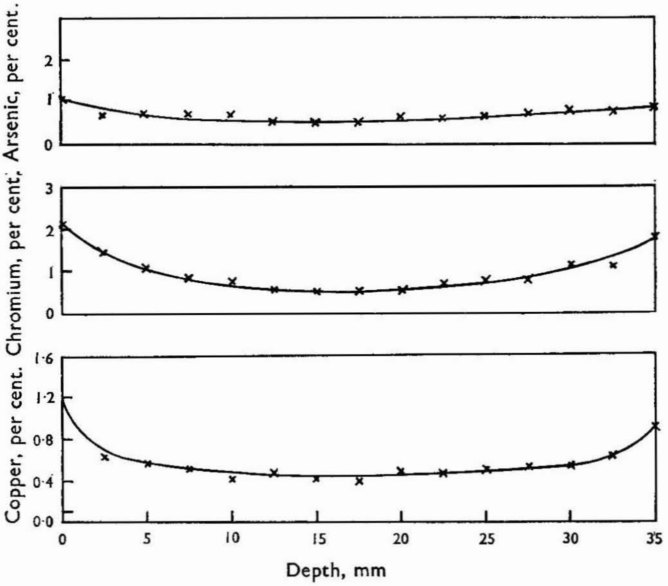

Fig. 1. Distribution of copper, chromium and arsenic preservative in Scots pine

It can be seen from Fig. 1 that it is possible to evaluate rapidly the distribution of copper, chromium and arsenic-containing preservatives over very small areas. This is not possible by previously available methods of chemical analysis.

METHODS

COPPER

REAGENTS—

Use high purity reagents when possible.

Zinc dibenzyldithiocarbamate solution—Dissolve 0·5 g of zinc dibenzyldithiocarbamate in 500 ml of carbon tetrachloride.

PROCEDURE—

Weigh the sample and place it in a 150-ml separating funnel, add 10 ml of concentrated hydrochloric acid and swirl it to wet the wood. Allow to stand for at least 5 minutes, add 90 ml of water and swirl the funnel to mix the solution; add, from a burette, 10 ml of zinc dibenzyldithiocarbamate solution and shake the separating funnel for 90 seconds. Allow the organic phase to separate, run off the carbon tetrachloride layer through a 7·0-cm Whatman No. 1 filter-paper into a 10-mm cell, discarding the first runnings. Measure the optical density of the yellow complex against a reagent blank, prepared in a similar way, at wavelength 435 nm on a Unicam SP 600 spectrophotometer. To obtain the copper content of the test solution compare the spectrophotometer reading with a calibration graph.

CALIBRATION—

Preparation of standard solution A—Dissolve 3·9689 g of analytical-reagent grade copper sulphate, $CuSO_4.5H_2O$, in water. Transfer the solution to a 500-ml graduated flask, add 10 ml of concentrated hydrochloric acid, dilute to the mark with water and mix.

1 ml of standard solution A $\equiv$ 2000 μg of copper.

Preparation of standard solution B—Transfer, by pipette, 10 ml of standard solution A into a 1-litre graduated flask, dilute to the mark with water and mix.

1 ml of standard solution B $\equiv$ 20 μg of copper.

Preparation of standard solution C—Transfer, by pipette, 10 ml of standard solution B into a 100-ml graduated flask, dilute to the mark with water and mix.

1 ml of standard solution C $\equiv$ 2 μg of copper.

Transfer aliquots of 1, 2, 4, 6, 8, 10, 12, 14, 16 and 20 ml of standard solution C to 150-ml separating funnels. Dilute to 90 ml with water and add 10 ml of concentrated hydrochloric acid. The aliquots contain 2, 4, 8, 12, 16, 20, 24, 28, 32 and 40 μg of copper, respectively. Continue as described under Procedure. Plot optical densities against micrograms of copper to obtain the calibration graph.

CHROMIUM

REAGENTS—

Use high purity reagents when possible.

Sodium hydroxide 2 N *solution*—Dissolve 8 g of sodium hydroxide pellets in 90 ml of water and dilute to 100 ml. Store in a polythene bottle.

Sulphuric acid 4 N *solution*—Add 28 ml of concentrated sulphuric acid, carefully with stirring, to 200 ml of water, cool, and dilute to 250 ml with water.

1,5-*Diphenylcarbazide solution*—Dissolve 0·5 g of 1,5-diphenylcarbazide in 40 ml of acetone containing 3 drops of 4 N sulphuric acid solution and dilute to 50 ml with acetone.

PROCEDURE—

Weigh the sample and place it in a covered 25-ml beaker. Add, from a burette, 2 ml of 2 N sodium hydroxide solution and 1 drop of 50 vol hydrogen peroxide. Heat the beaker on a hot-plate at a temperature of about 120° C for 5 minutes, but do not allow the solution to evaporate to dryness. Cool, wash the solution into a 100-ml graduated flask, dilute to about 85 ml with water, add, from a burette, 6 ml of 4 N sulphuric acid solution and mix the solution. Add 2 ml of 1·0 per cent. 1,5-diphenylcarbazide solution, dilute to the mark with water and mix. Measure the optical density of the violet - red chromium - diphenylcarbazide complex against a reagent blank, prepared in a similar way, in 10-mm cells at wavelength 540 nm on a Unicam SP 600 spectrophotometer. To obtain the chromium content of the test solution, compare the spectrophotometer reading with a calibration graph.

CALIBRATION—

Preparation of standard solution A—Dissolve 0·2828 g of potassium dichromate, $K_2Cr_2O_7$, in water. Transfer the solution to a 100-ml graduated flask, dilute to the mark with water and mix.

1 ml of standard solution A $\equiv$ 1000 μg of chromium.

Preparation of standard solution B—Transfer, by pipette, 10 ml of standard solution A into a 100-ml graduated flask, dilute to the mark with water and mix.

1 ml of standard solution B $\equiv$ 100 μg of chromium.

Transfer aliquots of 0·1, 0·2, 0·4, 0·6, 0·8, 1·0, 1·2 and 1·3 ml of standard solution B to covered 25-ml beakers. The aliquots contain 10, 20, 40, 60, 80, 100, 120 and 130 μg of chromium, respectively. Continue as described under Procedure. Plot the optical densities against micrograms of chromium to obtain the calibration graph.

ARSENIC

REAGENTS—

Use high purity reagents when possible.

Ammonium molybdate solution—Dissolve 1 g of ammonium molybdate in 80 ml of water containing 14 ml of concentrated sulphuric acid and dilute to 100 ml with water.

Hydrazine sulphate solution—Dissolve 0·15 g of hydrazine sulphate in water and dilute to 100 ml with water.

Ammonium molybdate - hydrazine reagent solution—Just before use mix 10 ml of ammonium molybdate solution and 10 ml of hydrazine sulphate solution, and dilute to 100 ml with water.

PROCEDURE—

Transfer the weighed sample to a covered 50-ml beaker and add 20 ml of reagent solution. Warm the solution on a steam-bath until the blue reduction complex appears, and then continue heating for 15 minutes. Cool the solution, wash it into a 25-ml graduated flask, dilute to the mark with reagent solution, and mix. Measure the optical density of the molybdenum-blue complex against a reagent blank, prepared in a similar way, in 10-mm cells at wavelength 840 nm on a Unicam SP 600 spectrophotometer. To obtain the arsenic content in the test solution, compare the spectrophotometer reading with a calibration graph.

CALIBRATION—

Preparation of standard solution A—Dissolve 1·3203 g of arsenic trioxide in a minimum volume of N sodium hydroxide solution. Transfer the solution to a 1-litre graduated flask, dilute to the mark with water and mix.

1 ml of standard solution A $\equiv$ 1000 μg of arsenic.

Preparation of standard solution B—Transfer, by pipette, 10 ml of standard solution A, with suitable precautions, into a 100-ml graduated flask, dilute to the mark with water and mix.

1 ml of standard solution B $\equiv$ 100 μg of arsenic.

Transfer aliquots of 0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7 and 0·8 ml of standard solution B to 50-ml beakers. The aliquots contain 10, 20, 30, 40, 50, 60, 70 and 80 μg of arsenic, respectively. To each beaker, add 2 ml of concentrated nitric acid and 1 ml of 50 vol hydrogen peroxide and evaporate the solution just to dryness. Add 1 ml of concentrated nitric acid, evaporate the solution to dryness and heat the residue for 30 minutes at a temperature not exceeding 130° C. Continue as described under Procedure. Plot the optical densities against micrograms of arsenic to obtain the calibration graph.

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Measurement of the Oxygen Content of Cider and Fruit Juices

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A method is described for measuring the dissolved oxygen content of non-carbonated samples under nitrogen at atmospheric pressure by using the Clark electrode. For carbonated samples the determination must be carried out at 30 p.s.i. nitrogen pressure to prevent loss of dissolved oxygen. A method is also described for measuring the oxygen content of the headspace gas in either carbonated or non-carbonated products.

THE importance of dissolved oxygen in the production of beer,[1,2] wines[3,4] and fruit juices[5,6,7] is well recognised and various methods have been proposed for determining the dissolved oxygen content. The introduction of the Clark[8,9] electrode marked a big advance in this field; it is simple to operate and readily adaptable for use under various conditions. The mechanism and factors affecting the performance of this electrode have been described by Kinsey and Bottomley,[10] who also emphasise the distinction between oxygen concentration and oxygen tension (*i.e.*, partial pressure).

Several versions of the Clark electrode are available commercially; the one used in the present experiments was the Beckman oxygen analyser (No. 777), which has the advantage of a 5-fold magnification for reading low levels of dissolved oxygen. The instrument consists essentially of a gold cathode and silver anode, with a gel of potassium chloride electrolyte and a thin polytetrafluorethylene ("Teflon") membrane protecting the electrodes from direct contact with the sample.

The Teflon is permeable to oxygen, and the response of the cell depends on the amount of oxygen penetrating the membrane, which is determined by the partial pressure of oxygen in the sample. Because of this, the cell gives the same response in free air as in air-saturated water. It is convenient, therefore, to calibrate the instrument by exposing the electrode to air and to express subsequent measurements of dissolved oxygen content in terms of percentage saturation. To convert these results into parts per million of dissolved oxygen, they must be multiplied by the solubility of oxygen, representing 100 per cent. saturation with air at atmospheric pressure, in the particular medium at the temperature of measurement.

For comparative purposes and routine testing it is usually assumed that the solubility of atmospheric oxygen in a juice or cider is the same as it would be in water. Kielhöfer and Würdig[11] showed that this was a close approximation for table wines, because of the opposing effects of alcohol increasing the solubility, and of soluble solids decreasing it. The same would be true for a dry cider but, with sweet ciders and fruit juices, the effect of sugars would predominate to decrease the solubility of oxygen in the sample. When the concentration of oxygen must be known accurately, the solubility of oxygen in air-saturated juice or cider can be determined polarographically, the polarograph being calibrated with a solution standardised by Winkler titration. The validity of this procedure was shown by Rentschler and Tanner,[12] who found that polarographic determination of the solubility of atmospheric oxygen in grape juice agreed with Winkler determinations on sucrose solutions of the same specific gravity. Winkler titrations cannot be used directly with juices because of interference from juice constituents.

Certain precautions must be observed when measuring dissolved oxygen with the Beckman oxygen analyser. It is essential that the sample should be stirred vigorously to prevent the formation of a gradient of oxygen concentration at the surface of the Teflon film; the tip of the electrode must be free from adhering bubbles, and it should be mounted in such a way that it can be inspected when readings are being taken; great care is needed when handling samples to avoid contact with air.

These conditions are fulfilled in the two procedures described below, which were developed for measuring the dissolved oxygen content of ciders and fruit juices at different stages of processing up to, and including, the final bottled product. A third procedure is described for collecting and measuring the oxygen content of the headspace gas from a bottled sample.

MEASUREMENT OF DISSOLVED OXYGEN AT ATMOSPHERIC PRESSURE—

It is convenient to collect the sample of cider or juice by siphoning it into a bottle previously filled with nitrogen. The bottle should be sealed with a minimum of headspace and the contents analysed for dissolved oxygen without delay.

The electrode vessel consists of a 250-ml conical flask with a B19 socket joint in the side, near the base. The Beckman oxygen sensor is fitted into this tapered socket with a sleeve of rubber tubing, so that the tip of the electrode is at the circumference of the flask.

Before use the apparatus is standardised to read 100 per cent. saturation with the electrode exposed to air. The blank reading (zero current) is then determined by passing nitrogen into the flask via the arrangement of tubes and T-piece shown in Fig. 1; the electrode should be loosened temporarily to allow nitrogen to flow out through the socket.

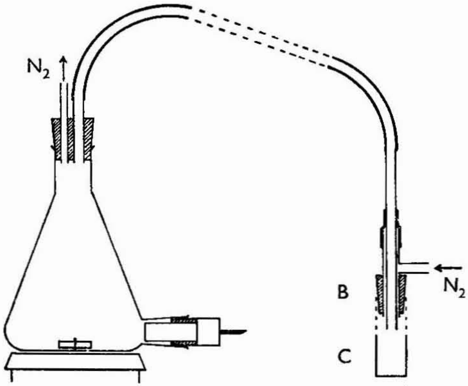

Fig. 1. Apparatus for determinations in non-carbonated samples: B, bung; and C, cap

When a sufficiently low blank reading has been obtained (less than 2 per cent. saturation) the cap, C, is removed from the bung, B, which is then fitted into the neck of the sample bottle, allowing the nitrogen flow to sweep out the headspace of the bottle before final closure.

With the nitrogen stream still flowing, the sample bottle is raised and tipped so that its contents run into the electrode flask, filling it up to the neck to give a minimum exposure of liquid surface. The flow of nitrogen should now be shut off, or greatly reduced.

The contents of the flask are stirred rapidly with a magnetic stirrer, and the tip of the electrode should be examined to ensure that the Teflon film is not obscured by adhering bubbles. A stable meter reading is usually obtained in a few seconds. The previously measured blank is subtracted from the observed reading to give the dissolved oxygen in terms of percentage saturation. If this is to be converted into concentration of oxygen, the temperature of the sample must also be recorded.

The following results are quoted as an example of the use of the method to follow the disappearance of dissolved oxygen in apple juice (by oxidase activity). The freshly pressed juice was oxygenated by shaking in air in a flask and then transferred to the conical electrode vessel.

Time, minutes	Saturation, per cent.	Dissolved oxygen, p.p.m.
3	44	4·1
5	34	3·1
7	24	2·2
9	17	1·6
10	13	1·2
12	7·8	0·7
15	3·8	0·3
90	1·6	0·1

All measurements were made at 20° C, at which temperature the solubility of atmospheric oxygen (in water) is 9·2 p.p.m.

A further example shows the uptake of oxygen by a perry during sweetening and filtering prior to bottling. (Measurements at 17° C; solubility of atmospheric oxygen, 9·7 p.p.m.)

	Saturation, per cent.	Dissolved oxygen, p.p.m.
Perry in storage vat	5·4	0·5
Pumped to blending vat and sweetened ..	12·6	1·2
Filtered into tank for bottling	15·6	1·5

This procedure gives stable and reproducible results with normal "still" samples, but with carbonated products the bubbles of carbon dioxide, released by stirring, frequently adhere to the electrode. The meter readings are erratic, decrease progressively, and do not become stable until most of the carbon dioxide has been stirred out of solution. The final value, however, is much lower than it should be because of the removal of dissolved oxygen with the carbon dioxide evolved. This is illustrated by the following results obtained on duplicate bottles of carbonated perry analysed (*a*) under pressure (as described below), (*b*) at atmospheric pressure after loss of most of the carbon dioxide, and (*c*) after longer stirring; the temperature was 20° C.

	Saturation, per cent.	Dissolved oxygen, p.p.m.
(*a*)	44, 46	4·0, 4·2
(*b*)	18, 13	1·7, 1·2
(*c*)	8, 7	0·7, 0·6

It is essential, therefore, to prevent the escape of carbon dioxide by carrying out the determination under pressure.

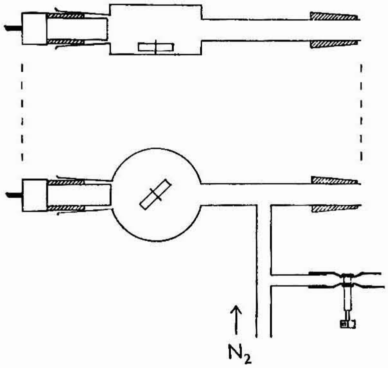

Fig. 2. Electrode vessel for determinations in carbonated samples

MEASUREMENT OF DISSOLVED OXYGEN UNDER PRESSURE—

The electrode vessel (Fig. 2) has a flat cylindrical shape, about 2 inches in diameter and 1 inch deep, with a B19 socket for the electrode and a wide tube ($\frac{1}{2}$ inch o.d.) with a rubber bung, by which it is attached to the sample bottle. Nitrogen enters this tube via a side-arm, which also carries a T-piece. As before, the electrode is sealed into the socket with a sleeve of rubber tubing.

Before use, the electrode is standardised in air in the usual way. The electrode vessel is then swept out with nitrogen, the rubber bung being loosely covered with a cap while the gas is allowed to escape past the electrode, which is temporarily loosened in its socket. When a sufficiently low zero-current reading is obtained, the electrode is made firm and the loose cap removed to allow the nitrogen to escape via the bung. The sample bottle is now opened and the electrode vessel attached to it, briefly allowing the gas-flow to sweep out the headspace of the bottle before tightening the bung firmly. The bottle and electrode vessel are clamped securely in a retort stand and the electrode itself held in its socket by a clip or bracket extending from the stand. The nitrogen pressure is increased to prevent the escape of carbon dioxide from the sample (about 30 p.s.i. is needed for products containing 2 to 2$\frac{1}{2}$ volumes of carbon dioxide). The nitrogen supply is then clipped off and the retort stand is inverted to allow the sample to flow into and completely fill the electrode vessel. No bubbles of carbon dioxide will be formed if the nitrogen pressure exceeds the carbonation pressure. The stand is now supported horizontally with the electrode vessel lying on the plate of the magnetic stirrer. The sample is stirred rapidly and the electrode surface checked for the absence of bubbles when the meter reading is taken. The zero current is subtracted from the observed reading to obtain the percentage saturation with dissolved oxygen.

To remove the bottle, the stand is returned to the vertical position and the sample drained back into the bottle; the gas pressure is released via the clip on the T-piece. A slow stream of nitrogen is now admitted to the electrode vessel so that it can be removed from the bottle without the entry of air. If this is done, the electrode vessel can be attached immediately to another bottle for further readings.

Certain practical points may usefully be mentioned.

The volume of the electrode vessel should be as small as conveniently possible, especially if it is to be used with small bottles, *e.g.*, 4 fluid oz.

Some slight loss of dissolved oxygen undoubtedly occurs as the sample flows from the bottle into the electrode vessel; the sample is in fact being extracted with oxygen-free nitrogen. Obviously the transference should be made with minimum of turbulence and repeated transfer should be avoided.

The apparatus can also be used without pressure for non-carbonated samples, but is less convenient for this purpose than the conical-flask electrode vessel previously described.

MEASUREMENT OF OXYGEN IN THE HEADSPACE GAS—

If the dissolved oxygen content of a bottled product is to be controlled it is important also to minimise the air in the headspace of the bottle, as the gaseous oxygen will ultimately go into solution. Thus, 1 ml of air dissolved in 100 ml of cider will yield 3 p.p.m. of dissolved oxygen. In practice, the oxygen does not dissolve completely, but distributes itself between the gaseous and liquid phases.

The relationship between gaseous and dissolved oxygen in a bottled product can be calculated theoretically. Consider a bottle containing V ml of cider and v ml of headspace where the gaseous oxygen is in equilibrium (at 20° C) with oxygen in solution.

(*i*) The oxygen in the headspace gas can be determined experimentally and calculated as the equivalent volume of air (x ml) at 760 mm and 20° C.

(*ii*) The concentration of dissolved oxygen in the cider is then proportional to the partial pressure of the oxygen in the headspace and is given by

$$9{\cdot}2 \times \frac{x}{v} \text{ p.p.m.}$$

where the solubility of oxygen in air-saturated cider at 760 mm and 20° C is assumed to be 9·2 p.p.m. (as for water).

Note—This calculation is unaffected either by the volume of cider or by the carbonation pressure. The ratio $\frac{x}{v}$ represents the concentration of air in the headspace gas.

(*iii*) The actual amount of oxygen dissolved in V ml of cider is given by

$$9{\cdot}2 \times \frac{x}{v} \times \frac{V}{1000} \text{ mg of oxygen.}$$

(*iv*) The amount of oxygen in x ml of air in the headspace gas at 20° C is given by

$$x \times 0{\cdot}209 \times \frac{32}{22{\cdot}4} \times \frac{273}{293}$$
$$= x \times 0{\cdot}278 \text{ mg of oxygen.}$$

(*v*) Thus the distribution of oxygen between the headspace gas and the cider is determined by the volumes v and V (at a given temperature, 20° C), and

$$\frac{\text{headspace oxygen}}{\text{dissolved oxygen}} = \frac{0{\cdot}278x}{9{\cdot}2x} \times \frac{1000v}{V}$$
$$= 30{\cdot}2 \times \frac{v}{V}.$$

Thus, if a bottle contains 302 ml of cider and 10 ml of headspace, the oxygen is equally distributed between gaseous and dissolved states.

The oxygen content of the headspace gas in a bottle sealed with a "crown-cork" can be measured with the Beckman headspace sampler incorporating a Clark electrode. This apparatus, originally designed for use with canned products, has been criticised, and modifications have been suggested.[13] In the absence of this apparatus, or if the closures of the bottles are unsuitable, the following method of collecting and measuring the headspace gas can be used.

The headspace gas in a bottle of carbonated beverage may occupy a volume of between 5 and 10 ml at a pressure of about 30 p.s.i. Thus the volume, when collected at atmospheric pressure, would be about 15 to 30 ml. To determine the amount of oxygen in the headspace gas it is necessary to measure both its volume and oxygen content, at atmospheric pressure. In addition to the Beckman oxygen analyser, other items required are a large tank of water (at least 15 × 12 × 9 inches deep), a reduction adaptor B34 to B19 (Quickfit and Quartz Ltd.), a 50-ml graduated cylinder and a 4-inch diameter glass funnel with its stem cut short and closed with rubber tubing and a screw clip.

The electrode is first standardised to read 21 per cent. of oxygen in air and its blank determined in pure nitrogen. It is fitted into the B19 socket of the adapter under water and is then suspended in the tank in such a way that no air is present within the electrode vessel.

The headspace gas can now be collected by opening the bottle under water and allowing the bubbles to rise into the inverted funnel. From here the gas is transferred into the inverted cylinder, by opening the screw clip. A rubber band is placed round the cylinder to mark the gas level so that the volume can be read more easily (when the cylinder is finally removed from the tank).

To measure the oxygen content of the gas a portion of it must be transferred from the cylinder into the bell of the electrode vessel. A little care is needed to ensure that the electrode tip is not covered by a hanging droplet of water, but the Teflon film does not wet so that drops are easily shaken off. A meter reading can now be taken and, when corrected for the zero current, gives the percentage of oxygen in the gas samples. As the total volume of the headspace gas has been measured, the actual volume of oxygen present, or its equivalent as air, can be calculated. The whole process should be carried out as rapidly as possible to minimise any gaseous exchange during manipulation of the sample under water. A small error in measuring the volume of the gas, *e.g.*, that caused by carbon dioxide dissolving in the water, does not greatly affect the final estimate of dissolved oxygen, but the accuracy of the method is necessarily limited by such practical considerations.

In certain samples, particularly uncarbonated juices transferred while hot into the bottle, the volume of headspace gas at atmospheric pressure is too small to be handled and measured as described above. For such samples, a suitable volume (5 to 10 ml) of nitrogen is first bubbled into the inverted funnel before collecting the headspace gas. The latter is then diluted with this nitrogen to facilitate manipulation. Tests of this procedure by adding 1-ml volumes of air to known volumes of nitrogen have given recoveries of 94 to 106 per cent.

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A Metabolite of *Macrophomina phaseoli* (Maubl) Ashby, with Thin-layer Chromatographic Behaviour Similar to that of Aflatoxin B

BY P. C. CROWTHER

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A metabolite of the fungi *Macrophomina phaseoli* has been found to have similar thin-layer characteristics on Kieselgel G Merck to that of aflatoxin B. A simple method is described for differentiating the *Macrophomina* metabolite from that of the *Aspergillus flavus* metabolite aflatoxin B.

IN 1965–66, a study carried out in the Gambia of the incidence of aflatoxin in groundnuts demonstrated an apparently high aflatoxin B contamination, as determined by conventional chemical assay procedures.[1,2] In these methods, the closely related aflatoxins, B_1 and B_2, are not separated but appear as a single spot, referred to as aflatoxins B throughout this paper.

Many of the groundnut samples tested were found to be infected with two fungi, *viz.*, *Macrophomina phaseoli* (Maubl) Ashby and *Botryodiplodia theobromae* Pat., which cause the common condition known as "black nuts."

Conventional aflatoxin analysis carried out on these black groundnuts revealed a compound that appeared at a similar position to the aflatoxins B on Merck Kieselgel G chromatoplates when using a developing system of 5 per cent. of methanol in chloroform. Like the aflatoxins B, this compound fluoresced bright blue under ultraviolet light (365 nm).

Examination of the extracted media from pure cultures of the two fungi showed that only *M. phaseoli* produced metabolites exhibiting a thin-layer pattern similar to that of the infected nuts.

Groundnuts infected with *M. phaseoli* contain, in addition to the blue fluorescent compound, a metabolite fluorescing strongly green under ultraviolet light. These metabolites were not toxic to mice or ducklings (P. C. Crowther, M. O. Moss and Mrs. M. Rose, Tropical Products Institute, unpublished results). Consequently, it was suspected that the aflatoxin-like fluorescence noted was attributable to another compound.

It was found that aflatoxin and the new blue compound were readily separable by a simple procedure with thin-layer chromatography. As the metabolite with a green fluorescence was always found on material infected with *M. phaseoli*, extracts yielding a green fluorescence at an R_{F} value of 0·6 to 0·75 were re-examined by developing the chromatoplate in a tank containing diethyl ether. The blue and green compounds reached R_{F} values of 0·9 and 1·0, respectively, while aflatoxin did not move appreciably from its original position. Table I gives the R_{F} values of aflatoxins B and the two main metabolites of *M. phaseoli*.

TABLE I

R_{F} VALUES ON 500-μ THICK KIESELGEL G (MERCK) THIN-LAYER CHROMATOPLATES

	Aflatoxins B (metabolites of *Aspergillus flavus*)	Metabolites of *M. phaseoli*	
Developing systems		Blue fluorescence	Green fluorescence
Methanol (2 per cent.) in chloroform	0·24	0·20	0·62
Methanol (5 per cent.) in chloroform	0·45	0·40	0·75
Acetone (10 per cent.) in chloroform (commonly used in aflatoxin assays)	0·40	0·40	0·75
Diethyl ether	0·05	0·75	0·98
Methanol (5 per cent.) in chloroform, followed by diethyl ether, R_{F} value relative to ether front	0·50	0·90	1·00

From Table I it will be seen that there is a risk of confusing the blue *Macrophomina* compound with aflatoxins B. To eliminate this risk, plates apparently aflatoxin-positive, and showing a green ultraviolet fluorescence near the solvent front, should be re-developed in diethyl ether. Blue fluorescent spots that reach a high R_F value are definitely not aflatoxin.

Many other foodstuffs, such as maize, sunflowerseed meal, cocoa and cassave have been found to be naturally infected with *M. phaseoli*. The thin-layer patterns obtained from these extracted foodstuffs were similar to those obtained from infected groundnuts.

Thanks are given to G. Gilman, formerly Plant Pathologist, Department of Agriculture, the Gambia, now at the Tropical Stored Products Centre, Slough, for the provision of pure cultures of the fungi, also to the Director of this Institute for his permission to publish this paper.

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Book Reviews

ASPECTS OF ANALYTICAL CHEMISTRY. By R. A. CHALMERS, B.Sc., Ph.D., F.R.I.C. Pp. viii + 144. Contemporary Science Paperbacks 19. Edinburgh and London: Oliver & Boyd. 1968. Price 7s. 6d.

This little book comes along at an opportune time when there is much interest in analytical chemistry amongst students in the universities and technical colleges of this country. The breakaway from exclusive use of balance, beaker and burette, which has characterised analytical chemistry recently, has revealed it to be one of the most exciting and diversified areas of study and research available in modern chemistry. Not only are all the techniques of modern inorganic, organic and physical chemistry used, but also many of those of physics and the biochemical sciences. What is more, these techniques are used to good practical purpose. These are undoubtedly some of the thoughts that underlie the production of this book and that will become apparent to readers, particularly student readers.

The subject matter is divided into chapters entitled General Principles, Classical Methods, Spectroscopic Methods, Methods using Radioactive Emission, Electrochemical Methods, Separation Methods and Automation. There is a selected list of books for further reading, a list of references and a subject index. Naturally, the author has had to select his coverage of material carefully because of the limitations imposed upon him by the space available in a book such as this. Although the reviewer does not altogether agree with the balance struck between the individual sections, this is a subjective choice. I personally would have preferred to have seen less attention paid to the classical aspects and more to the modern "key" methods that are more representative of the modern analytical scene. However, having said this, it must be borne in mind that the author's title is "*Aspects* of Analytical Chemistry," and that he has deliberately chosen some in preference to others. Many modern text-books do indeed cater rather well for these "key" techniques, but my feeling is that they do so in a highly specialised way and in great depth.

The author has painted a fairly panoramic picture of analytical chemistry with particularly good brushwork in the classical techniques and general principles areas. The style is lucid and the text is pleasant to read, and is well illustrated with diagrams and tabular presentation of data. The author stamps it with a refreshing image of his own personality and his views on many issues. It is a book that all students should read for general information and oversight of the area of modern analytical chemistry. It makes an excellent complement to the late H. N. Wilson's "Approach to Analytical Chemistry." The latter is written by an industrial analytical chemist and, not unnaturally, pays more attention to the applied aspects of modern instrumental techniques. Both books really deserve to be read in sequence.

Undoubtedly, Dr. Chalmers has performed an outstanding service to analytical chemistry in presenting us with this fine paperback. I hope that it will be as widely read as it deserves to be by students and by general readers. Few books make more interesting reading.

T. S. WEST

HANDBUCH DER ANALYTISCHEN CHEMIE. Edited by W. FRESENIUS and G. JANDER. Part 3. Band VII$\alpha\beta$. ELEMENTE DER SIEBENTEN HAUPTGRUPPE. II. CHLOR, BROM, JOD. By PROFESSOR DR. A. OTTO GÜBELI. Pp. viii + 614. Berlin, Heidelberg and New York: Springer-Verlag. 1967. Price (paper) DM 163, $40.75; (bound) DM 168, $42.00.

This volume of the Handbuch contains full details of the quantitative analytical chemistry of chlorine, bromine and iodine.

The first section (305 pp.) deals with chlorine, and the chloride, hypochlorite, chlorate and perchlorate ions. All types of method, gravimetric, titrimetric, colorimetric, electrometric, radiometric, etc., are described as well as many separation procedures. Moreover, full details are given for the quantitative analysis of materials such as air, water, organic compounds, plastics, insecticides, oils, biological substances, metals and glasses. Virtually every aspect of the quantitative analysis of anything containing chlorine atoms in any form is covered with full experimental procedures; the literature is referenced up to 1963.

In the second section (218 pp.), the determination of bromine and bromine-containing ions, and the analysis of materials containing them, are dealt with in a similar fashion. In the third section (79 pp.), which covers iodine and iodine-containing ions, the treatment is less exhaustive. The methods for the determination of the various ions are given in detail, but the author has, understandably, quailed before the prospect of listing the multitudinous applications to various materials.

As is customary in the Handbuch, the treatment is comprehensive and uncritical. Perhaps it is too detailed, for experimental detail is given for practically every method mentioned. In most cases, procedures differing in only minor detail and those based on extravagant flights of imagination, would have been better dismissed in a sentence or two.

This is a book that could not have been written by three authors without a vast amount of repetition, yet the welter of methods available for the halogens and their ions makes their compilation barely within the compass of a single author. Professor Gübeli is to be congratulated on his fortitude and organisational techniques. The volume is indispensable for analytical reference libraries.

A. M. G. MACDONALD

HANDBUCH DER ANALYTISCHEN CHEMIE. Edited by W. FRESENIUS and G. JANDER. Part 3. Band IVaα. ELEMENTE DER VIERTEN HAUPTGRUPPE. I. KOHLENSTOFF, SILICIUM. By H. GRASSMANN and W. PRODINGER. Pp. xxiv + 563. Berlin, Heidelberg and New York: Springer-Verlag. 1967. Price (paper) DM 153, $38·25; (bound) DM 158, $39.50.

The greater part of this volume (443 pp.) is concerned with the determination of carbon and its important simple compounds, and has been written by H. Grassmann. The various chapters deal with carbon and carbides, simple hydrocarbons and ethylene oxide, carbon oxides, and, in the final chapter, COS, $COCl_2$ and analogous compounds, cyanide, cyanate, thiocyanate and formic, acetic and oxalic acids. All types of method seem to be listed. The author properly resists the temptation to become too far entangled with organic analysis; the organic compounds that he does deal with are those which tend to be badly neglected in conventional organic analysis texts.

The section on silicon, written by W. Prodinger, covers gravimetric, colorimetric and titrimetric methods in a straightforward fashion. In both parts, procedures are given not only for the pure substance or ion, but also for applications to very many materials.

As this reviewer has said of previous volumes, the coverage is exhaustive; in this volume the literature dates up to 1963. The entirely uncritical nature of these compilations does, however, become depressing; one yearns for some note of guidance, even some personal prejudice, about which of the various procedures of a particular type might be the most suitable for some mundane purpose. Here are the principles, the procedures and some notes for multitudes of methods, in sufficient detail for recourse to the journal literature to be almost unnecessary. The work involved merely in their collection is enormous and extremely valuable, so that it is perhaps too much to ask for some evaluation also.

Like the rest of the Handbuch, this volume should be available in all reference libraries and it would be particularly useful for laboratories without access to good library facilities.

A. M. G. MACDONALD

AUTOMATIC DISPENSING PIPETTES. Scientific Report No. 3. An Assessment of Thirty-Five Commercial Instruments. Pp. 27. Association of Clinical Biochemists. 1967. Price 10s. (7s. 6d. to members of A.C.B.).

Obtainable from Mr. J. T. Ireland, Biochemistry Laboratory, Alder Hey Children's Hospital, Liverpool 12.

As laboratory workers learned from their post-war experiences, if apparatus was available commercially, it was, in the long run, cheaper to buy it than to make it with their own unskilled hands, and, as manufacturers of scientific equipment flourished as never before, the more discerning laboratory chiefs began to spend an unprecedented amount of time selecting the best buy from the range of equipment offered. It was against this background that the Association of Clinical Biochemists set up its Scientific and Technical Committee to simplify and to ensure a more satisfactory outcome to these decisions. The result has been (amongst other things) a most valuable series of Technical Bulletins and a shorter series of Scientific Reports, of which this is the third to appear. Most are still available and are listed in this Report.

The automatic dispensers tested include 6 based on a pipette; 19 syringe pipettes, of which 11 do not have a fixed reservoir; 5 double-action pipettes, and 5 more elaborate instruments designed to be operated electrically. Speed of operation may be of importance when many deliveries are to be made and the instruments vary from 2 to 30 seconds in the time they take to deliver 5 ml. Of greater importance is the accuracy and precision of the deliveries and, in instruments designed to be used for a range of volumes, the extent to which a particular volume can be reproduced after a change in the setting. These have been examined, and for the latter measurement it is useful to know that a 5-ml volume can, in most instances, be set with a coefficient of variation of less than 1 per cent., but for 5 instruments this value lay between 1·1 and 5·3 per cent. The error in actually delivering 5 ml exceeded the class B tolerance in 12 instruments, and the mean error in the worst was over 0·2 ml. Tests were made on instruments delivering between 0·5 and 10 ml.

The testing committee lists the faults they encountered, such as breakages in transit, and report the response of manufacturers to their complaints. The question of guarantee is mentioned and the electrical safety of the more complex instruments discussed. Finally, 6 pipettes "considered sufficiently precise and easy to use" are listed.

The value of such a comprehensive and carefully executed study is immediately apparent, and laboratory chiefs can hardly afford to be ignorant of its findings. Others may be concerned to learn, if they have not yet tested them, the limitations of the instruments already in use.

All of these instruments cost less than £75 and were bought specially for this study. The Ministry of Health is to be applauded for this service to many outside hospital laboratories, and it is hoped that they will continue their support when the Association of Clinical Biochemists wishes to make similar studies of more costly instruments in everyday use. D. N. RAINE

NON-DESTRUCTIVE NEUTRON ACTIVATION ANALYSIS OF BIOLOGICAL MATERIAL. By M. RAKOVIČ. Pp. 101. Prague: Acta Universitatis Carolinae Medica. Monograph 28 (in English). 1967. Price 20 Kčs.

This monograph, which somewhat resembles a Ph.D. thesis, describes the determination of sodium, potassium and phosphorus in biological material by neutron activation followed by simple β- or γ-counting. The author gives full practical details of techniques for avoiding mutual interference when counting mixtures of sodium-24, potassium-42 and phosphorus-32, and concludes that while sodium-24 and phosphorus-32 can be determined by direct counting of the activated sample, potassium must be separated chemically to obtain reliable results. There is a useful nomograph for correcting counts from sodium-24 in the presence of potassium-42, and a section describing how the precision (not the accuracy, as in the text) of activation analysis can be evaluated.

The work will be useful for chemists and biochemists engaged in determining these three elements by neutron activation. It lacks any reference to competing techniques, such as flame photometry and atomic-absorption spectrometry, which are commonly used for determining sodium and potassium today. In addition, the only references given subsequent to 1964 are to the author's own work, and several references in the text are not listed in the bibliography.

H. J. M. BOWEN

RADIOMETRIC TITRATIONS. By T. BRAUN and J. TÖLGYESSY. Translated by I. FINÁLY. General Editors R. BELCHER and L. GORDON. Pp. x + 168. Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris and Braunschweig: Pergamon Press. 1967. Price 55s. *International Series of Monographs in Analytical Chemistry. Volume* 29.

Radiometric titration methods in which the radioactive tracer is added to the titrant or to the solution to be analysed, sometimes to both, depend on the measurement of radioactivity for the location of the end-point. The main practical problem is the separation of excess of reactants from the reaction product for the measurement of the radioactivity of either, or both, fractions. And on the effectiveness of this separation depends the success of the titration. It is straightforward in methods based on precipitation reactions and those involving the use of solid radioactive indicators, as filtration can be used. For methods based on complex formation, in which reactants and products remain in the same phase, recourse must be had to solvent extraction or ion exchange.

The authors aim, by writing this book, to ensure an objective evaluation of a topic that they consider has not received the attention it warrants in monographs and reviews published during the last decade. They are well qualified to do this by their considerable contributions to the subject in recent years.

A theoretical discussion of the principles of the various methods is followed by a description in some detail, with diagrams or photographs of the apparatus used, of examples from the literature. It is doubtful, however, if there is always enough information to permit an objective evaluation of the utility of a method to be made, without reference to the original publications. Nevertheless, it is a valuable review of the present state of the art with an excellent bibliography. The translation is good and the book well produced. It is a valuable addition to the analyst's library.

D. A. LAMBIE

ANWENDUNG VON ISOTOPEN IN DER ORGANISCHEN CHEMIE UND BIOCHEMIE. Band I. Bestimmung der Isotopenverteilung in markierten Verbindungen. By H. SIMON and H. G. FLOSS. Pp. x + 247. Berlin, Heidelberg and New York: Springer-Verlag. 1967. Price DM 54: $13.50.

This volume on the determination of isotope distribution in labelled compounds is the first of a projected series of three. The second is to deal with isotope effects and the third with analysis.

The determination of the distribution of labelling, in labelled compounds, is so important in tracer work generally that it is (as the authors observe in their foreword) a little surprising that no attempt at an extended review of the subject has hitherto appeared. In preparing labelled compounds for metabolic researches, and even more widely in degrading metabolic products, chemical and biochemical reactions must be used to degrade molecules into fragments so that the position of the isotopic label may be quantitatively determined. It is commonplace knowledge that such reactions are hardly ever themselves quantitative. The widespread use of tracers has focused attention on this, as on other aspects of purity and analysis of organic compounds. And yet (setting aside exceptional situations in which direct physical methods may be used) these degradative reactions are the only means of finding labelling patterns. If the side reactions and by-products are overlooked, they may lead to completely erroneous conclusions; and unfortunately, one does not often have a thorough knowledge of the side reactions and by-products.

This is perhaps the most valuable aspect of Professor Simon's and Dr. Floss's book. It is a systematic exposition of general degradative reactions, methods of handling and measuring common small-molecular degradation products, and then general methods for the conventional chemical classes, such as carboxylic acids, hydrocarbons, alcohols and derivatives, aldehydes and ketones and carbohydrates, ending up with special groups and natural products such as isoprenoids, steroids, vitamins and alkaloids. The authors do not profess that their work is comprehensive, but they have, in fact, achieved a creditably wide coverage. They describe their work as a practical book, a collection of useful methods; to prompt the reader to select the best known methods, to improve on them, and to be on the look-out for pitfalls. Many practical methods for degradative reactions are given in brief, clear form and the generous provision of formulae (which are clearly set out) helps to make the book convenient in use. There are more than eight-hundred references to publications in the original literature, some of them as recent as 1966. There is a good subject index, and also a formulae index, and the reader with only a limited knowledge of German will be able to find his way about the book without much difficulty.

The authors deal only with the "statistical" and not with the "intramolecular" pattern of labelling. This is sensible as it is only very exceptionally that intramolecular labelling (referred to briefly on page 3) is significant for the user.

Even a superficial study of the book will alert the reader to the many known and documented sources of error in degradation reactions, and to the need for caution in making assumptions about any such reactions. Methods can often be checked by using known, authentic labelled samples and also, in a lesser degree, by careful quantitative study of the reactions used. These precautions have not been used often enough in tracer work generally, and the information and guidance given in "Bestimmung der Isotopenverteilung in markierten Verbindungen" will be particularly valuable.

As would be expected, most of the examples discussed deal with carbon-isotope labelling, but there is also much valuable information about tritium and deuterium. There is (as one would expect) very little about other tracer isotopes.

To conclude, this book meets a very real need, and should be in the hands of everyone working with labelled compounds as tracers. One can foresee that the authors will be called upon to produce updated revisions at suitable intervals. We may hope that they will indeed do so.

The printing and production are of the high standard that one has come to expect of such a publishing house as Springer-Verlag. J. R. CATCH

Errata

JUNE (1968) ISSUE, p. 358, 18th line. *For* "a standard error of the mean of ±1·0" *read* "a standard error of the mean of ±0·001."

AUGUST (1968) ISSUE, p. 554, 1st two lines under **Book Reviews**. *For* EXTRA PHARMACOPOEIA (MARTINDALE). Twenty-fifth Edition. Edited by R. G. TODD. Pp. xxviii + 1804. London: Pharmaceutical Press. 1967. Price 50s. *read* EXTRA PHARMACOPOEIA (MARTINDALE). Twenty-fifth Edition. Edited by R. G. TODD. Pp. xxviii + 1804. London: Pharmaceutical Press. 1967. Price 150s.

Summaries of Papers in this Issue

Inorganic Ion Exchange in Organic and Aqueous - Organic Solvents

A Review

SUMMARY OF CONTENTS

G. J. MOODY and J. D. R. THOMAS

Chemistry Department, University of Wales Institute of Science and Technology, Cathays Park, Cardiff, CF1 3NU, Wales.

Analyst, 1968, **93**, 557–588.

REPRINTS of this Review paper will soon be available from The Society for Analytical Chemistry, Book Department, 9/10 Savile Row, London, W.1, at 7s. 6d. per copy, post free.

A remittance for the correct amount, made out to The Society for Analytical Chemistry, MUST accompany every order; these reprints are not available through Trade Agents.

Polarographic Determination of Caesium in the Presence of Other Alkali Metals Based on Interaction with the Cinnamaldehyde Radical Anion

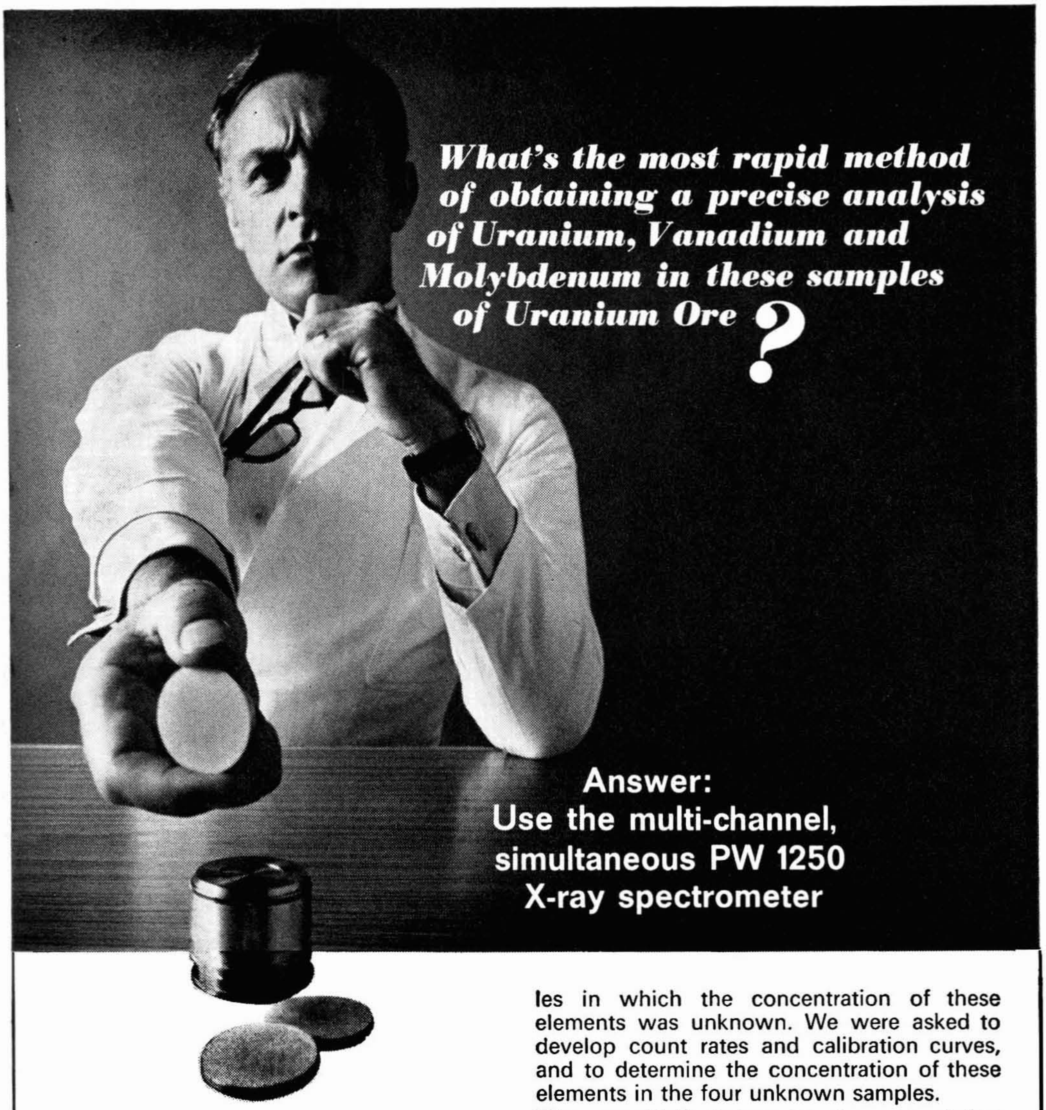
In this determination of caesium the wave i_M, corresponding to the reduction of a species formed by interaction of a cinnamaldehyde radical anion with alkali-metal ions, is measured. This wave appears in 0·1 M lithium hydroxide solutions between the first two one-electron reduction steps of cinnamaldehyde.

The height of this wave i_M increases with increasing alkali-metal concentration, and is most sensitive to caesium, which can be determined in the range 0·003 M to 0·1 M in the presence of less than 0·03 M rubidium, 0·05 M potassium and 0·1 M sodium, to within an accuracy of 5 per cent. The only observed interference was from short-chain tetra-alkyl ammonium cations.

D. BARNES and P. ZUMAN

Department of Chemistry, University of Birmingham, Birmingham 15.

Analyst, 1968, **93**, 589–594.



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Studies in the Analytical Chemistry of Selenium: Absorptiometric Determination with 2-Mercaptobenzoic Acid

Selenium(IV) forms a 1:3 complex with 2-mercaptobenzoic acid that shows maximal absorption at 268 nm in the pH range 0·5 to 2·5. The formation of the complex provides the basis of a rapid and sensitive method for the determination of selenium in the presence of a wide range of elements. When the complex is extracted into ethyl acetate, 22 of 36 other ions investigated do not interfere, even at 200-fold excess. The interference of the others, including tellurium, is readily overcome by a simple technique of total-ion exchange, by masking or by solvent extraction. Of the ions examined only mercury(II) still interferes.

The molar absorptivity of the complex at 268 nm is 15,600 and the sensitivity index 5×10^{-3} μg per cm^2. The complex is formed instantaneously and maintains an unchanging absorbance for over 2 hours. The method is suitable for the determination of selenium in the range 0·008 to 1·5 p.p.m. in aqueous solution.

M. S. CRESSER and T. S. WEST

Chemistry Department, Imperial College, London, S.W.7.

Analyst, 1968, **93**, 595–600.

The Purification of Commercial Alizarin Red S for the Determination of Aluminium in Silicate Minerals

Sephadex G-10 has been used to isolate sodium alizarin sulphonate from commercial samples of Alizarin Red S that contained variable and large amounts of inorganic salts. Aluminium in silicate minerals can be reliably determined with the purified reagent, which gives a linear response up to 180 μg of aluminium.

H. G. C. KING and G. PRUDEN

Rothamsted Experimental Station, Harpenden, Herts.

Analyst, 1968, **93**, 601–605.

The Extraction of Iron with Di-(2-ethylhexyl)orthophosphoric Acid, and its Direct Determination with Bathophenanthroline

A simple, direct determination of iron(III) extracted from chloride solutions with di-(2-ethylhexyl)orthophosphoric acid is described. Iron in the organic phase is first reduced with ascorbic acid, bathophenanthroline and pyridine are then added and the colour developed measured at 533 nm. With this procedure, which involves extraction of the iron with a phase-volume ratio of 1:1, an improvement on the already appreciable selectivity of other bathophenanthroline procedures is obtained.

Extremely small amounts of iron can be determined with satisfactory precision when extraction is carried out with an inorganic-to-organic phase-volume ratio of 100:1. Results for the determination of iron in high-pressure boiler water are reported.

E. CERRAI and G. GHERSINI

Laboratori CISE, Casella Postale 3986, 20100 Milano, Italy.

Analyst, 1968, **93**, 606–610.

The Chemical Analysis of Copper, Chromium and Arsenic Preservative-treated Wood

Methods are described for the rapid determination of copper, chromium and arsenic in preserved timber. These preserving compounds are leached from thin sections of wood with hydrochloric acid, sodium hydroxide and dilute sulphuric acid, respectively. Copper, chromium and arsenic are reacted with zinc dibenzyldithiocarbamate, diphenylcarbazide and ammonium molybdate - hydrazine reagent, respectively, and the determinations completed by spectrophotometric measurement of the coloured complexes formed.

The procedure is particularly useful for the study of the distribution, over small areas, of copper, chromium and arsenic-containing preservatives in wood.

A. I. WILLIAMS

Ministry of Technology, Forest Products Research Laboratory, Princes Risborough, Aylesbury, Bucks.

Analyst, 1968, **93**, 611–617.

Measurement of the Oxygen Content of Cider and Fruit Juices

A method is described for measuring the dissolved oxygen content of non-carbonated samples under nitrogen at atmospheric pressure by using the Clark electrode. For carbonated samples the determination must be carried out at 30 p.s.i. nitrogen pressure to prevent loss of dissolved oxygen. A method is also described for measuring the oxygen content of the headspace gas in either carbonated or non-carbonated products.

L. F. BURROUGHS

Long Ashton Research Station, University of Bristol.

Analyst, 1968, **93**, 618–622.

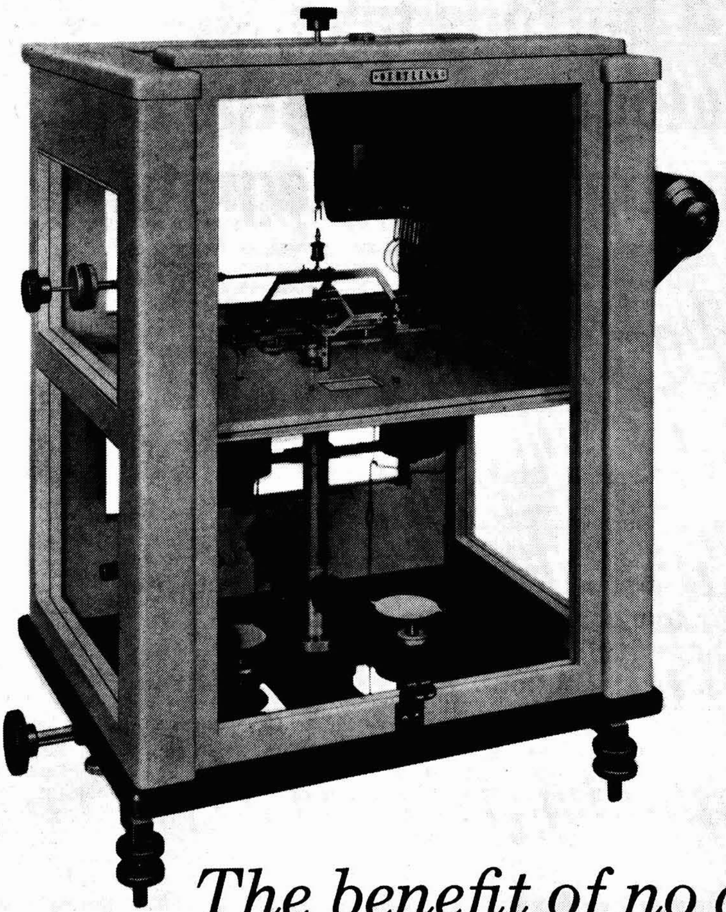
A Metabolite of *Macrophomina phaseoli* (Maubl) Ashby, with Thin-layer Chromatographic Behaviour Similar to that of Aflatoxin B

A metabolite of the fungi *Macrophomina phaseoli* has been found to have similar thin-layer characteristics on Kieselgel G Merck to that of aflatoxin B. A simple method is described for differentiating the *Macrophomina* metabolite from that of the *Aspergillus flavus* metabolite aflatoxin B.

P. C. CROWTHER

Tropical Products Institute, Ministry of Overseas Development, 56–62 Gray's Inn Road, London, W.C.1.

Analyst, 1968, **93**, 623–624.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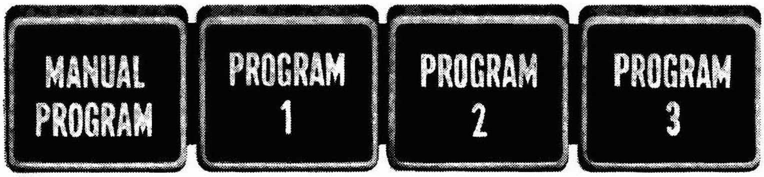

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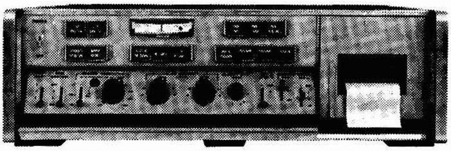

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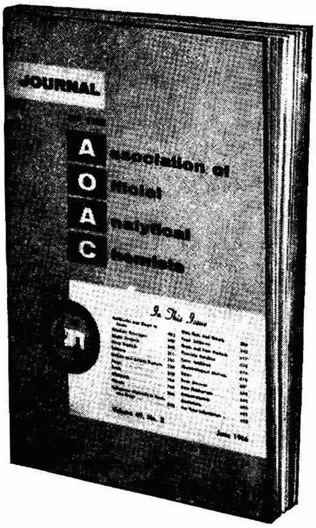
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General Medical Council

British Pharmacopoeia 1968

Publication: SEPTEMBER 4, 1968
Official in U.K.: MARCH 3, 1969

The British Pharmacopœia is published under the direction of the General Medical Council in accordance with the Medical Act 1956 and provides standards for the quality of substances and preparations used in medicine and pharmacy.

The British Pharmacopœia 1968 supersedes the British Pharmacopœia 1963 and the Addenda 1964 and 1966. It contains 1149 monographs, including 93 not in the previous edition.

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British Pharmacopœia 1968

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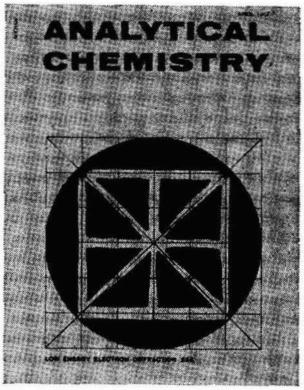
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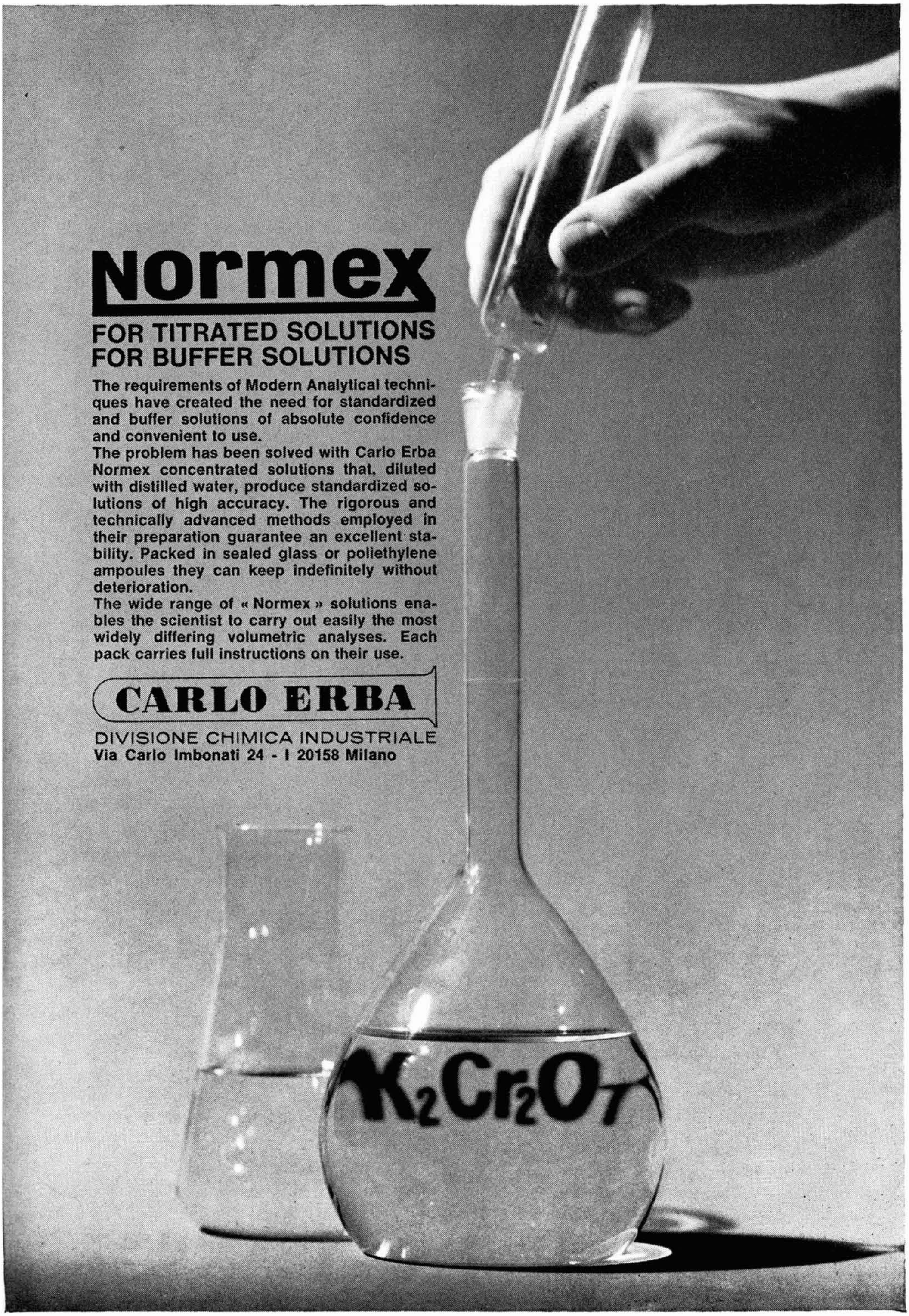

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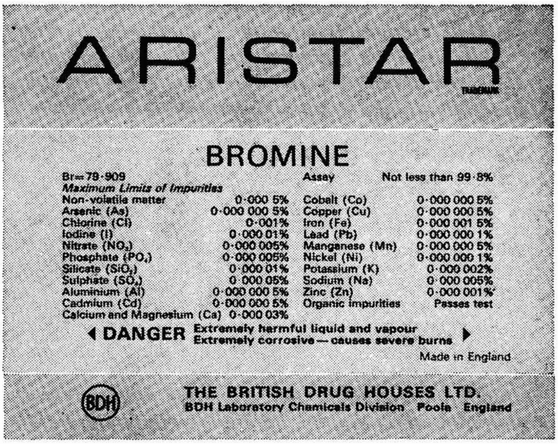

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Br = 79·909		Assay	Not less than 99·8%
Maximum Limits of Impurities			
Non-volatile matter	0·000 5%	Cobalt (Co)	0·000 000 5%
Arsenic (As)	0·000 000 5%	Copper (Cu)	0·000 000 5%
Chlorine (Cl)	0·001%	Iron (Fe)	0·000 001 5%
Iodine (I)	0·000 01%	Lead (Pb)	0·000 000 1%
Nitrate (NO_3)	0·000 005%	Manganese (Mn)	0·000 000 5%
Phosphate (PO_4)	0·000 005%	Nickel (Ni)	0·000 000 1%
Silicate (SiO_2)	0·000 01%	Potassium (K)	0·000 002%
Sulphate (SO_4)	0·000 05%	Sodium (Na)	0·000 005%
Aluminium (Al)	0·000 000 5%	Zinc (Zn)	0·000 001%
Cadmium (Cd)	0·000 000 5%	Organic impurities	Passes test
Calcium and Magnesium (Ca)	0·000 03%		

◀ **DANGER** Extremely harmful liquid and vapour
Extremely corrosive — causes severe burns ▶

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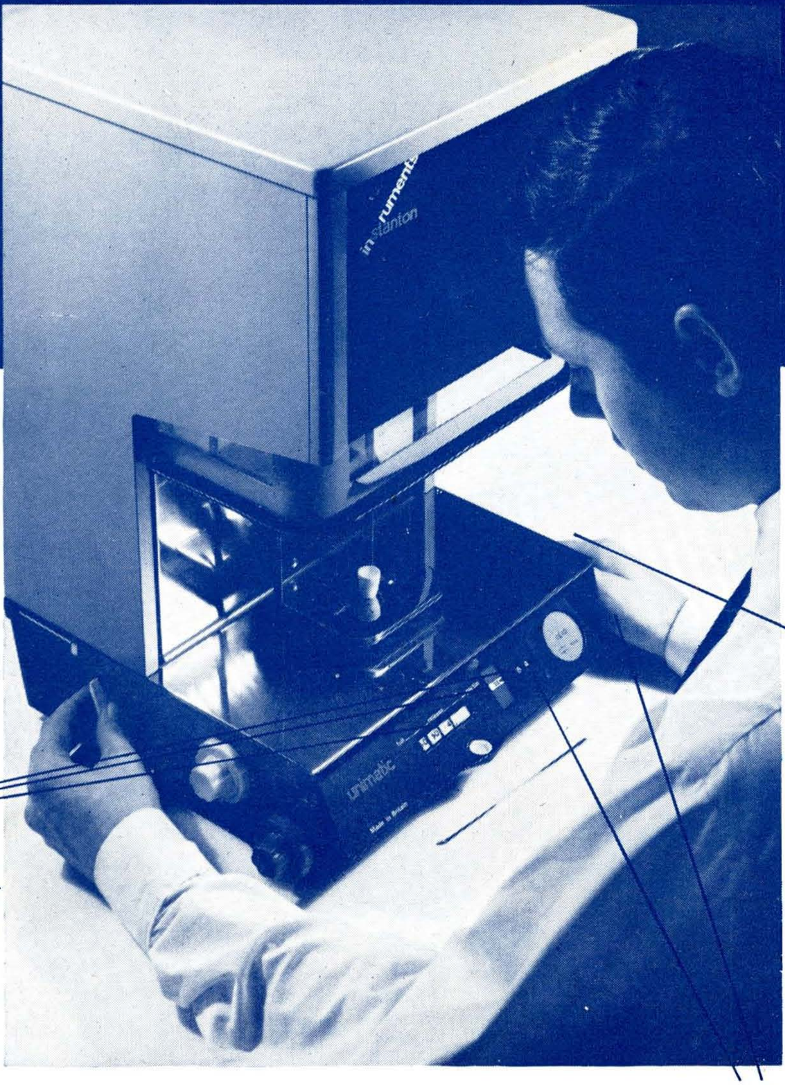
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