An International Journal of Analytical Chemistry

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ION EXCHANGE AND SOLVENT EXTRACTION OF METAL COMPLEXES

by **Y. Marcus** *and* **A. S. Kertes,** *both at the Department of Inorganic Chemistry, The Hebrew University of Jerusalem.*

This comprehensive work treats solutions of electrolytes in aqueous and non-aqueous solvents and complex formation in solution as a general background. On this basis it discusses ion exchangers and their role in complex chemistry, and solvent extraction of acids and metal complexes with various types of solvents, singly and in mixtures. It concludes with a comparative review of several illustrative systems, from a unified view of the two methods discussed.

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The Contents are as follows:-

Preface; Aqueous Solutions of Electrolytes; Non-aqueous Solutions of Electrolytes; Complex Formation in Solution; Ion Exchangers; Cation Exchange of Complexes; Anion Exchange of Complexes; Principles of Solvent Extraction; Extraction by Compound Formation; Extraction by Solvation; Extraction by Ion-pairing; Synergistic Extraction; Application of Distribution Methods; Appendices; Author Index; Subject Index.

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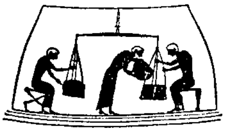

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TALANTA REVIEW

APPLICATIONS OF DIGITAL COMPUTERS IN ANALYTICAL CHEMISTRY—II*†

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(*Received* 30 *December* 1968. *Accepted* 14 *January* 1969)

Summary—This review deals with applications of digital computers to the evaluation of ionization constants of acids and bases, stability constants of metal complexes, concentrations of equilibrium mixtures, and the solution of rate equations. The use of computers permits systems of greatly increased complexity to be studied, and introduces additional methods of calculation such as numerical integration and Monte Carlo techniques.

EQUILIBRIUM CONSTANTS

Calculation of p*K* values from pH-titration or spectrophotometric data, by using the Henderson–Hasselbach equation, becomes difficult when species have two or more similar p*K* values. A further difficulty arises if the anions of the acids being titrated can form ionic complexes with the cations of the titrating base. Hamann and Johnson[1] allowed for this possibility when they solved species- and charge-balance equations, using a high-speed computer to calculate titration curves for weak dibasic acids. Roth and Bunnett[2] have described a computer programme for use in spectrophotometric determinations of overlapping p*K* values. They selected five well spaced points on the pH–absorbance curve, at a suitable wavelength, and used Thamer's method[3] in computing the absorbance of the three species and also the two p*K* values. The main disadvantage of this programme is that it uses only a few of the experimental results. An alternative approach utilizes all of the available data, including the limiting absorbances of two of the species, and, by orthogonal matrix transformations,[3a] evaluates the two p*K* values and the absorbance of the intermediate species, together with estimates of the standard deviations of these quantities.[4]

Neither of these programmes requires initial estimates of the desired p*K* values, and hence they are more convenient than the programme SWING described by Nagano and Metzler[5] which uses an iterative least-squares fit of the pH-absorbance curve to obtain the p*K* values. Another programme, PITMAP, is based on a treatment by Sillén and his co-workers.[6–9] In the "LETAGROP" or "pit-mapping" approach, the error-square sum function for the *n* variables in a system is defined as a "paraboloid in *n*-dimensional space", and the calculation is designed to seek the minimum, or "pit", in such a surface. This method works well if good initial guesses can be made at the values of the constants to be refined. Both SWING and PITMAP provide thorough tests of experimental data because they use all readings at up to 75

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* Pt. I. *Talanta*, 1969, **16**, 629.

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wavelengths (for up to three successive pK values), a final check including the comparison of computed and experimental absorption spectral curves.[5]

Computations of overlapping pK values from potentiometric titrations use similar programmes to those for the stepwise formation constants of metal complexes. Thus, Irani and Callis[10] used a non-linear least-squares computer programme to fit pH-titration curves of linear phosphoric acids and hence to obtain their successive pK values. The computations were based on a quantity, the average number of hydrogen ions associated with the anion, which is formally similar to Bjerrum's formation function. For this reason, it is convenient to discuss potentiometric methods for stability constants and pK values at the same time.

Since Bjerrum's pioneering work on metal ammine formation,[11] the methods of choice for evaluating stability constants have used relations involving the formation function, $\bar{n}$, and the free ligand concentration. The arithmetical calculations are tedious but not difficult, and computer programmes to give $\bar{n}$ and free ligand concentrations are straightforward. Similarly, the graphical technique of Irving and Rossotti[12] can be replaced by a least-squares treatment for obtaining stepwise formation constants of mononuclear complexes. Computers have been used in this way.[13,14] Datta and Grzybowski[15] calculated $\bar{n}$ and free ligand concentrations, then applied weighting factors and variances in a computer programme, based on a graphical method,[16] to obtain K_1 and K_2: computation of the theoretical titration curve, using these values, served as a check on the closeness of fit. The programme described by Unwin, Beimer and Fernando[17] applies only to simple systems in which the two mononuclear complexes ML and ML_2 are formed, and requires the prior calculation of $\bar{n}$ and free ligand concentrations. Another set of programmes[18] is based on the use of $\bar{n}$ and hence also seems to be limited to mononuclear and non-protonated complexes.

However, computers are capable of doing far more than this, and the recent tendency has been to develop more general programmes of greater mathematical complexity. Two papers serve as an introduction to this field. One of these concerns the general mathematical formulations necessary for the calculation of stability constants of complex ions,[19] and the other examines weighted least-squares methods using computers, for the same purpose.[20] Conventional methods of stability constant calculation, based on the use of $\bar{n}$, cannot be applied to systems containing protonated, hydrolysed or polynuclear metal complexes, because $\bar{n}$ cannot be obtained from the titration data. To overcome this difficulty, two main types of programme have been developed.

These employ Gaussian methods and "pit-mapping" as described above. Tobias and Yasuda[21] used both of these to obtain pK values of ligands, acid dissociation constants of aquo-metal ions, and stability constants of metal complexes, refining them jointly or individually. The necessary input data comprised the analytical hydrogen ion concentrations, total metal ion concentration, total ligand concentration, pH values, and estimates of errors (needed in computing variances). Both types of programme were designed to minimize the sums of squares of weighted residuals in analytical hydrogen ion concentration. (The residual is the difference between the experimental value and the amount calculated from the pH and the concentrations of all species by using computed equilibrium constants.) Initial values of free metal ion and free ligand concentrations were computed with approximate values of the constants, and then Newton-Raphson[22] iteration was used in the mole-balance equations for total metal ion and total ligand. The two equations were solved simultaneously, except when the values of the constants being refined were for hydrolysed metal ion (equation for total metal ion only) and the protonated ligand (equation for total ligand only).

The Gauss method used a conventional[23] non-linear least-squares programme to calculate the shifts in the constants, the partial derivatives being obtained numerically by incrementing the constants. Weighting was important unless the residuals were defined in terms of $\bar{n}$ or a similar function because, in the mole-balance equation, small errors in measured pH have much bigger effects at low pH than they do at higher pH.

The "pit-mapping" programme differed mainly in the way the constants were incremented (initially by a specified amount, then by the use of estimated standard errors). Tobias and Yasuda concluded that the Gauss method is slightly easier to programme and has somewhat shorter running times. Also, if initial estimates are too "wild", large overshifts can occur in "pit-mapping", and the shifts can even be in the wrong direction.[21] Difficulties that arise in cases where the "pits" are skew (*i.e.*, covariant with the constants) can be overcome by transforming the co-ordinates, using a "twist matrix", so that refinement is along the main axis of the pit: this is done in Sillén's programme LETAGROP VRID.[8,9] With this refinement, and reasonably good initial guesses, there is probably little to choose between Gaussian and "pit-mapping" methods.

The Gaussian method can also fail if the matrix is ill-conditioned (the vectors of the A matrix may be nearly linearly dependent) and if the starting values are not close enough for a truncated Taylor series to be a useful approximation. The likelihood of failure can be decreased in various ways, one of the most effective being to approach the minimum by the iterative method of Davidon as improved by Fletcher and Powell.[24]

A modified form of the GAUSS programme of Tobias and Yasuda[21] is intended for all kinds of equilibria in a one metal–one ligand system.[25] It has a shorter running time and more reliable convergence in cases where initial estimates of the constants are poor. The input includes a list of possible species giving, in each case, the number of metal ions, ligand molecules, protons or hydroxyl groups in the postulated species and an estimate of its stability constant. Examples of the use of GAUSS are references 26 and 27.

Recently, a more general programme SCOGS which also uses a conventional non-linear least-squares approach has become available.[28] It can be applied to systems containing up to two different kinds of metal ions and two different kinds of ligands. Constants for mixed-ligand species can readily be obtained.[29] In principle, SCOGS is capable of extension to more complicated systems. A related programme, SCOSUS, can be used to obtain the stability constant of a single unknown species (which can be a mixed-ligand or a mixed-metal complex) from pH titration data, if all the other constants are known.[30] The mixed species can contain up to 10 different kinds of metal ion, 10 different kinds of ligands, and also be protonated or hydrolysed, and the value of the constant is computed at each point in the titration. GAUSS, SCOGS and SCOSUS all include in their final print-outs a tabulation of the computed concentrations of all species throughout the titrations, so that the importance of individual species can be assessed. SCOGS uses a refinement technique which minimizes the sum of the squares of residuals in titre, so that the application of equal weighting for all points in the titration is a satisfactory simplification.

The use of computers in obtaining equilibrium constants is, of course, independent of the technique by which the experimental data are obtained. For example, Rydberg and Sullivan[31] applied a computer programme to solvent extraction measurements to calculate, by a least-squares fit, the stability constants of mononuclear complexes in the uranium(IV)–acetylacetone system. In another case the species extracted in some solvent extraction studies, and their relevant constants, were determined by means of a least-squares polynomial curve-fitting computer programme, including weighting calculated from error propagation theory.[32] Similarly, Momoki, Sato and Ogawa[33] used a least-squares method to compute successive formation constants from polarographic data. Equilibrium constants have also been computed from NMR chemical shift data.[34]

Wallace and Katz[35] described a computer method for determining the number of significant species in a solution, from spectrophotometric measurements. They set up an $m \times n$ matrix, comprising measurements at m wavelengths and n metal–ligand (or similar) ratios. The programme corrects for estimated errors in the measured quantities when it computes the rank of the matrix which, in turn, gives the number of species present. The method was used by Varga and Veatch,[36] along with contour mapping and iterative analysis of absorption spectra, to determine the nature of hafnium–chloranilic acid complexes, including their spectra and stability constants.

Conrow, Johnson and Bowen[37] have made an analysis of errors in the determination of association constants by spectrophotometry, pointing out the sensitivity of the results to errors in initial guesses of values used in any iterative approach. Their programmes, which apply both to self-association and to complex formation, compute equilibrium constants and molar absorptivities. Eberle's[38] computer programme for obtaining the stepwise formation constants of ML and ML_2 requires that only metal-containing species contribute to the light absorption. From the dependence of absorbance on pH it computes the values of K_1 and K_2, and the extinction coefficient of ML, that best fit the experimental results. The principles involved in obtaining the equilibrium constant for a system $A + B \rightleftharpoons C$, from spectrophotometric data, have been discussed and a simple computer programme to calculate quantities for a linear plot has been outlined.[39] The method of Wentworth, Hirsch and Chen[40] for a single intermolecular complex is much more rigorous: it includes weighting and allowance for propagation of error in a least-squares adjustment technique which is basically that of Lansbury, Price and Smeeth.[20] Other programmes have been described for computing self-association constants from spectrophotometric measurements, usually by least-squares fitting procedures.[41–44]

EQUILIBRIA IN CHEMICAL SYSTEMS

In principle, a knowledge of the stability constants of metal complexes and the dissociation constants of acids and bases permits calculation of the composition of equilibrium mixtures in solution. This information is valuable to the analytical chemist seeking to devise optimum conditions for quantitative separations or determinations, especially by complexometric titration. It is not, in general, an easy task to perform the necessary calculations manually although, under particular conditions, very good approximate methods are available.[45] Nevertheless, it is only recently that computers have been applied in this field, and the earliest computer applications to equilibrium studies were concerned with gas mixtures. Manual, iterative methods for calculating complex compositions of gas mixtures at equilibrium, from the relevant constants, have been devised.[46–49] One method was based on a linearization technique by Taylor's series expansions of equations involving differences between arithmetical solutions and trial values, neglecting terms above the first order, and requiring initial guesses at the equilibrium values. Another method used initial guesses aimed at satisfying mass-balances. Subsequently, Zeleznik and Gordon[50] applied a computer to show that all of the methods gave the same results.

Villars[51] described a method of successive approximations for computing combustion equilibria, in which only one reaction at a time was considered. All equilibrium constants were then calculated, and for the next cycle of refinement the programme selected the reaction showing the greatest discrepancy between calculated and given values of equilibrium constants. The necessary adjustment to composition was computed, and the process was continued until values fell within tolerances. Anthony and Himmelblau[52] applied a search technique[53] (requiring a large computer) to the calculation by an iterative procedure of complex equilibria in a gas mixture, using free energy relations. Two other procedures[54] for determining equilibrium compositions in complex mixtures also sought minimum values for the free energies (using chemical potentials). One method used the steepest descent technique, applied to a quadratic fit; the other was based on linear programming. A method for evaluating rocket propellants could handle up to 12 chemical elements and 70 combustion products: it computed flame temperature, chemical composition, enthalpy, entropy, specific heat ratios and various velocities.[55] Cruise[56] subsequently combined this with Villars's[51] method to reduce computer time and memory requirements. More recently, a programme has been described[57] for dealing with up to 20 elements, 250 gaseous chemical species and 20 condensed phases.

A paper by Emery[58] provides a convenient introduction to the arithmetical treatment of equilibria in aqueous systems. He described a programme for calculating acid-base titration curves and the compositions of solutions during titrations. Input information comprises the p*K* values, the number of replaceable hydrogen ions, the concentrations, and the amount of acid or base added at any stage. In regions where the specified pH increment is exceeded, the titration increments are automatically diminished to a tenth or a hundredth of their normal amounts. The output of the computer is tabulated and also plotted by a line printer. Like many other computer programmes, it does not require the approximations that are commonly needed for the corresponding manual calculations, especially for systems containing very weak acids or bases, or where successive p*K* values overlap.

An iterative procedure was used to compute the effects of dilution and ionic strength on weak acid–strong base titration curves, and on the Van Slyke buffer index.[59] (The ionic strength affects the activity coefficients and, in turn, depends on the fraction of the acid that has been titrated.) For instructional purposes, Jajicek[60] modified Sillén's KUSKA programme[7] for obtaining equilibrium concentrations in metal complex, or acid-base, systems so as to have a general programme to which specific subroutines could be added for the particular case being considered.

Given the total metal ion and total ligand concentrations, pH, p*K* and stability constant values for a system containing one kind of metal ion and one kind of ligand, an iterative process enables the computation to be made of equilibrium concentrations of all species present.[61] The species can include protonated, hydrolysed, or polynuclear metal complexes, hydrolysed metal ions, and protonated ligands. The programme described by Ropars and Viovy[62] extends the possible range of systems to include one kind of metal ion and two different complexing agents, able to form mixed complexes. It is based on the Newton-Raphson method[22] of successive approximations to solve the mathematical equations obtained from material-balance sums, electroneutrality, and the equilibrium constant relationships. Supplementary information enables the stability constant of a mixed-ligand complex to be computed.[63] The programme is similar to an earlier but less general one.[64]

The pH–concentration profiles for mixtures of pyridoxal, amino-acids and their Schiff bases have been obtained by using a computer.[65]

Bard and King[66] described a programme which they applied to the ionization of a polybasic acid and to equilibria in a system of one metal ion and two kinds of ligands. The programme was used to solve n algebraic equations in n unknowns by first guessing values for two of the variables and then using them to evaluate the others, in turn, from $n - 2$ equations. All but one of the constants were used in the last two equations to evaluate the remaining constant and, if the two estimates did not agree, the first constant was increased or decreased: the process was continued until adequate agreement was reached. Ways in which the programme could be made more efficient were subsequently pointed out.[67]

Equilibrium concentrations in systems containing two kinds of metal ions and two kinds of ligands were computed by Botts, Chashin and Schmidt[68] but by that time a more general programme was available[69] for multi-metal–multi-ligand mixtures in which the complexes were of the types ML, ML_2, $ML_3 \ldots ML_n$. This, in turn, was replaced by an entirely general treatment of equilibria in a single phase, such as a solution or a gas, and the system can contain such species as mixed-ligand, hydrolysed, protonated, polynuclear or mononuclear metal complexes, protonated ligands and hydrolysed metal ions.[70] One of the examples to which the programme was applied was a ten metal–ten ligand system containing 195 species. The input information comprises the total concentration of each metal and each complexing agent, the relevant equilibrium constants, and the pH of the solution. The programme begins with the initial crude approximation that complex formation is negligible, and then rapidly refines the estimates of free metal ion and free ligand concentrations until all equations are satisfied simultaneously. Johansen[71] has also described a method, based on linear programming, for determining the equilibrium composition of a complex mixture.

The programme HALTAFALL[72] extends possibilities to systems containing more than one phase. HALTAFALL calculates equilibrium concentrations of all species in mixtures of any number of components, which can include solid phases, provided equilibrium constants and gross composition are known. The form the programme takes depends on the nature of the input, but examples have been described for one fluid phase, two fluid phases (two liquids or a gas and a liquid), and fluids with solid phases present.[72] A computer programme has also been described for calculating fluid balance and electrolyte distribution for selected compartments of the human body.[73]

REACTION KINETICS

The integration of rate equations is often difficult, even for relatively simple systems, and this has, in the past, been a seriously limiting factor in the study of reaction mechanisms. Where the rate equations have been integrated, there is usually little difficulty in numerical evaluation to obtain rate constants. Simple computer programmes are available to do this for first-,[74,75] pseudo-first-,[74] second-[75] and third-order[75] rate constants. Wiberg[76] has given a group of programmes for dealing with kinetic data. The first programmes compute, from spectrophotometric or titrimetric data, first- or second-order rate constants through one, two and three half-lives, comparing observed and calculated data through each of these intervals (to reveal any drifts). Two other programmes are for consecutive first-order reactions, followed spectrophotometrically, in cases where the absorptivities of the intermediate and the product are unknown. Estimated values of these quantities and the rate constants are inserted, and they are adjusted automatically to give the best fit, either by successive incrementing or by the method of steepest descent (which computes partial derivatives of the average deviation with respect to change in each of the parameters, and increments the parameters proportionately).

Analogue computers enable approximate representations to be made of conditions in systems containing small numbers of components, but digital computers, by their greater accuracy, capacity, speed and ability to be programmed, are now much preferred for the processing of kinetic data.

There is no doubt that computer techniques have greatly extended the possibilities of interpreting kinetic measurements. Thus Garfinkel[77] used a digital computer to simulate conditions in a biochemical system in which 49 differential equations described the rates of change of concentration of 49 chemical species. Numerical integration of the differential equations was by an Euler point-slope method, using Taylor expansions, with a regulated step-size to keep truncation errors small. Cleland[78] has also described general computer programmes, based on an approach due to Wilkinson,[79] for processing enzyme kinetic data. The methods compute rate constants to give the best fit (by a non-linear, least-squares, matrix-inversion technique, with assigned weighting factors) to the assumed reaction scheme.

DeTar and DeTar[80] have reviewed the general computer techniques that are available for elucidating time–concentration relationships for reacting systems, including equilibrium and steady-state conditions. The problem can be stated as follows: "Given the rate equations (expressed as differential equations) and reactant concentrations at some specified time, to express the concentrations of all species as a function of time". Unlike the traditional methods, which give rise to a wide range of integrated expressions for the variation of concentration with time, the computer technique is general and involves direct numerical integration: the trapezoidal method[81] is faster than the more elaborate fourth-order Runge-Kutta method,[82] and is usually adequate. Results of the computer operations are expressed in tabular or graphical form.

Where steady-state conditions apply, a different approach is necessary, and an iterative perturbation method can be used. An alternative procedure is to decrement each reaction step by a small amount, and make two sums, one being the decrements for the reactions where a given species is a product, and the other for the decrements where the species is a reactant. If the ratio of these sums is greater than unity, the estimate of that species concentration is too small, and conversely. Estimates for each species are adjusted iteratively until the ratio is unity to within specified limits. Examples of applications of computer programmes using the above methods have been discussed.[80] A simplified computer programme has also been described[83] for treating complex reaction mechanisms, providing there are no steady-state intermediates. A further, general, programme covers this contingency.[84] Wiberg[76] also described a general programme for computing, by numerical integration, concentrations of species as a function of time, given the relevant rate equations. The programme includes an automatic plotting routine.

The greatest advantage to be obtained from the application of a digital computer to the interpretation of kinetic measurements is by the use of numerical integration programmes in which an iterative procedure is included for adjusting the values of the rate constants to give the best fit (by a least-squares method) between the time-dependent computed and experimental concentrations.

MONTE CARLO METHODS

An alternative approach to the integration of rate equations is a statistical one, based on the use of a Monte Carlo[85] model of the reacting system, from which concentration–time curves can be obtained directly by digital computer.[86] A portion of the computer storage (*e.g.*, 1000 registers) represents the total concentrations of all reactants, and these registers are filled proportionately with 1's, 2's, 3's, *etc.*, corresponding to initial concentrations of species 1, 2, 3, ... A computer programme generates random numbers from 0 to 999 and these are used in searching the corresponding storage register in ways that depend on the particular rate equations. For example, for the reaction $A \rightarrow B$, if the specified register contains a 1 it will be replaced by a 2; otherwise no action will be taken. After a specified number of such random searches, the numbers of 1's, 2's, 3's, *etc*, in the storage are counted and recorded, and the process continues. For competing reactions such as $C \leftarrow A \rightarrow B$, the corresponding random searches must be set equal to the ratio of the rate constants. Second-order reactions (such as $2A \rightarrow B$, or $A + B \rightarrow C$) can be simulated by randomly choosing two locations (for 2A's and an A and a B, respectively). The method is, of course, far slower and less accurate than the methods based on numerical integration. Nevertheless, its error of about 1% is tolerable for most chemical purposes. Lindblad and Degn[87] have described a more sophisticated Monte Carlo method for computing concentrations as a function of time for any system of first- and second-order reactions, given the reaction scheme, rate constants and initial concentrations. The computer programme can also deal with autocatalytic reactions. Other examples of the use of Monte Carlo methods have been discussed by Cohen[88] and by Spielman and Levenspiel.[89] Similar techniques are used in "random walk" methods for studying properties of lattices,[90] chains[90] and hard spheres.[91]

Zusammenfassung—Diese Übersicht behandelt die Anwendung von Digitalrechnern auf die Bestimmung der Dissoziationskonstanten von Säuren und Basen, Stabilitätskonstanten von Metallkomplexen, Konzentrationen von Gleichgewichtsgemischen und Lösung von Geschwindigkeitsgleichungen. Die Verwendung von Rechenanlagen gestattet die Untersuchung sehr viel komplizierterer Systeme und führt zusätzliche Rechenverfahern ein, wie numerische Integration und Monte-Carlo-Brechnungen.

Résumé—Cette revue traite des applications des ordinateurs analogiques à l'évaluation des constantes d'ionisation d'acides et bases, des constantes de stabilité de complexes métalliques, des concentrations de mélanges à l'équilibre et à la solution d'équations de vitesse. L'utilisation d'ordinateurs permet l'étude de systèmes de complexité grandement accrue, et introduit des méthodes supplémentaires de calcul comme l'intégration numérique et les techniques de Monte Carlo.

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DETERMINATION OF SMALL QUANTITIES OF XANTHATE

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Summary—A new spectrophotometric method for the determination of very small amounts of xanthate in solutions, particularly cyanide solutions from gold-extraction plants, is described. It is based on the formation and extraction of copper(II) xanthate. The coefficient of variation is 1·0% at the 40-ppm level and 3·4% at the 4-ppm level and the lower limit of determination is approximately 0·5 ppm. Copper(II) xanthate normally decomposes into copper(I) xanthate and dixanthogen, but in the proposed method the decomposition is delayed.

THE determination of trace quantities of xanthate in solutions is frequently required for the control of flotation processes for the recovery of minerals. Furthermore, some gold mines recover gold by cyanide treatment of the residue after the pyrite has been floated from the ore, and residual xanthate used in the flotation step interferes with this process. The solutions containing xanthate also contain 0·3–0·4% of potassium cyanide, varying amounts of gold, cobalt, nickel, copper, and iron present as thiocyanates or other complex cyanides, calcium, and sulphur compounds such as sulphate, sulphite, and thiosulphate. In the development of a method for the determination of xanthate, attention was focused on these cyanide solutions, because it was felt that a method that was found to be applicable to them would also be applicable to the simpler solutions in a flotation circuit.

Bičovsky and Bičovská[1] have published a method for determining xanthate, based on the formation of a nickel-xanthate complex and its extraction into chloroform. The nickel is titrated in the chloroform solution with mercury(II) acetate solution, diphenylcarbazone being used as indicator. This method is unsuitable for the determination of very small amounts of xanthate, but the present authors felt that it might be possible to measure the concentration of the xanthate complex in the chloroform spectrophotometrically.

Exploratory work showed that a suitable procedure could not be based on nickel xanthate because copper interfered by preferentially combining with the xanthate; so the apparently analogous formation of a copper xanthate complex was investigated.

EXPERIMENTAL

Reagents

Potassium ethyl xanthate. This reagent is referred to as xanthate in this paper. Aqueous solutions of the salt are unstable, and so they were used immediately after preparation. The solution was prepared by dissolving 0·1 g of the analytical-grade reagent (Riedel-de Häen) in water adjusted to pH 10, and diluted to 100 ml with similar water.

Potassium copper cyanide solution. Prepared by dissolving 6·2 g of Cu_2Cl_2 in 200 ml of 1*M* potassium cyanide and adding enough copper(II) chloride to bring the copper(II) content to 2–4%.

Copper(I) chloride that is dark green because of excessive copper(II) content (>10%) should not be used.

Nickel sulphate solution. Prepared by dissolving 7·5 g of analytical-grade $NiSO_4.xH_2O$ (20·7–22·0% Ni) in water, and diluting to 250 ml.

Potassium cyanide solution, 2% *w/v.*

Sodium chloride solution, 25% *w/v.*

Analytical-grade reagents were used when available.

Procedure

The sample containing 15–100 μg of xanthate was transferred to a 100-ml separating-funnel, 1·5 ml of 2% potassium cyanide were added, and the solution was diluted to 50 ml. Then exactly 10 ml of chloroform were added.

Three ml (±0·1) of nickel sulphate solution were added. The solution was mixed, and 30–60 sec were allowed for a precipitate of nickel cyanide to appear. If no precipitate had appeared in 60 sec, nickel sulphate solution was added in drops until a slight precipitate became visible. From this stage the remaining steps of the method were carried out without delay and as rapidly as possible.

Three ml of copper cyanide solution and 5 ml of sodium chloride solution were added with a rapid dispenser, and the mixture was shaken for 10 min. The chloroform phase was filtered through a dry Whatman No. 41 filter paper into a 125-ml tall beaker, and the absorbance immediately measured at 305 nm in a 20-mm quartz cell. A xanthate-free solution was prepared for use as a reference blank by adding 1·5 ml of 2% potassium cyanide solution to distilled water in a 100-ml separating-funnel and continuing as described above for the sample. A calibration curve (15–100 μg of xanthate) was prepared in the usual way.

Note. The addition of sodium chloride does not appear to be essential. It was added initially because we erroneously thought that it would have a salting-out effect and thus favour the extraction of the complex into chloroform. However, it was noticed that sodium chloride had a beneficial effect in retarding the precipitation of copper(I) cyanide and, for this reason, it was retained.

RESULTS AND DISCUSSION

Absorption spectrum and stability of copper xanthate in chloroform

The absorption spectrum of a chloroform solution of the copper xanthate complex is given in Fig. 1, curve *A*, which shows that the wavelength of maximum absorption is 305 nm. The transmittance was measured at intervals of time with the following results:

Time, *min*	1	2	5	10	15	20	25
Transmittance, %	13·5	15·0	17·0	18·5	19·5	20·0	21·0

The copper xanthate decomposed rapidly in the chloroform solution, but the error should not be serious if the absorbance is measured as soon as possible after the separation of the chloroform phase.

The absorption spectrum of the chloroform solution, measured after 24 hr, is given in Fig. 2, curve *A*. This curve is similar to that obtained when dixanthogen is dissolved in chloroform (Fig. 2, curve *B*), and it is probable that the compound that is extracted into chloroform gradually decomposes with the formation of dixanthogen. The biquinoline test[2] failed to detect copper(I) in the chloroform solution immediately after the extraction. However, a positive test was obtained on solutions that had aged, and this suggests that copper(I) xanthate is formed in addition to dixanthogen. If the chloroform solution containing the decomposition products is shaken with a mixture of potassium cyanide, nickel sulphate, and copper cyanide, the reaction is reversed and the original compound is re-formed.

Stability of the copper xanthate complex in aqueous solutions

Aqueous solutions of the copper xanthate complex, prepared as described in the procedure, were extracted with chloroform at varying time intervals between the addition

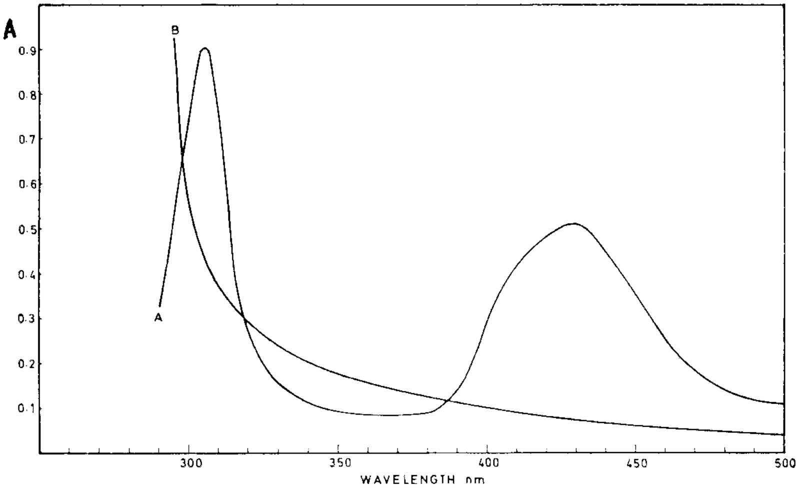

FIG. 1.—Absorption spectra of chloroform extract and copper(I) xanthate in chloroform.
A—100 μg of xanthate treated by described procedure; *B*—100 μg of copper(I) xanthate; 20-mm cell, 10 ml of chloroform; chloroform as reference.

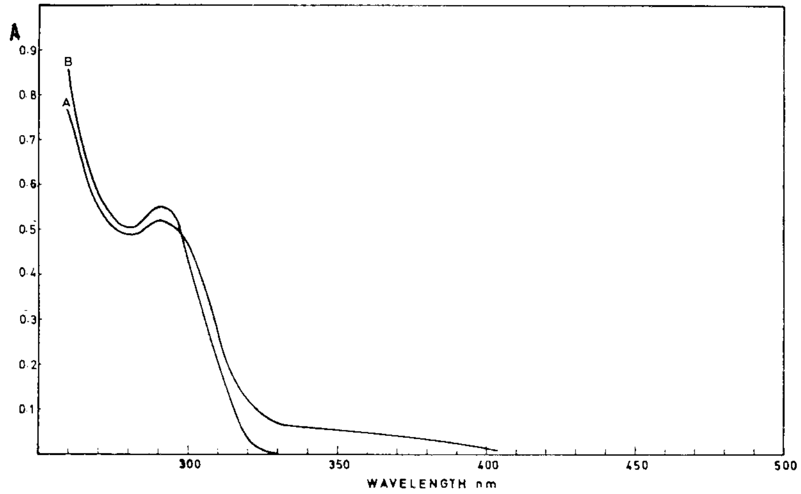

FIG. 2.—Absorption spectra of chloroform extract after 24 hr and of dixanthogen. *A*—as Fig. 1, curve *A*; *B*—100 μg of dixanthogen in chloroform; 20-mm cell; chloroform as reference.

of the copper cyanide solution and the extraction. The transmittance of the chloroform solutions was read immediately after the extraction, with the following results:

Time between formation and extraction, *min*	0·5	1	3	5	10	15
Transmittance, %	14·0	13·5	14·0	14·5	20·5	24·0

The complex is stable in aqueous media for up to 5 min, but then decomposes fairly rapidly.

Tests also showed that the interval between addition of the nickel sulphate and the copper cyanide solution is not important and that 10 min of shaking is adequate for the extraction of the copper xanthate.

Effect of concentration of nickel sulphate and copper cyanide

The formation of copper xanthate does not take place in a solution containing an excess of free cyanide, but the presence of nickel cyanide is necessary. This is why sufficient nickel sulphate solution is added to form a small precipitate of nickel cyanide.

Potassium cyanide is added initially to all samples to allow for those that may not contain sufficient cyanide. It was decided that 1·5 ml of 2% potassium cyanide solution was an adequate amount to add, and tests showed that 2·7–3·2 ml of nickel sulphate solution are required for this amount of cyanide.

A flocculent precipitate of copper(I) cyanide formed when potassium copper cyanide solution was added to those solutions to which had been added more than 3·2 ml of nickel sulphate solution. The low results obtained for these solutions were thus due to the removal of copper from the solution by precipitation. The amount of nickel sulphate solution that should be added can be gauged by the formation of a small amount of fine-grained precipitate. This precipitate, which has been identified as nickel cyanide, is readily distinguishable from the flocculent copper(I) cyanide.

Effect of other species

Thiocyanate (12 mg), thiosulphate (18 mg), sulphate (50 mg), cyanate (12·5 mg), zinc cyanide (9·6 mg), tetracyanoaurate(III) (7·5 mg), hexacyanoferrate(II) (1 mg) and cobalt (0·15 mg), when present in the amounts stated, cause less than 5% error in the determination of 100 μg of xanthate.

Precision and accuracy

The precision was tested on samples of cyanide solution from a gold-extraction plant (two analysts, two samples each, 12 variates for each sample; one analyst had no experience of the method) and the coefficients of variation were 3% for solutions containing 4·0, 5·0 and 54 ppm of xanthate, and 1% for a 38-ppm solution. The 3% coefficient of variation for the 54-ppm solution was obtained by the inexperienced analyst. The accuracy was tested by spiking samples with known amounts of xanthate; the recoveries are shown in Table I. If the small amounts of xanthate present are taken into account, the accuracy and precision of the method are satisfactory.

TABLE I.—RESULTS OBTAINED ON A CYANIDE SOLUTION SPIKED WITH XANTHATE

Volume of sample, *ml*	Xanthate added, *μg*	Xanthate recovered, *μg*	Deviation, *μg*
1·0	50	48	−2
2·0	100	101	+1
3·0	50	49	−1
4·0	100	99	−1
5·0	50	47	−3
10·0	100	101	+1
20·0	50	47	−3

Chemistry of the reactions

The nature of the coloured complex has been investigated and it is concluded that it is copper(II) xanthate.

Analysis of the chloroform extract showed that the compound extracted contained copper, but not cyanide, nickel, sodium or potassium, and when 200 μg of xanthate were used, an average of 41·4 μg (7 results, 2·1 μg range) of copper was found in the organic phase by atomic-absorption spectrophotometry. The mole ratio of copper to xanthate calculated from these results is very close to 1:2, which corresponds to that in copper(II) xanthate.

The absorption spectrum of the chloroform extract (Fig. 1, curve *A*) is different from that of copper(I) xanthate in chloroform (Fig. 1, curve *B*). The copper(I) xanthate was prepared by adding copper(II) sulphate to a solution of potassium ethyl xanthate in the correct molar proportions, $2Cu(II) + 4RX = 2CuRX + (RX)_2$.[3] The dixanthogen formed was removed by extraction with chloroform, and the residue of copper(I) xanthate was dissolved in chloroform containing 1% of pyridine [copper(I) xanthate is insoluble in chloroform in the absence of pyridine; pyridine does not affect the adsorption spectrum of the copper(II)]. Copper(I) in copper(I) xanthate dissolved in a mixture of chloroform and pyridine can be identified by the biquinoline test.[2] Copper(I) was not detected by this test in the chloroform solution obtained by the procedure described unless the copper was first reduced with hydroxylamine hydrochloride. Reducing conditions (acid sulphite solutions) inhibit the formation of the compound, and the inhibition is most pronounced when the reducing conditions are strongest. This suggests that copper in the complex is in the bivalent rather than in the univalent state.

Role of cyano-complexes in the formation of the compound. Under some conditions, when potassium cyanide is added to a solution containing copper(II) ions, complex cyano-compounds of copper(II) are formed; $K_2Cu(CN)_4$, $K_2Cu[Cu(CN)_4]_2$, and $Cu[Cu(CN)_4]$.[4] As a small amount of copper(II) chloride was present in the copper(I) chloride used for the experimental work, the cyanide solution prepared from it probably contained one or more of the copper(II) cyanide complexes in addition to copper(I) cyanides such as $K_2Cu(CN)_3$. Thus it was observed that a transient violet colour formed when the cyanide solution was prepared from copper(I) chloride. According to Moles and Itzaguirre,[4] a solution of $K_2Cu[Cu(CN)_4]_2$ is violet and decomposes to $K_2Cu(CN)_4$ and $Cu[Cu(CN)_4]$.

If the violet solution of $K_2Cu[Cu(CN)_4]_2$ [a copper(II) compound prepared by the addition of potassium cyanide to copper(II) sulphate solution or the decomposition products mentioned above], is added to an aqueous solution of potassium ethyl xanthate and the solution is shaken with chloroform, a compound is extracted that has the same spectral properties (Fig. 3) as the compound formed when the method described (Fig. 1, curve *A*) is used. The reaction is probably

$$K_2Cu[Cu(CN)_4]_2 + 6C_2H_5OCSSK \rightleftharpoons 3Cu(C_2H_5OCSS)_2 + 8KCN \qquad (1)$$

or, if the decomposition product of $K_2Cu[Cu(CN)_4]_2$ is added,

$$K_2Cu(CN)_4 + 2C_2H_4OCSSK \rightleftharpoons Cu(C_2H_5OCSS)_2 + 4KCN \qquad (2)$$

In both cases a copper(II) xanthate is formed. The conclusion is that the compound formed in the method is copper(II) xanthate.

The reactions mentioned above do not take place when there is a large excess of free cyanide ions, hence the necessity to add nickel sulphate until all the free cyanide ions are complexed or precipitated.

The presence of nickel cyanide has a disturbing effect on reactions (1) and (2). If the violet solution of $K_2Cu[Cu(CN)_4]_2$, or a solution of its decomposition products, is added to xanthate in cyanide solution after the addition of nickel sulphate, relatively small amounts of the copper(II) xanthate are formed, a green-yellow precipitate of unknown composition being obtained instead. If, on the other hand, copper(I) cyanides such as $KCu(CN)_2$ or $K_2Cu(CN)_3$, together with the copper(II) cyanide complexes $K_2Cu[Cu(CN)_4]_2$ or $K_2Cu(CN)_4$, are added, the formation of copper(II) xanthate takes place readily. An equation that accounts for the reaction of copper and xanthate in the presence of nickel cyanide is

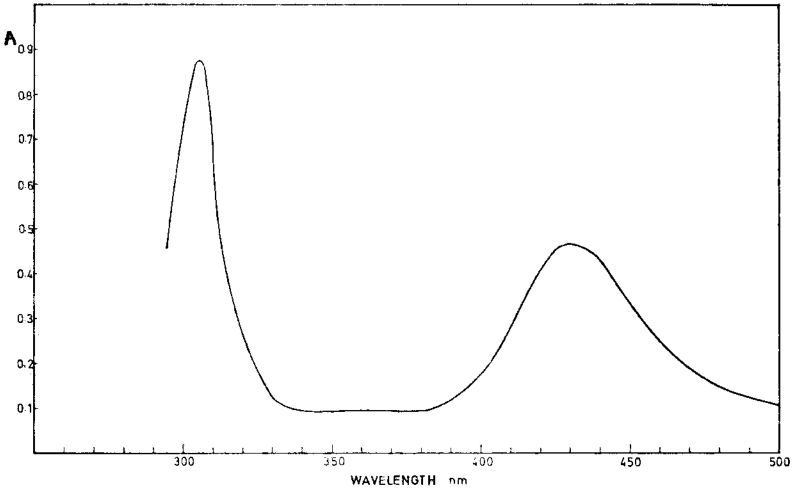

FIG. 3.—Absorption spectrum of copper(II) xanthate in chloroform.

$$Ni(CN)_2 + K_2Cu(CN)_4 + K_2Cu(CN)_3 + 2C_2H_5OCSSK \rightarrow KCu(CN)_2 + K_2Ni(CN)_4 + Cu(C_2H_5OCSS)_2 + 3KCN$$

It is generally accepted that copper(II) ions and xanthate react to form copper(I) xanthate and dixanthogen.[3,5] As our observations leave little doubt that the compound extracted into chloroform is copper(II) xanthate, copper(II) ions and xanthate must react in two stages, the formation of copper(II) xanthate and the decomposition of this compound into copper(I) xanthate and dixanthogen.

A notable feature of the analytical method is that the decomposition is delayed by the choice of appropriate conditions under which the compound can be extracted into chloroform and measured.

Acknowledgement—The authors wish to thank the Director of the National Institute for Metallurgy for permission to publish the work described in this paper.

Zusammenfassung—Ein neues spektrophotometrisches Verfahren zur Bestimmung sehr kleiner Mengen Xanthogenat in Lösungen, speziell in Cyanidlösungen aus Goldextraktionsbetrieben, wird beschrieben. Es beruht auf der Bildung und Extraktion von Kupfer(II) xanthogenat. Der Variationskoeffizient beträgt im 40 ppm-Bereich 1,0% und im 4 ppm-Bereich 3,4%; die untere Nachweisgrenze liegt bei etwa 0,5 ppm. Kupfer(II) xanthogenat zersetzt sich normalerweise zu Kupfer(I) xanthogenat und Dixanthogen; beim hier vorgeschlagenen Verfahren ist diese Zersetzung verlangsamt.

Résumé—On décrit une nouvelle méthode spectrophotométrique pour le dosage de très petites quantités de xanthate dans des solutions, en particulier des solutions de cyanure d'usines d'extraction d'or. Elle est basée sur la formation et l'extraction du xanthate de cuivre(II). Le coefficient de variation est de 1,0% à la teneur de 40 ppm et de 3,4% à la teneur de 4 ppm et la plus faible limite de détermination est d'approximativement 0,5 ppm. Le xanthate de cuivre(II) se décompose normalement en xanthate de cuivre(I) et dixanthogène mais, dans la méthode proposée, la décomposition est retardée.

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SIMULTANEOUS DETERMINATION OF PALLADIUM, PLATINUM AND RHODIUM IN CRUDE PLATINUM SAMPLES BY ACTIVATION ANALYSIS AND HIGH-RESOLUTION GAMMA SPECTROMETRY

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Summary—Instrumental neutron-activation analysis using a Ge(Li) detector has been investigated for the simultaneous determination of platinum, palladium and rhodium in crude platinum samples contained in lead cupels. This technique proved feasible and appears promising for extension to the determination of most of the noble metals.

SEVERAL methods are used by assaying laboratories to concentrate the platinum metals from platinum-bearing ores, and include collection in lead, iron–nickel–copper alloys, and tin. When lead is used as collector, the metals present in the resulting lead beads are sometimes transferred to silver or gold by cupellation. Platinum and palladium, and to a lesser extent rhodium and ruthenium, appear as main constituents in the lead beads, while gold, silver, rhenium, osmium and iridium are present as minor constituents, depending on the concentration of the individual metals in the ores,[1] but segregation may occur, especially with ruthenium and osmium.

Several analytical techniques can be used to determine the individual platinum metals in a variety of materials, ranging from rocks to highly purified noble metals.[2,3] Classical methods are being superseded by physical methods such as X-ray fluorescence, polarography, *etc*,[4–11] but insufficient sensitivity and the lack of agreement in results for the same samples by different physical methods render their use somewhat unsatisfactory. Neutron-activation procedures, however, have been used for obtaining improved sensitivities,[12] and for determination of mg and μg amounts of the noble metals in platinum metals, minerals, meteorites, etc[13–31] Usually, however, radiochemical separations were involved, and a Geiger-Müller tube or NaI(Tl) scintillation counter was used. These methods are still not entirely satisfactory, owing to the many precautions which have to be taken,[32] apart from the lengthy radiochemical procedures involved. Most of these disadvantages can be eliminated if non-destructive activation analysis can be used.

During the past few years high-resolution lithium-drifted germanium [Ge(Li)] detectors have been intensively developed for gamma-spectrometry and at present find wide use in activation analysis, especially for multiple-element analysis. More gamma-photopeaks can be detected, observed and identified than by earlier methods.

An attempt has been made to apply high-resolution gamma-spectrometry directly to reactor-irradiated samples in order to assess the possibilities for determining platinum, palladium and rhodium in lead beads.

TABLE I.—NUCLEAR DATA FOR RADIONUCLIDES PRODUCED FROM NOBLE METALS BY (n, γ) REACTIONS

Target isotope	Abundance, %	Cross-section, *barn*	Product isotope	Half-life	Gamma-ray energy, *MeV*
^{96}Ru	5·51	0·21	^{97}Ru	2·7 d	0·216 0·325
^{102}Ru	31·61	1·2	^{103}Ru	40 d	0·498 0·611 0·040(^{103m}Rh)
^{104}Ru	18·6	0·7	^{105}Ru	4·5 hr	0·265 0·316 0·472 0·725 0·130(^{105m}Rh) 0·322(^{105}Rh)
^{103}Rh	100	12	^{104m}Rh	4·4 min	0·051 0·077
		140	^{104}Rh	42 sec	0·556 1·24
^{102}Pd	0·96	4·8	^{103}Pd	17 d	0·365 0·040(^{103m}Rh)
^{106}Pd	27·33		^{107m}Pd	21 sec	0·213
			^{107}Pd	$7·5 \times 10^6$ *y*	—
^{108}Pd	26·71	0·07	^{109m}Pd	4·8 min	0·188
			^{109}Pd	13·6 hr	0·088(^{109m}Ag)
^{110}Pd	11·81		^{111m}Pd	5·5 hr	0·17
			^{111}Pd	22 min	0·068(^{111m}Ag)
^{107}Ag	51·35	30	^{108}Ag	2·3 min	0·430 0·511 0·618 0·633
^{109}Ag	48·65	2·8	^{110}Ag	270 d	0·656 0·706 0·764 0·884
			^{110m}Ag	24·2 sec	0.656
^{185}Re	37·07	100	^{186}Re	91 hr	0·137 0·123
^{187}Re	62·93	75	^{188m}Re	18·7 min	0·063 0·105
			^{188}Re	17 hr	0·155 0·478 0·633
^{184}Os	0·018	< 200	^{185}Os	95 d	0·647 0·875
^{188}Os	13.3		^{189}Os	5·7 hr	0·031
^{189}Os	16·1		^{190m}Os	9·5 min	0·186 0·356 0·510 0·614
^{190}Os	26·4	8	^{191m}Os	14 hr	0·074
			^{191}Os	16 d	0·042(^{191m}Ir) 0·129(^{191m}Ir)
^{192}Os	41	1·6	^{193}Os	32 hr	0·139 0·281 0·321 0·559

Table 1. (*cont.*)

Target isotope	Abundance, %	Cross-section, *barn*	Product isotope	Half-life	Gamma-ray energy, *MeV*
^{191}Ir	38·5	260	^{192m}Ir	1·4 min	0·058
		700	^{192}Ir	74·5 d	0·295
					0·309
					0·316
					0·468
					0·484
					0·588
					0·604
					0·613
^{193}Ir	61·5	130	^{194}Ir	19 hr	0·325
					0·645
					0·937
^{190}Pt	0·012	150	^{191}Pt	3 d	0·130
					0·172
					0·360
					0·409
					0·539
^{192}Pt	0·78	8	^{193m}Pt	3·5 d	0·136
^{194}Pt	32·8	1·2	^{195m}Pt	3·5 d	0·031
					0·099
					0·130
^{196}Pt	25·4		^{197m}Pt	80 min	0·337
		0·8	^{197}Pt	18 hr	0·077
					0·191
					0·269
^{198}Pt	7·2	4	^{199}Pt	31 min	0·074
					0·189
					0·247
					0·318
					0·475
					0·540
					0·159(^{199}Au)
					0·208(^{199}Au)
^{197}Au	100	98	^{198}Au	2·7 d	0·412

EXPERIMENTAL

Nuclear data

The application of reactor neutron activation to the platinum metals results in the formation of several radioisotopes.[14,18–23,26,30] The most important radioisotopes produced by thermal neutron bombardment of these metals are given in Table I. Interfering nuclear reactions, such as (n, p) and (n, α) reactions, can be neglected in the determination of platinum, palladium[20] and rhodium. In the determination of rhodium, interference due to the reaction ^{104}Pd(n, p) ^{104m}Rh,^{104}Rh can be ignored since the thermal-neutron cross-section of rhodium is much higher than the fast-neutron cross-section of palladium. The influence of other elements which may be present in the lead bead can be neglected since these elements are present only in trace amounts.

Procedure

Weighed samples (<10 mg) of lead beads in which the platinum metals had been concentrated were sealed in polyethylene containers. The beads were obtained by evaporating lead from the original beads, and contained about 15% lead. Standards were mixtures of weighed portions of standard solutions of $RhCl_3$ (90 μg Rh/ml), $PdCl_2$ (670 μg Pd/ml) and $PtCl_2$ (830 μg Pt/ml) in polyethylene containers. All reagents used were of analytical or spectrographical purity, and were used without further purification. The liquid mixture was carefully evaporated to dryness, after which the containers were sealed. For convenience of counting in the determination of rhodium, the samples and standards were irradiated separately and in fixed sequence for precisely 1 min. The relative value of the integrated neutron fluxes were determined for each sample and standard by using gold monitor samples. Irradiations were done in the pneumatic facility of SAFARI 1, an ORR-type reactor, in a thermal-neutron flux of about 10^{11} n. mm.$^{-2}$. sec.$^{-1}$ Westcott's epithermal index, r, for this irradiation

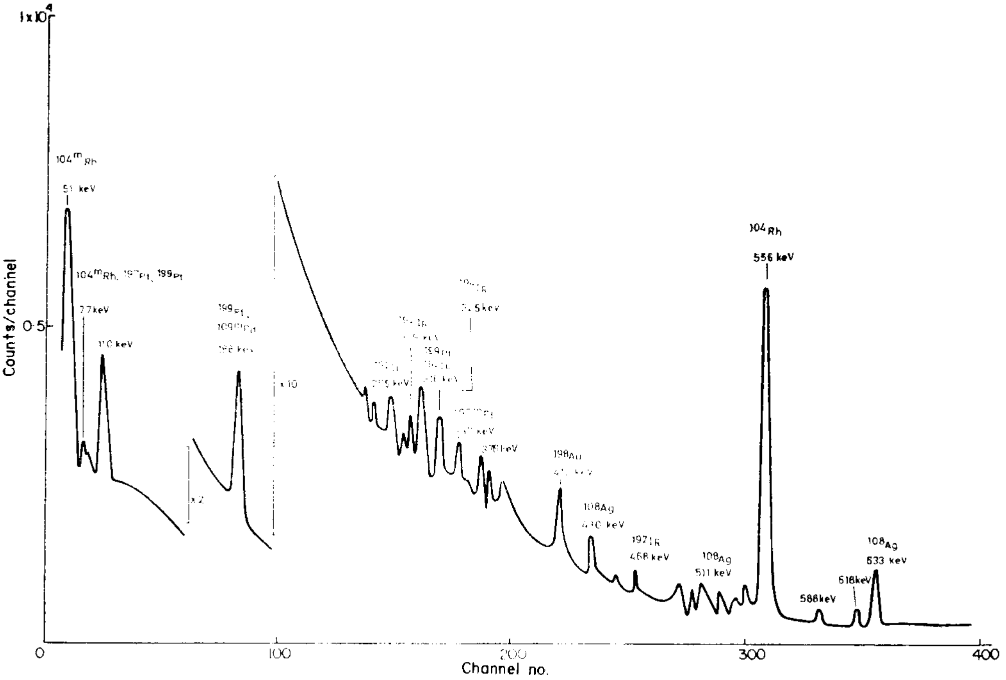

FIG. 1.—Low-energy gamma-spectrum of an irradiated lead bead sample 3 min after irradiation.

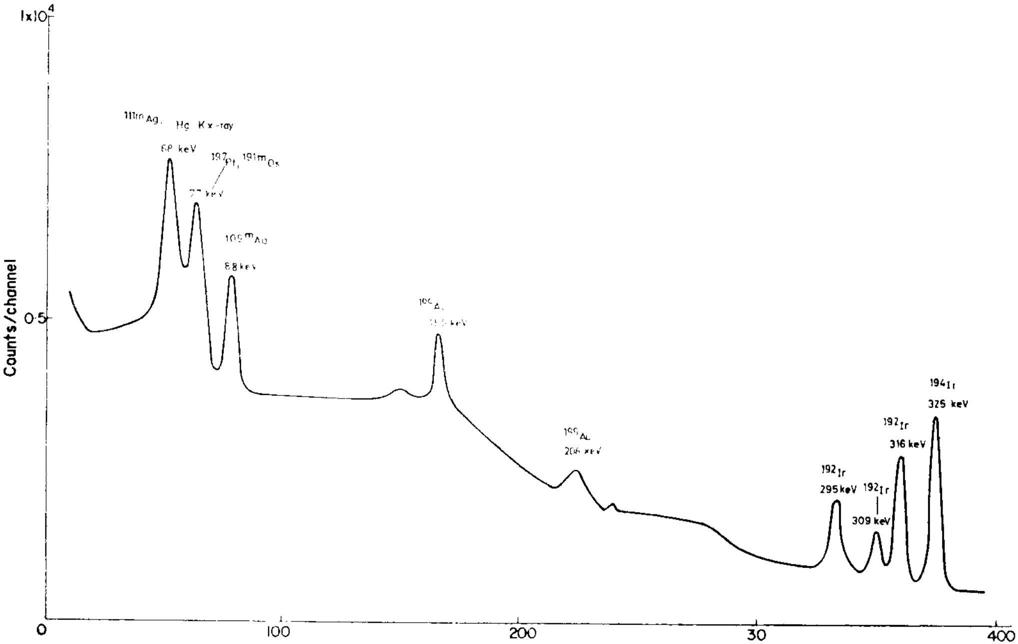

FIG. 2.—Low-energy gamma-spectrum of an irradiated lead bead sample 18 hr after irradiation.

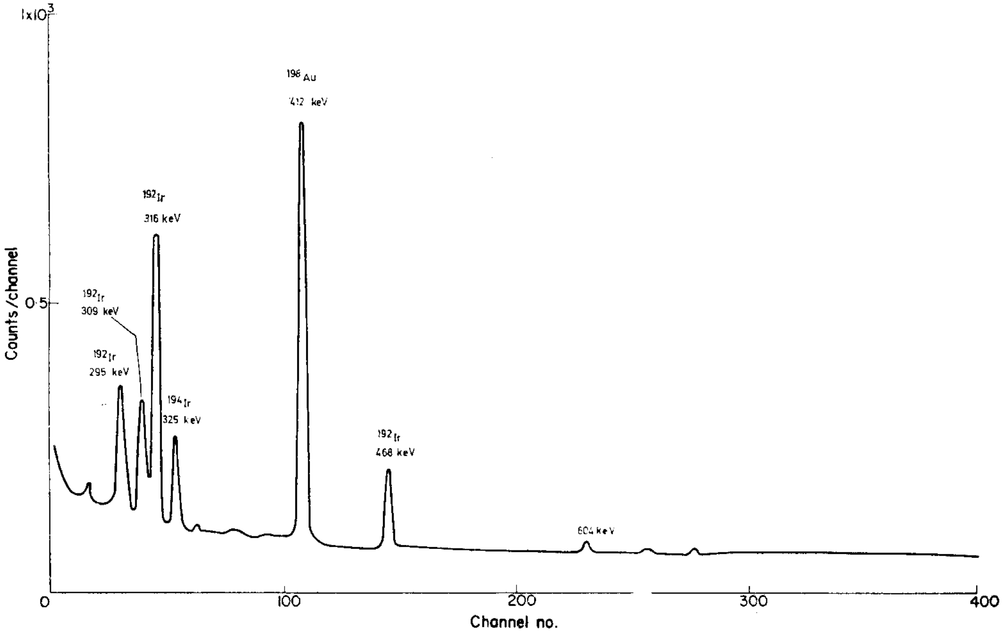

FIG. 3.—Gamma-spectrum of an irradiated lead bead sample 30 hr after irradiation in the intermediate energy region.

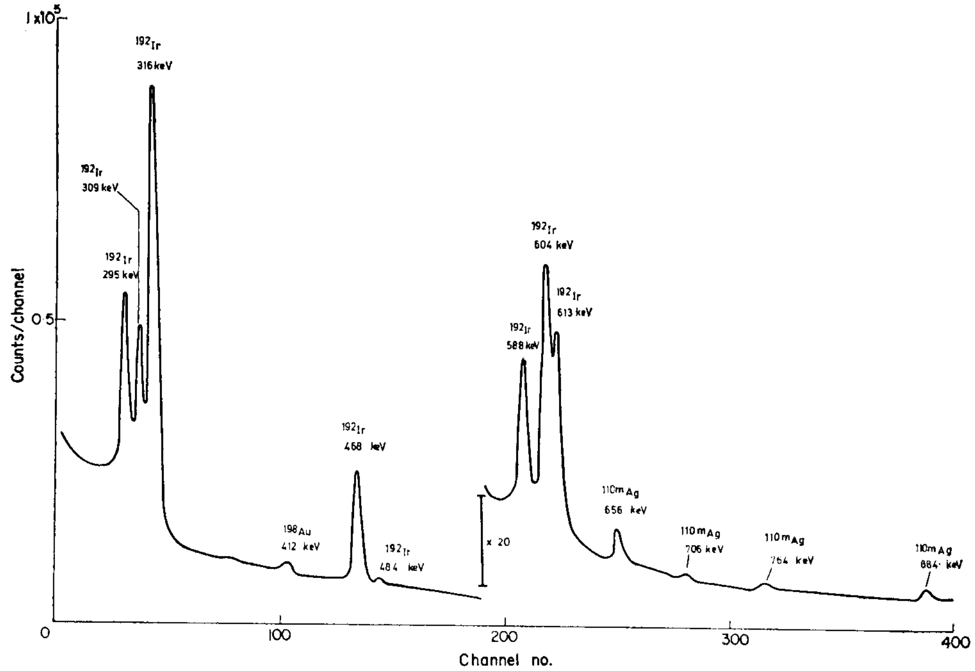

FIG. 4.—Gamma-spectrum of an irradiated lead bead sample 4 weeks after irradiation in the intermediate energy region.

position is 0.0148. Gamma-spectrometry of the irradiated samples and standards was done exactly 3 min after each irradiation by placing them 70 mm below a Ge(Li) detector in a system described elsewhere.[33] The irradiated gold standards were measured after about 2 hr of cooling, with the same counting equipment. Rhodium and gold were determined by measuring the counts under the 0·556-MeV and 0·412-MeV photopeaks of ^{104}Rh and ^{198}Au respectively.

About 5 hr after the first irradiation the samples and standards were re-irradiated in the same position for 30 min for the determination of palladium and platinum, and measured about 18 hr after irradiation, 0·088-MeV and 0·159-MeV photopeaks of ^{109m}Ag (daughter of ^{109}Pd) and ^{199}Au (daughter of ^{199}Pt), respectively, being used. Gamma spectra of these samples were also recorded 30 hr after irradiation. One sample was subjected to long irradiation and counted after a month's cooling.

Graphical analysis[34] was used to obtain the true counts under the different photopeaks. The resolution of the counting equipment was 4·6 keV for the 0·662-MeV photopeak of ^{137m}Ba.

RESULTS AND DISCUSSION

A gamma spectrum of a lead bead sample after 1 min of irradiation and 3 min of cooling is shown in Fig. 1. The 0.556-MeV photopeak of ^{104}Rh which is predominant in the gamma spectrum, has been used as a measure of the rhodium content of the sample. That the activity of the 0·556-MeV photopeak was due only to ^{104}Rh was confirmed by following the decay of one of the samples for about six half-lives.

Figure 2 shows a gamma spectrum of a lead bead sample irradiated for 30 min and cooled for about 18 hr. The prominent 0·088-MeV and 0·159-MeV photopeaks of ^{109m}Ag and ^{199}Au (daughters of ^{109}Pd and ^{199}Pt) are well separated from other gamma-photopeaks and have been used as a measure of the palladium and platinum contents of the sample. The samples used appeared to contain $\sim$3% Rh, $\sim$10% Pd and $\sim$30% Pt.

As can be seen even from Fig. 1 which also shows distinct photopeaks of ^{108}Ag, ^{192}Ir and ^{198}Au, it should be possible to extend the non-destructive analysis to other elements of the noble-metal group. To obtain better sensitivity for these elements longer irradiation times and cooling periods have to be used. This is clearly seen in Figs. 2–4. Thirty hours after a bead sample had been irradiated for 30 min at a neutron flux of 10^{11} n.mm^{-2}.sec^{-1}, ^{194}Ir and ^{198}Au were easily detected (Fig. 3), while ^{110m}Ag and ^{192}Ir could be distinctly observed after 12 hr of irradiation and 4 weeks of cooling (Fig. 4). In a number of papers[14,18,21,31] it has been mentioned that in an almost-thermal neutron flux ($<10\%$ fast neutrons) the interference due to fast-neutron reactions can be ignored in the determination of silver, iridium and gold in platinum samples. For gold determination, however, care should be taken to avoid the second-order reaction $^{196}\mathrm{Pt}(n, \gamma)^{197}\mathrm{Pt}\beta\text{–}^{197}\mathrm{Au}(n, \gamma)^{198}\mathrm{Au}$.[31]

No indications of photopeaks from ruthenium and osmium were observed in the gamma spectra of the lead beads. These elements are known to be easily lost by volatilization and the rather drastic procedures used in forming the lead beads are presumably responsible for their absence. If the techniques were modified so that these elements were not lost, no difficulties should be encountered in their determination either. The determination of rhenium in the lead beads appears to be impossible owing to its concentration being too low.

Acknowledgement—The authors are indebted to Dr. P. W. de Lange for use of his Ge(Li) detector.

Zusammenfassung—Zur gleichzeitigen Bestimmung von Platin, Palladium und Rhodium in Rohplatinproben aus Bleikupellen wurde die Neutronenaktivierungsanalyse mit einem Ge(Li)-Detektor untersucht. Die Methode erwies sich als durchführbar und eröffnet Möglichkeiten der Ausdehnung auf die Bestimmung der meisten Edelmetalle.

Résumé—On a étudié l'analyse instrumentale par activation de neutrons en utilisant un détecteur à Ge(Li) pour la détermination simultanée des platine, palladium et rhodium dans des échantillons de platine brut contenus dans des coupelles de plomb. Cette technique se révèle réalisable et paraît prometteuse pour l'extension au dosage de la plupart des métaux nobles.

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SEPARATION OF TERVALENT RARE EARTHS AND SCANDIUM FROM ALUMINIUM, IRON(III), TITANIUM(IV), AND OTHER ELEMENTS BY CATION-EXCHANGE CHROMATOGRAPHY IN HYDROCHLORIC ACID–ETHANOL

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Summary—Tervalent rare earths and Sc are separated from the silicate-forming elements Al, Fe(III), Mg and Ti(IV), and also from Mn(II), U(VI), Be, Ga, In(III), Tl(III), Bi(III), Ni, Zn, Cu(II), Cd and Pb by cation-exchange chromatography. The other elements are eluted with $3{\cdot}0M$ HCl containing 50% ethanol from a column of 60 ml of AG50W-X8 resin (200–400 mesh) while the rare earths are retained. Separation factors are larger than in aqueous hydrochloric acid. Th, Zr, Hf, Ba, Sr, Ca, K, and Rb are the only elements which accompany the rare earths group, but these can easily be separated by other methods which are described. Relevant distribution coefficients, elution curves and accurate results of quantitative separations of synthetic mixtures are presented.

WHILE much information is available on the separation of individual rare earths from their mixtures, the number of procedures described for the ion-exchange separation of the rare earths as a group from the bulk of other elements is rather limited.

Rare earths can be absorbed as nitrate complexes from nitric acid–organic solvent[1–5] or nitric acid–acetic acid[6] mixtures on anion-exchange resins. Many elements are not absorbed and can be separated quantitatively, but Th, U(VI), Bi, Tl(III), Pb, Ba, Sr, Ca and Cd are absorbed and cannot be separated from some of the rare earths.[3] Furthermore, Sc has low distribution coefficients in nitric acid–organic solvent media and does not accompany the other rare earths, while Ti(IV) cannot be separated from the rare earths because of precipitate formation.[3] Zr also cannot be separated and the conditions for the separation of Cu(II) are rather critical.[3]

Bivalent cations such as Ca, Sr, Cu, Ni and Cd can be separated from rare earths by elution with $1{\cdot}5M$ nitric acid from a column of Dowex 50W-X8 cation-exchange resin, while the rare earths are retained.[7] Common tervalent ions such as Fe and Al accompany the rare earths. By use of $1{\cdot}75M$ hydrochloric acid as eluent, these elements can also be separated and the separation of many bivalent ions which have some tendency to form chloride complexes is improved considerably.[8] Only Zr, Hf, Th, Ba and Sr are retained by the resin together with the rare earths, but can easily be separated by other methods. Al has the highest distribution coefficient of the elements eluted with $1{\cdot}75M$ hydrochloric acid and also shows some tailing, while Sc has the lowest coefficient of the rare earth group.[8] The separation factor for these two elements is only $\alpha_{\mathrm{Al}}^{\mathrm{Sc}} \sim 2{\cdot}3$, and only up to about 2·5 mequiv of Sc can be separated quantitatively from 5 mequiv of Al on a column of 60 ml of AG50W-X8 resin.[8] During a systematic study of cation-exchange distribution coefficients in hydrochloric acid–ethanol media, it was found that the coefficients for the rare earths increased considerably more with increasing ethanol concentrations than did the coefficients for aluminium. This is because the smaller aluminium cation has a higher charge density and hence has more resistance to reduction of the size of its hydration sheath than the larger rare earth cations. As a result the separation of the rare earths from Al and also from Ga and other elements can be improved considerably by using 3·0*M* hydrochloric acid in 50% ethanol as eluent for these elements instead of 1·75*M* hydrochloric acid. The separation factor α_{Al}^{Sc} increases from 2·3 to 13, and α_{Al}^{Yb} increases from 2·3 to 4·2. With this eluent Yb becomes the least strongly absorbed of the rare earth elements, except Lu which was not investigated. The behaviour of Yb during elution experiments and in quantitative separations from Al and other elements has therefore been studied in more detail.

EXPERIMENTAL

Reagents and apparatus

Chemicals of analytical grade purity were used when possible. The cation-exchanger was BioRad AG50W-X8 resin, a specially purified sulphonated polystyrene. Borosilicate glass tubes of 20 mm bore, fitted with a B19 ground-glass joint at the top and a No. 2 sintered-glass plate and a tap at the bottom were used as columns.

Distribution coefficients

Distribution coefficients were determined by the batch method with 2·500 g of dry resin, 5 mequiv of the cation and a total solution volume of 250 ml. The resin was dried at 60° over phosphorus pentoxide in a vacuum pistol. The solutions were equilibrated by shaking for 24 hr at 20° and then filtered. The amounts of the elements in the aqueous and, when possible, in the resin phase, were determined by appropriate methods, and the distribution coefficients *D* calculated from

$$D = \frac{\text{amount on resin}}{\text{amount in solution}} \times \frac{\text{ml of solution}}{\text{g of dry resin}}$$

Comparative coefficients in 1·75*M* hydrochloric acid and in 3·00*M* hydrochloric acid in 50% ethanol are presented in Table I.

Elution curves

Table I shows that Al is the most strongly absorbed of the elements which are to be separated from the rare earths, while Yb is the least strongly absorbed of the rare earths. An elution curve for these two elements was therefore prepared, a 20-mm diameter column of 20 (60 ml) of AG50W-X8 resin, 200–400 mesh, being used.

Al (1·7 mmole) and Yb (1·0 mmole) in 50 ml of 0·1*M* hydrochloric acid were added to the column and absorbed on the resin. Aluminium was then eluted with 3·00*M* hydrochloric acid in 50% ethanol (flow-rate 1·5 ± 0·3 ml/min, the maximum obtainable without application of external pressure). The elution was continued until Yb also appeared in the eluate, thus providing information about the limitations of the method with regard to the amounts which can be separated. An automatic fraction-collector took 25-ml portions, in which the two elements were subsequently determined. The experimental curve is shown in Fig. 1.

Figure 2 presents a similar elution curve for the Mg–La pair, but elution with 3·00*M* hydrochloric acid in 50% ethanol was stopped after 500 ml and the La(III) was then eluted with 3·00*M* aqueous hydrochloric acid. An elution curve for the Ti(IV)–La pair on the same column is shown in Fig. 3. In this case absorption took place from 0·5*M* hydrochloric acid containing 0·1% of hydrogen peroxide to suppress the hydrolysis of Ti(IV). Elution carried out with 3·00*M* hydrochloric acid in 50% ethanol containing 0·5% of hydrogen peroxide was stopped after 500 ml and the La then eluted with 4·00*M* aqueous hydrochloric acid.

Ga, Fe(III), Ni, Mn(II), Be and U(VI) are eluted ahead of Al and have elution curves which are more or less comparable to those of Mg and Ti(IV), while In(III), Tl(III), Bi(III), Zn and Cu(II) appear in the eluate at the elution front.

TABLE I.—EQUILIBRIUM DISTRIBUTION COEFFICIENTS

Element	1·75*M* HCl†	3·00*M* HCl in 50% ethanol
La	70	123
Ce(III)	67	119
Sm	56	101
Gd	48·2	92
Er	41·8	54
Y	40·1	61
Yb	39·9	43·5
Sc	38·8	134
Al	17·0	10·1
Ga	16·4	3·7
In(III)	0·7	<0·5
Tl(III)	<0·5	<0·5
Bi(III)	<0·5	<0·5
Fe(III)	7·1	4·2
*Ti(IV)	5·4	5·9
Mn(II)	7·8	6·9
Ni(II)	8·8	5·6
Mg	7·9	8·3
U(VI)	8·6	5·9
Be	6·9	4·2
Zn	5·4	<0·5
Cu(II)	6·0	1·6
Ca	15·8	30·0
Sr	22·5	62

* 1 ml of 30% H_2O_2 present.

† Published previously, included for comparison.

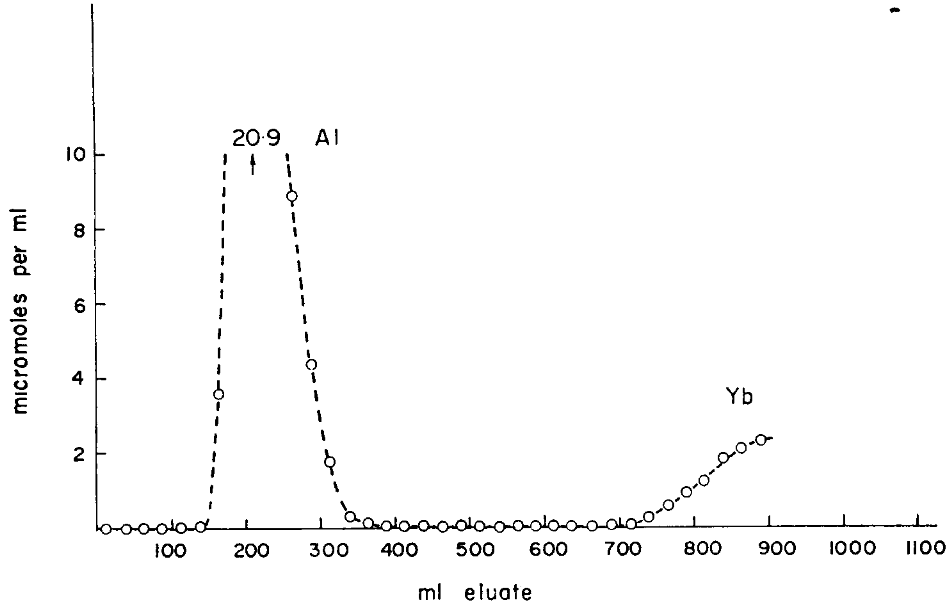

FIG. 1.—Elution curve for Al–Yb with 3·0*M* HCl in 50% ethanol.
Column of 60 ml (20 g) of AG50W-X8 resin, 200–400 mesh. Flow-rate 1·5 ± 0·3 ml/min.

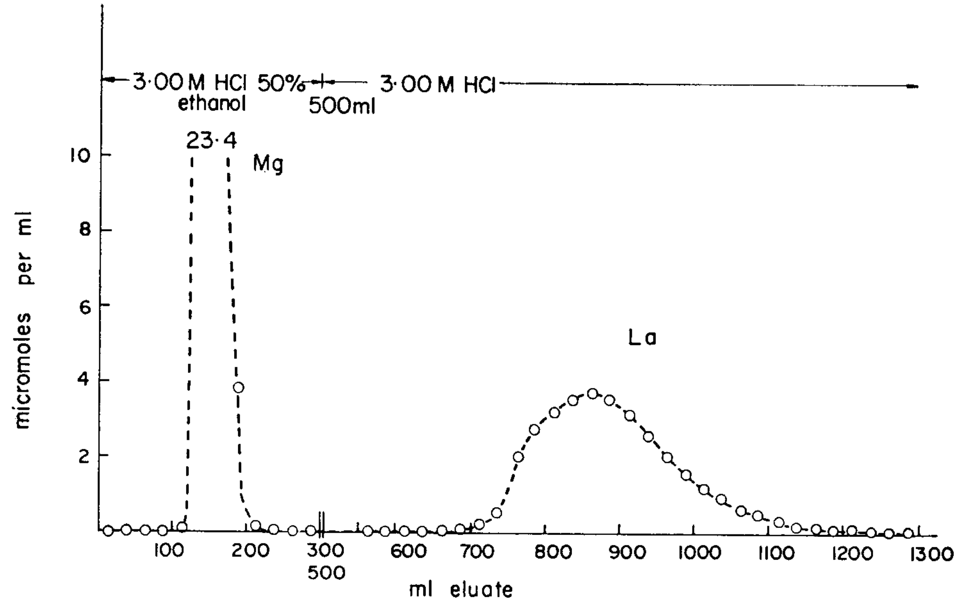

FIG. 2.—Elution curve for Mg–La.
Column of 60 ml (20 g) of AG50W-X8 resin, 200–400 mesh. Flow-rates 1·5 ± 0·3 ml/min for ethanolic, 3·0 ± 0·3 ml/min for aqueous solution.

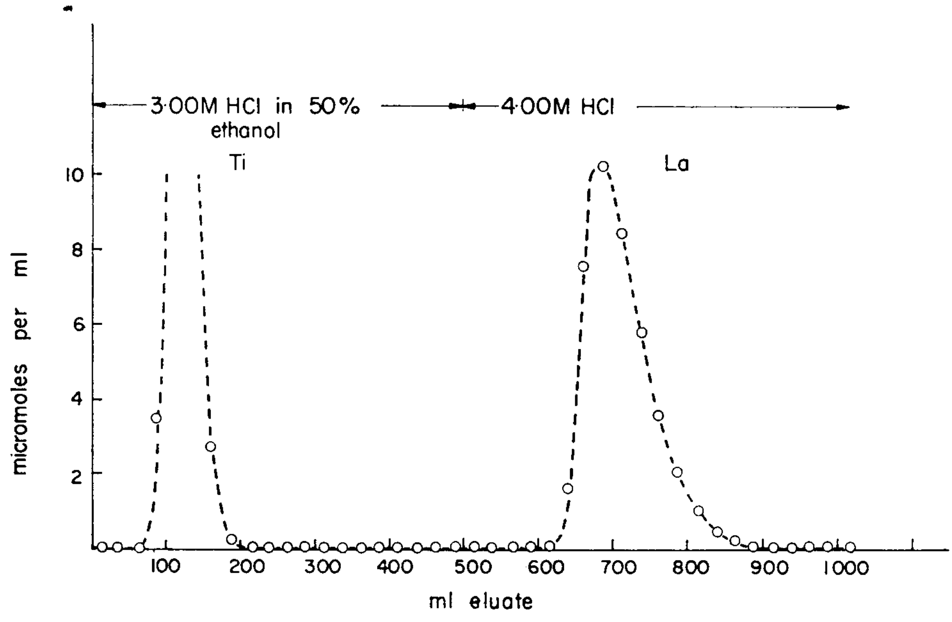

FIG. 3.—Elution curve for Ti(IV)–La.
Column of 60 ml (20 g) of AG50W-X8 resin, 200–400 mesh. Flow-rates 1·5 ± 0·3 ml/min for ethanolic, 3·0 ± 0·3 ml/min for aqueous solution.

Quantitative separations

Volumes of standard solutions of one rare earth and one other element in 0·1*M* hydrochloric acid were measured out in triplicate, mixed, and absorbed on a column of AG50W-X8 resin as described above. Solutions containing Ti(IV), Tl(III) and Bi(III) were absorbed from 0·5*M* hydrochloric acid. In the case of Ti(IV) these solutions also contained 0·5% of hydrogen peroxide Mixtures containing Pb were passed through the column in 3·0*M* hydrochloric acid in 50% ethanol. The "other elements" were then eluted with 300 ml of 3·00*M* hydrochloric acid in 50% ethanol. Aluminium required 500 ml of this eluent. Flow-rates were 1·5 ± 0·3 ml/min. The eluates for Pb, Bi(III) and Tl(III) were taken from the beginning of the absorption step, the others from the beginning of the elution step. The rare earths were finally eluted with 500 ml of 4·00*M* hydrochloric acid at a flow-rate of 3·0 ± 0·3 ml/min. Ethanol and excess of acid were removed from the eluates by evaporation and the amounts of the elements determined. The results are presented in Table II, and the methods used are summarized in Table III.

TABLE II.—QUANTITATIVE SEPARATIONS

Taken, *mg*		Found, *mg**	
Rare earth	Other element	Rare earth	Other element
Yb 168·1	Al 56·12	168·0 ± 0·2	56·10 ± 0·06
Yb 252·2	Al 1·403	252·1 ± 0·3	1·405 ± 0·005
†Yb 2·52	Al 224·5	2·54 ± 0·04	224·4 ± 0·2
Sc 45·10	Al 56·12	45·08 ± 0·05	56·10 ± 0·05
†Sc 0·451	Al 224·5	0·448 ± 0·005	224·6 ± 0·2
Gd 148·9	Al 56·12	148·8 ± 0·3	56·13 ± 0·06
La 140·1	Al 56·12	140·1 ± 0·2	56·09 ± 0·06
Yb 168·1	Ga 75·35	168·2 ± 0·2	75·40 ± 0·08
Yb 168·1	In(III) 112·5	168·1 ± 0·2	112·4 ± 0·2
Yb 168·1	Fe(III) 54·96	168·1 ± 0·1	54·98 ± 0·06
Yb 168·1	Ti(IV) 56·12	168·0 ± 0·2	56·10 ± 0·05
Yb 168·1	Be 18·22	168·2 ± 0·2	18·24 ± 0·04
Yb 168·1	Mg 24·81	168·1 ± 0·2	24·82 ± 0·03
Yb 168·1	U(VI) 229·6	168·2 ± 0·2	229·7 ± 0·2
Yb 168·1	Bi(III) 102·9	168·1 ± 0·2	102·8 ± 0·2
Yb 168·1	Tl(III) 103·6	168·1 ± 0·3	103·6 ± 0·1
Yb 168·1	Pb(II) 205·4	168·0 ± 0·2	205·5 ± 0·2
Yb 168·1	Cd 114·3	168·1 ± 0·2	114·2 ± 0·2
Yb 168·1	Zn 65·91	168·2 ± 0·2	65·90 ± 0·06
Yb 168·1	Cu(II) 64·33	167·9 ± 0·3	64·30 ± 0·08
Yb 168·1	Mn(II) 58·41	168·0 ± 0·2	58·43 ± 0·05
Yb 168·1	Ni(II) 55·98	168·2 ± 0·2	55·95 ± 0·08

* Mean of triplicate determinations.

† Al eluted with 600 ml of eluent.

DISCUSSION

The method described provides a useful means for the quantitative separation of the rare earths and scandium as a group from the common silicate-forming elements Al, Fe(III), Mg and Ti(IV), and also from Mn(II), U(VI), Be, Ga, In(III), Tl(III), Bi(III), Ni, Zn, Cu(II), Cd and Pb. Actual separations have been performed mainly for element-pairs with Yb as the rare earth. Because Yb is the least strongly absorbed of the rare earths (except Lu), it is reasonable to assume that separations will also be quantitative for the other rare earths. Elements such as Co(II), Hg(II), Li, Na, V(V), Mo(VI), Au(III) and the platinum metals have not been investigated in detail, but according to their distribution coefficients[9] they should also be eluted with 3·0*M* hydrochloric acid in 50% ethanol.

The presence of the organic solvent increases the separation factor for the Yb–Al pair, the most critical one, to $\alpha_{\mathrm{Al}}^{\mathrm{Yb}} = 4{\cdot}2$ as compared with 2·3 in aqueous 1·75*M*

TABLE III.—ANALYTICAL PROCEDURES

Element	Method
Sc, Zn, Pb, Bi(III)	Titration with EDTA, Xylenol Orange as indicator.
Tl(III)	Titration with EDTA in the presence of tartrate at pH 10, Methylthymol Blue as indicator.
Mg	Titration with EDTA, Eriochrome Black T as indicator.
Mn(II)	Titration with EDTA in presence of hydroxylamine hydrochloride, Methylthymol Blue as indicator.
Cd	Titration with EDTA, Methylthymol Blue as indicator.
Ni	Titration with EDTA, Murexide as indicator.
Al	Excess of CDTA, back-titration with Zn(II), Xylenol Orange as indicator.
Fe(III)	Dichromate titration after reduction to Fe(II).
Cu(II)	Iodide–thiosulphate titration.
La, Gd, Yb	Gravimetrically as oxides after precipitation with oxalic acid.
In(III), Ga, Ti(IV), U(VI)	Gravimetrically as oxides after precipitation with ammonia solution.
Be	Gravimetrically as benzoylacetonate.

hydrochloric acid,[8] while that for the La–Al pair increases from 4·1 to 12·2. As a result larger amounts of rare earths can be separated from other elements in hydrochloric acid–ethanol mixtures. Furthermore, the tailing which Al shows on elution with 1·75*M* hydrochloric acid[8] is reduced considerably, mainly because the distribution coefficient of Al is lower in 3·0*M* hydrochloric acid in 50% ethanol than in 1·75*M* aqueous hydrochloric acid (Table I).

Separations are sharp and quantitative for amounts up to 1·5 mmole of Yb from several mmole of other elements on a 60-ml resin column. As little as 0·451 mg of Sc can be separated from about 200 mg of Al or even larger amounts of other elements and determined with an error of about 1%.

The only elements which accompany the rare earths are Th, Zr, Hf, Ba and Sr completely, and Ca, K and Rb partially. Up to at least 200 mg of Th are retained by the column when the rare earths are eluted with 4·0*M* hydrochloric acid. Zr and Hf can be separated from the rare earths and Sc by eluting the latter group with 0·25*M* sulphuric acid from a column of AG1-X8 anion-exchange resin, on which Zr and Hf are retained. Ba, Sr, Ca, K and Rb can be eluted from a 60-ml column of AG50W-X8 resin with 1·75 or 2·0*M* nitric acid, the rare earths and Sc being retained.

The separation of Al from the rare earths is much less satisfactory when 100–200 mesh resin is used instead of 200–400 mesh resin, yet Fe(III) and many of the other elements can be separated quite satisfactorily from the rare earths by use of resin of larger particle size.

Zusammenfassung—Dreiwertige seltene Erden und Sc werden durch Kationenaustauschchromatographie von den silikatbildenden Elementen Al, Fe(III), Mg und Ti(IV) sowie von Mn(II), U(VI), Be, Ga, In(III), Tl(III), Bi(III), Ni, Zn, Cu(II), Cd und Pb abgetrennt. Die anderen Elemente werden von einer Säule von 60 ml Harz AG50W-X8 (200–400 mesh) mit 3,0*M* HCl eluiert, die 50% Äthanol enthält; die seltenen Erden bleiben zurück. Die Trennfaktoren sind größer als in wäßriger Salzsäure. Th, Zr, Hf, Ba, Sr, Ca, K und Rb sind die einzigen Elemente, die die Gruppe der seltenen Erden begleiten; sie können jedoch mit anderen beschriebenen Methoden leicht abgetrennt werden. Die einschlägigen Verteilungskoeffizienten, Elutionskurven und genaue Ergebnisse quantitativer Abtrennungen synthetischer Gemische werden vorgelegt.

Résumé—On sépare, par chromatographie d'échange cationique, les terres rares trivalentes et Sc des éléments générateurs de silicate Al, Fe(III), Mg et Ti(IV) et aussi de Mn(II), U(VI), Be, Ga, In(III), Tl(III), Bi(III), Ni, Zn, Cu(II), Cd et Pb. Les autres éléments sont élués par HCl 3,0M contenant 50% d'éthanol d'une colonne de 60 ml de résine AG50W-X8 (200–400 mesh) tandis que les terres rares sont retenues. Les facteurs de séparation sont plus élevés qu'en acide chlorhydrique aqueux. Th, Zr, Hf, Ba, Sr, Ca, K et Rb sont les seuls éléments qui accompagnent le groupe des terres rares, mais ils peuvent être aisément séparés par d'autres méthodes que l'on décrit. On présente les coefficients de partage correspondants, les courbes d'élution et les résultats exacts de séparations quantitatives de mélanges synthétiques.

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COMPLEXES FORMED IN THE CHLOROFORM EXTRACTION OF URANIUM(VI) WITH OXINE

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Summary—Equilibrium distribution ratios have been determined for uranium(VI) with oxine between chloroform and $0{\cdot}1M$ perchlorate as a function of pH and reagent concentration at 20°. It is concluded that the extractable complex is UO_2Ox_2HOx. The equilibrium constants for the extraction of uranium have been determined as $K_{U,1} = [UO_2Ox_2HOx]_0/[UO_2^{2+}][Ox^-]^3[H^+] = 10^{36.18}$ at low pH and $K_{U,2} = [UO_2Ox_2HOx]_0/[UO_2Ox_2OH^-][Ox^-][H^+]^2 = 10^{25.40}$ at high pH.

THE first stoichiometric study of the distribution equilibrium of uranium(VI) with oxine (HOx refers to the neutral oxine molecule) was carried out by Dyrssen and Dahlberg.[1] They reported that uranyl ion was extracted as UO_2Ox_2 but not as UO_2Ox_2HOx, because the distribution ratio was proportional to the square of the concentration of oxinate anion, though the data were somewhat scattered. Clifford, Bullwinkel, McClaine, and Noble[2] found that uranyl ion was extracted from a carbonate solution at high pH into isobutyl methyl ketone containing oxine and quarternary alkylammonium chloride, as the uranyl trioxinate ion associated with the ammonium cation. Starý,[3] who carried out a systematic study of the solvent extraction of 32 metal oxinates, reported that uranyl ion was extracted into chloroform as UO_2Ox_2HOx.

The inconsistencies in the literature regarding the extractable uranium(VI)–oxine complex indicate the need for further studies of the distribution behaviour of uranium between chloroform and an aqueous perchlorate solution. It is of interest to know whether the uranium–oxine complex in the organic phase has an additional molecule of oxine and to what extent the additional molecule of oxine influences the distribution curve.

EXPERIMENTAL

Reagents

All the reagents used were of guaranteed reagent grade. The chloroform used contained 0·5% v/v ethanol. The distilled water was boiled before use, to remove carbon dioxide. Sodium hydroxide solutions were prepared by diluting aqueous saturated solution of sodium hydroxide with air-free water, and stocked in polyethylene bottles.

Procedures

Preparation of UO_2Ox_2HOx. To 200 ml of a solution containing 1 g of uranyl nitrate hexahydrate, was added 1 g of oxine in 100 ml of $1M$ hydrochloric acid. The solution was heated to about 70° and $2M$ ammonia was added dropwise, with stirring by magnetic stirrer, until no further precipitate appeared on addition of ammonia. After digestion for an hour the precipitate was filtered off on a glass filter and washed with hot distilled water. The product was then dried in a desiccator over phosphorus pentoxide. The composition of the complex was verified from the weight loss on ignition to uranium oxide in platinum crucibles at 950° and by bromometric titration of oxine in the complex.

Distribution measurements. A volume (5 ml) of chloroform containing known amounts of oxine and UO_2Ox_2HOx was shaken with an equal volume of an aqueous perchlorate solution for an

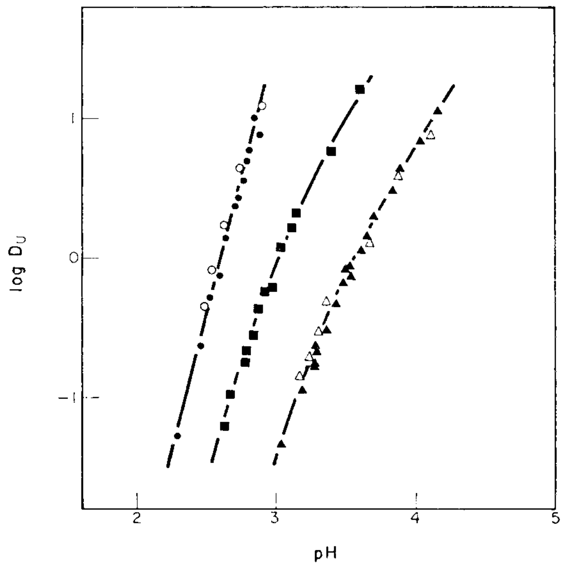

FIG. 1.—Distribution of U as a function of pH (acid region).
Init. conc. of U in the organic phase: solid symbols, 1·42 × $10^{-4}M$; open symbols, 1·42 × $10^{-5}M$. Init. conc. of HOx in the organic phase: circles 0·100M; squares, 0·030M; triangles, 0·010M.

$$\left(\frac{\Delta \log D_U}{\Delta \log [\mathrm{HOx}]_i}\right)_{\mathrm{pH}=3} \sim 3$$

hour. The pH was adjusted by addition of sodium hydroxide and perchloric acid, and sodium perchlorate was added to give a constant ionic strength of 0·1M. After equilibrium had been reached, the mixture was centrifuged and a portion (1–2 ml) of the organic phase was taken for uranium determination with arsenazo-III. The pH of the aqueous phase was measured.

Determination of uranium with arsenazo-III. Uranium in the organic phase was determined by the procedure of Onishi and Toita.[4] The sample solution was heated to remove chloroform and excess of oxine. The remaining residue was dissolved in 6M hydrochloric acid and fine zinc powder was added. After about 30 min, when the zinc powder had dissolved completely, 1 ml of 0·1% solution of arsenazo-III was added per 10 ml of aqueous solution and the absorbance at 670 nm was measured against a reagent blank.

Determination of pOx. The value of pOx (−log [Ox^-]) is calculated by equation (1) from the pH and the initial concentration of oxine in the organic phase, $[\mathrm{HOx}]_i$.

$$\mathrm{pOx} = \log\left(1 + \frac{D_R[\mathrm{H}^+]}{K_1} + \frac{[\mathrm{H}^+]}{K_2} + \frac{[\mathrm{H}^+]^2}{K_1K_2}\right) - \log\,[\mathrm{HOx}]_i \qquad (1)$$

where K_1 and K_2 are the acid dissociation constants of oxinium ion and oxine, D_R is the distribution coefficient of oxine, HOx, and the concentration of hydrogen ion is calculated as pH = −log [H^+] for convenience. D_R, pK_1, and pK_2 were determined from the distribution results for oxine, obtained in preliminary experiments under the same distribution conditions as for uranium. The analysis of the distribution data was carried out according to Dyrssen.[5] The following values were obtained and adopted in this work: log D_R = 2·64, pK_1 = 5·14, and pK_2 = 9·74; they are in good agreement with published values.[5,6]

All experiments were carried out in a temperature-controlled room at 20°.

RESULTS AND DISCUSSION

Distribution of uranium(VI) at low pH

The distribution curves for uranium in the low pH region are given in Fig. 1 (D_U is the distribution ratio of uranium).

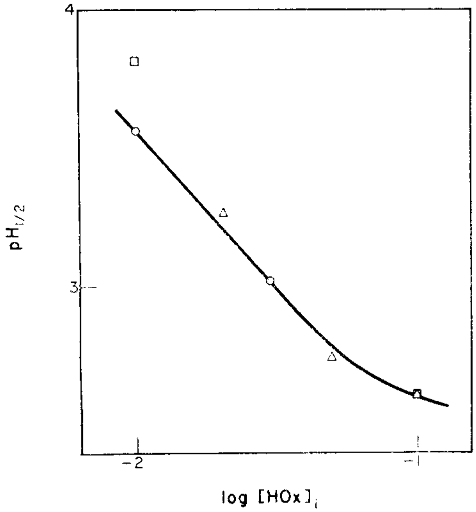

FIG. 2.—Comparison of published $pH_{1/2}$ values. Δ, Dyrssen;[1] □, Starý;[3] ○, this work.

The $pH_{1/2}$ values are determined to be 2·61, 3·02 and 3·56 for $0{\cdot}1M$, $0{\cdot}03M$, and $0{\cdot}01M$ oxine in chloroform respectively, and they are independent of the initial concentration of uranium examined ($1{\cdot}42 \times 10^{-5}$ and $1{\cdot}42 \times 10^{-4}M$).

Starý[3] reported the $pH_{1/2}$ values obtained under similar experimental conditions to be 2·60 and 3·81 for $0{\cdot}1M$ and $0{\cdot}01M$ oxine respectively. For $0{\cdot}1M$ oxine the $pH_{1/2}$ value determined in this experiment is in good agreement with that given by Starý, but that for $0{\cdot}01M$ oxine is a little smaller.

If the data given by Dyrssen and Dahlberg[1] are plotted as $\log D_U$ against pH ($-\log [H^+] + 0{\cdot}09$), the $pH_{1/2}$ values 2·61, 2·74 and 3·26 are obtained for 0·1, 0·05, and $0{\cdot}02M$ oxine respectively. The agreement is very good as shown in Fig. 2.

The curves in Fig. 1 become steeper at decreasing pH because oxine is transferred to the aqueous phase as oxinium ions. It can be seen that $\Delta \log D_U/\Delta \log [HOx]_i$ is close to 3 at pH 3, and a similar slope is obtained when the earlier data of Dyrssen and Dahlberg[1] are plotted. Thus the uranyl ion cannot be extracted as UO_2Ox_2 as suggested by them, and the dominating complex in the range 0·01–$0{\cdot}1M$ oxine is more likely to be UO_2Ox_2HOx.

In order to test the reaction

$$UO_2^{2+} + 3Ox^- + H^+ \rightleftharpoons UO_2Ox_2HOx\ (\text{org}), \tag{2}$$

$D_U \sim [UO_2Ox_2HOx]_0/[UO_2^{2+}]$ was plotted as $\log D_U + \text{pH}$ against pOx (Fig. 3). The points for the three different concentrations of oxine fall practically on a single curve with limiting slope −3. The fall-off from slope −3 can be explained by the appearance of uranyl oxinate complexes in the aqueous phase on increasing $[Ox^-]$. From the limiting slope it is possible to calculate the constant for equilibrium (2):

$$K_{U,1} = \frac{[UO_2Ox_2HOx]_0}{[UO_2^{2+}][Ox^-]^3[H^+]} = 10^{36\cdot18} \tag{3}$$

Distribution of uranium(VI) at high pH

The distribution curves in the high pH region are shown as a function of pH in

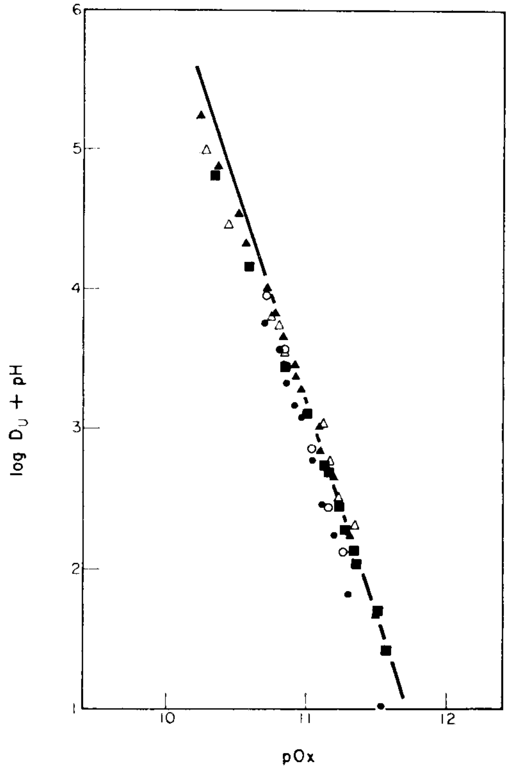

FIG. 3.—A plot of log D_U + pH *vs.* pOx.
For symbols see Fig. 1. Slope of the straight line is −3.

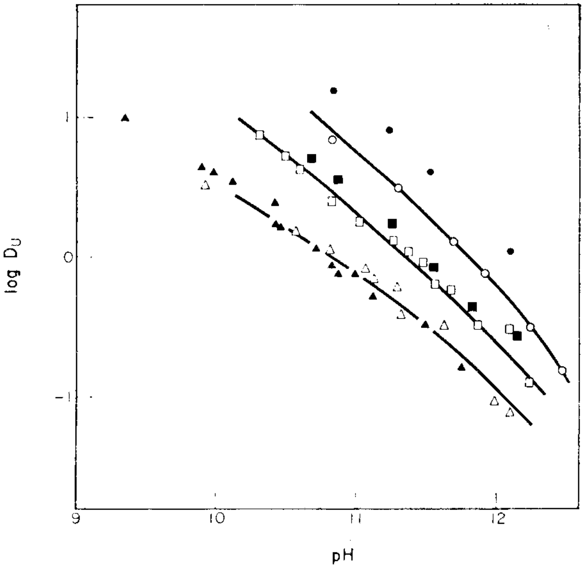

FIG. 4.—Distribution of U as a function of pH (alkaline region).
For symbols see Fig. 1.

$$\left(\frac{\Delta \log D_U}{\Delta \log [\mathrm{HOx}]_i}\right)_{\mathrm{pH}=11} \sim 1$$

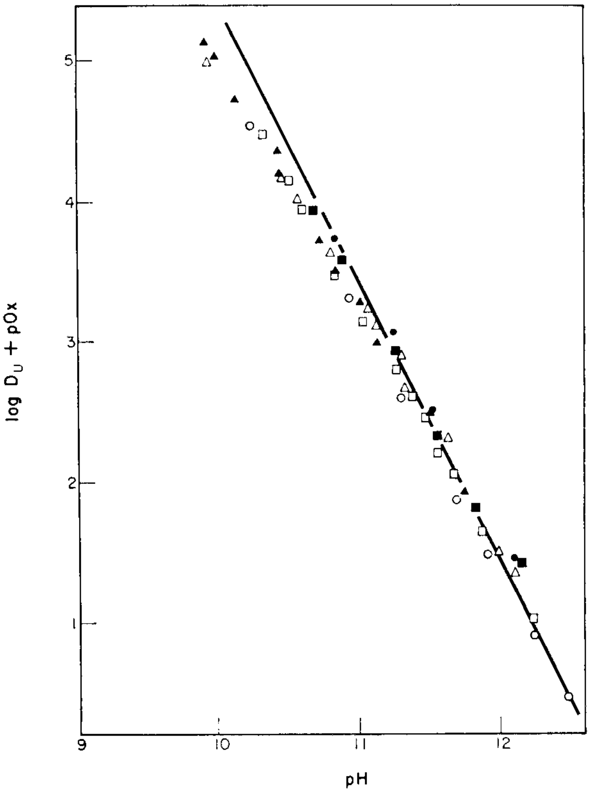

FIG. 5.—A plot of log D_U + pOx *vs.* pH.
For symbols see Fig. 1. Slope of the straight line is −2.

Fig. 4. The distribution ratio of uranium decreases with increasing pH in the alkaline region, as was pointed out by Dyrssen and Dahlberg.[1] An interesting fact is that the distribution ratio is higher with $1{\cdot}42 \times 10^{-4}M$ uranium than $1{\cdot}42 \times 10^{-5}M$. The difference becomes distinguishable with increasing concentration of oxine. These results may suggest that some polymerized uranium–oxine complexes are present in the organic phase in addition to UO_2Ox_2HOx when the concentration of uranium(VI) is $1{\cdot}42 \times 10^{-4}M$, and that oxine plays an important role in the formation of such complexes. However, the absorption spectra of uranium–oxine complex in the organic phase were not changed significantly by changes in the concentration of oxine (0·01–0·1*M*) or uranium ($7{\cdot}10 \times 10^{-5}$ and $1{\cdot}42 \times 10^{-4}M$).

The slopes of the distribution curves (approximately −1) in Fig. 4 indicate that a negatively charged complex is formed in the aqueous phase. Furthermore, $\Delta \log D_U / \Delta \log [HOx]_i$ is approximately 1 at pH 11. This indicates that $UO_2Ox_2OH^-$ is formed in the aqueous phase.

In order to test the reaction

$$UO_2Ox_2HOx(org) \rightleftharpoons UO_2Ox_2OH^- + 2H^+ + Ox^- \qquad (4)$$

$D_U \sim [UO_2Ox_2HOx]_0/[UO_2Ox_2OH^-]$ was plotted as $\log D_U$ + pOx against pH

(Fig. 5). The points for the three different concentrations of oxine fall practically on a single curve with a limiting slope of -2. From this slope

$$K_{\mathrm{U},2} = \frac{[\mathrm{UO_2Ox_2HOx}]_0}{[\mathrm{UO_2Ox_2OH^-}][\mathrm{H^+}]^2[\mathrm{Ox^-}]} = 10^{25\cdot 40} \qquad (5)$$

can be calculated. At lower pH the results deviate from the straight line with slope -2, indicating that UO_2Ox_2 is present in the aqueous phase in addition to $UO_2Ox_2OH^-$. Thus, the results do not support the existence of the complex, $UO_2Ox_3^-$, in the aqueous phase as suggested by Dyrssen and Dahlberg[1] or by Bullwinkel and Noble.[5] In fact Dyrssen and Dahlberg's results only prove the existence of a negatively charged complex, $UO_2Ox_n(OH)_{3-n}^-$, and the absorption spectra given by Bullwinkel and Noble[5] indicate that $UO_2Ox_3^-$ is changed when a salt (*e.g.*, $[(C_6H_5)_4As^+][UO_2Ox_3^-]$) is dissolved in aqueous solution.

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Zusammenfassung—Die Verteilungsverhältnisse im Gleichgewicht wurden für Uran(VI) mit Oxin zwischen Chloroform und 0,1*M* Perchlorat als Funktion von pH und Reagenskonzentration bei 20° bestimmt. Es wird geschlossen, daß der extrahierbare Komplex UO_2Ox_2HOx ist. Die Gleichgewichtskonstanten zur Extraktion von Uran wurden bestimmt als $\mathrm{K}_{\mathrm{U},1} = [UO_2Ox_2HOx]_0/[UO_2^{2+}][Ox^-]^3[H^+] = 10^{36,18}$ bei niedrigem pH und $K_{\mathrm{U},2} = [UO_2Ox_2HOx]_0/[UO_2Ox_2OH^-][Ox^-][H^+]^2 = 10^{25,40}$ bei hohem pH.

Résumé—On a déterminé les rapports de partage à l'équilibre pour l'uranium(VI) avec l'oxine entre le chloroforme et le perchlorate 0,1*M* en fonction du pH et de la concentration en réactif à 20°. On en conclut que le complexe extractible est UO_2Ox_2HOx. On a déterminé que les constantes d'équilibre pour l'extraction de l'uranium sont $K_{\mathrm{U},1} = [UO_2Ox_2HOx]_0/[UO_2^{2+}][Ox^-]^3[H^+] = 10^{36,18}$ à bas pH et $K_{\mathrm{U},2} = [UO_2Ox_2HOx]_0/[UO_2Ox_2OH^-][Ox^-][H^+]^2 = 10^{24,40}$ à pH élevé.

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BESTIMMUNG VON IONENBEWEGLICHKEITEN IN NICHTWÄSSRIGEN ELEKTROLYTLÖSUNGEN—I

DIE MESSUNG DER ÜBERFÜHRUNGSZAHL DER Na-IONENKOMPONENTE IN WASSERFREIEM METHANOL NACH DEM RADIOISOTOPENVERFAHREN MIT HILFE DES γ-STRAHLERS ^{24}Na

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Zusammenfassung—Zur Überprüfung der Anwendungsmöglichkeit des Radioisotopenverfahrens, das Überführungszahlen nach der Methode der direkten Grenzflächenwanderunggestattet, auf Bestimmungen in nichtwässrigen Elektrolytlösungen wurde die Überführungszahl der Na-Ionenkomponente in 0,01n wasserfreier NaCl-Methanol-Lösung bei 25° unter Verwendung des γ-Strahlers ^{24}Na ermittelt. Die erhaltenen Ergebnisse sind in guter Übereinstimmung mit den mit Hilfe herkömmlicher Meßverfahren erhaltenen Werte. Die Genauigkeit und Konzentrationsgrenze des Meßverfahrens und seine Vorteile gegenüber den optischen Methoden bei der Überführungsmessung in nichtwässrigen Medien werden diskutiert.

IONENBEWEGLICHKEITEN sind eine wichtige Größe zur Ermittlung der Struktur von Elektrolytlösungen, da sie Aussagen über den Zustand des gelösten Elektrolyten und somit über seine Wechselwirkung mit dem Lösungsmittel gestatten. Sie sind bekanntlich aus kombinierten Leitfähigkeits- und Überführungszahlmessungen zu errechnen.

Da die zu ermittelnde Abhängigkeit dieser Meßgrößen von den Versuchsbedingungen (Konzentration, Druck, Temperatur usw.) z.T. sehr gering ist, muß ihre Messung mit hoher Präzision erfolgen, um für theoretische Problemstellungen hinreichend genaue Aussagen zu erhalten.

In der Literatur ist nun eine große Anzahl von exakten Meßdaten der Leitfähigkeit und Überführungszahl in wässrigen Elektrolytlösungen bekannt.[1] Aus ihnen lassen sich die entsprechenden Ionenbeweglichkeiten im wässrigen Medium, ihre Temperatur- und Konzentrationsabhängigkeit und ihre Grenzionenleitfähigkeit mit hinreichender Genauigkeit ermitteln. Die von McInnes, Longsworth und Gordon[2–8] und ihren Schulen zu hoher Präzision entwickelte Methode der Überführungszahlbestimmung nach dem Grenzflächenverfahren ermöglicht ferner die Überprüfung der Debye-Hückel-Onsager-Theorie in wässrigem Medium, zu der Überführungszahlen insofern sehr geeignet sind, da ihre Konzentrationsabhängigkeit Aussagen über den speziellen Einfluß des elektrophoretischen Effektes zuläßt.[9] Dagegen liefern Leitfähigkeitsmessungen nur Aussagen über den gemeinsamen Einfluß des elektrophoretischen und Relaxations-Effektes.

Auf dem Gebiet der nichtwässrigen Elektrolytlösungen liegt ebenfalls eine große Zahl von exakten Leitfähigkeitsmessungen vor.[1,10] Dagegen sind Präzisionsmessungen von Überführungszahlen in nichtwässrigen Lösungsmitteln außerordentlich spärlich vorhanden. Dieser Mangel an exakten Überführungsmessungen beschränkt in vielen Fällen die Ermittlung der Einzelionenleitfähigkeit und damit der Ionenbeweglichkeit, so daß das reichhaltige Material an präzisen Leitfähigkeitsmessungen für die Bestimmung dieser Größe nicht voll ausgenutzt werden kann.

Von den verschiedenen Autoren wird daher auf die Notwendigkeit der Kenntnis der Ionenbeweglichkeit für die weitere Erforschung nichtwässriger Elektrolytlösungen immer wieder mit Nachdruck hingewiesen.[11–18] Überführungsmessungen in nichtwässrigen Medien würden auch eine weitere Überprüfung der Gültigkeit der Elektrolyttheorien für diese Lösungsmittel ermöglichen.

Die Kenntnis der Ionenbeweglichkeit in nichtwässrigen Elektrolytlösungen dürfte sich auch auf dem Gebiete der Papierchromatographie und Papierelektrophorese als sehr fruchtbar erweisen, da dann theoretische Voraussagen über die Trennbarkeit von Elektrolytmischungen in den betreffenden Lösungsmitteln möglich sind.

Zur Ermittlung der Grenzionenleitfähigkeit in nichtwässrigen Elektrolytlösungen müssen Überführungs- und Leitfähigkeitsmessungen in diesen Medien bis zu Elektrolytkonzentrationen von 10^{-3} bis 10^{-4}n bzw. bei noch geringerer Konzentration durchgeführt werden, um die Ionenassoziation in diesen Lösungsmitteln mit Sicherheit ausschließen zu können.

Leitfähigkeitsmessungen sind bei geringer Konzentration durchgeführt worden. Der Mangel an exakten Werten für die Ionenbeweglichkeit in nichtwässrigen Elektrolytlösungen beruht daher in erster Linie auf dem Unvermögen der herkömmlichen Meßverfahren, Überführungsmessungen bei derartig geringen Elektrolytkonzentrationen durchzuführen. Die drei Verfahren zur Bestimmung von Überführungszahlen sind *1.* das Hittorf-Verfahren, *2.* das EMK-Verfahren und *3.* die Methode der Grenzflächenwanderung.

Das Hittorf-Verfahren ist wegen seiner unteren Konzentrationsgrenze von 0,01n für Präzisionsmessungen von Überführungszahlen in stark verdünnten nichtwässrigen Elektrolytlösungen ungeeignet.[16]

Mit dem EMK-Verfahren sind einige Meßreihen der Überführungszahlen in nichtwässrigen Elektrolytlösungen bis herab zu einer Konzentrationsgrenze von 10^{-3}n durchgeführt worden.[19–22] Die Genauigkeit des Verfahrens beruht aber auf der Reversibilität und Reproduzierbarkeit der verwendeten Elektroden, die in nichtwässrigen Medien eingeschränkt sind, so daß dieses Verfahren nur bedingt einsatzfähig ist.

Dagegen ist das Grenzflächenverfahren bereits mit Erfolg zur Präzisionsmessung von Überführungszahlen in nichtwässrigen Medien herangezogen worden.[11,14,23–25] Seine Fehlergrenze beträgt 0,03 % und ist somit hinreichend.[16]

Bei der herkömmlichen Verfolgung der im elektrischen Felde stattfindenden Grenzschichtwanderung mittels optischer Methoden ist die untere Konzentrationsgrenze des Grenzflächenverfahrens durch die Empfindlichkeit begrenzt, mit der unter Ausnutzung des Unterschiedes in der Farbe bzw. in den Brechungsindices der überschichteten Lösungen die Grenzschicht noch lokalisiert werden kann. Diese Grenze liegt allgemein bei $5 \cdot 10^{-3}$n. Unter Anwendung der Schlieren-Methode auf die Grenzschichterkennung kann diese Konzentrationsgrenze noch unterschritten werden. Jedoch erfordert das Schlieren-Verfahren einen rechteckigen Querschnitt der Wanderungsstrecke, was eine unsymmetrische Temperaturverteilung im Meßrohr bedingt, die sich auf die Stabilität der Grenzschicht sehr nachteilig auswirkt.

Gordon versuchte diesen Nachteil des optischen Erkennungsverfahrens zu beseitigen, indem er den an der Grenzschicht erfolgenden Leitfähigkeitssprung der

Elektrolytlösungen zur Grenzschichtlokalisierung verwendete.[26] Mit diesem Leitfähigkeitsverfahren konnte er eine Konzentrationsgrenze von 10^{-3}n erreichen.

Am günstigsten dürfte die Messung von Überführungszahlen in nichtwässrigen Medien mit dem in unserem Labor entwickelten Radioisotopenverfahren erfolgen, das die Grenzschicht zwischen einer inaktiven und einer mit β- bzw. γ-Radioisotopen markierten radioaktiven Lösung mit Hilfe geeigneter Strahlendetektoren zu lokalisieren gestattet.[27–34]

H. J. Schiff hat zuerst im Rahmen seiner Dissertation die Wanderung einer mit β-Strahlern markierten Grenzschicht aktiv/inaktiv mit Hilfe von Endfensterzählrohren verfolgt. Da dieser Teil seiner Dissertation nicht veröffentlicht wurde, erhielten wir erst lange nach Beginn unserer eigenen Untersuchungen durch eine Monographie[16] davon Kenntnis. Schiff gelang es aber nicht, Überführungszahlen nach seiner Methode zu messen, da er aufgrund eines prinzipiell falschen Ausblendmechanismus radioaktive Lösungen einer Aktivitätskonzentration von >1 mCi/ml benötigt, die ihm nicht zur Verfügung standen. Die erforderlichen Aktivitäts-Konz. für unser β- bzw. γ-Radioisotopenverfahren liegen zwischen 0,1 bis 5 μCi/ml.

Mit diesem Verfahren gelingt es, Überführungszahlen in wässrigen Medien noch bei einer geringeren Konzentration als 10^{-4}n zu messen. Dabei zeigt es sich, daß eine prinzipielle untere Konzentrationsgrenze existiert, bis zu der Grenzschichten zwischen chemisch verschiedenen Lösungen noch stabil sind.[35] Diese prinzipielle untere Konzentrationsgrenze des Grenzflächenverfahrens kann mit Hilfe der Radioisotopenmethode überwunden werden, indem die Grenzschicht zwischen zwei chemisch identischen Lösungen erzeugt wird, die sich allein aufgrund ihrer radioaktiven Markierung voneinander unterscheiden.[33] Durch Anwendung dieser sogenannten "identischen Methode" entfällt auch das Problem der Auffindung einer geeigneten Indikatorlösung, das bei dem herkömmlichen Grenzflächenverfahren oftmals nur mit erheblichen Schwierigkeiten zu lösen war.

Um nun die Anwendbarkeit des γ-Radioisotopenverfahrens zur Messung von Überführungszahlen in nichtwässrigen Elektrolytlösungen nachzuweisen, haben wir es anhand eines Elektrolytpaares überprüft, dessen Überführungszahl bereits mit herkömmlichen Methoden sehr genau bestimmt worden ist. Dafür schien uns die von Gordon[14] bei 25° ermittelte Überführungszahl der Na-Ionenkomponente in einer 0,01n Lösung von Natriumchlorid in wasserfreiem Methanol am geeignetsten zu sein, da bei dieser Konzentration sowohl die Kationen- als auch die Anionen-Überführungszahl bestimmt worden ist und ihre Werte die Bedingung $\sum_{\mathrm{R}} T_{\mathrm{R}} = 1$ innerhalb der sehr geringen Fehlergrenze erfüllen.

Als Radioisotop haben wir den starken γ-Strahler ^{24}Na verwendet, da seine Strahlung gut nachweisbar ist und er sich leicht durch Beschuß mit thermischen Neutronen aus ^{23}Na mittels einer (n, γ)-Reaktion erzeugen läßt. Aufgrund seiner Strahleneigenschaften und kurzen Halbwertszeit bietet er auch aus Strahlenschutzgründen Vorteile.

EXPERIMENTELLER TEIL

Die Meßzelle

Die Grenzschicht ^{24}NaCl/CdCl$_2$ sollte nach dem autogenen Verfahren[2] erzeugt werden, damit in die Meßzelle keine Hähne, die Dichtungs- und Kriechstromprobleme aufwerfen können, eingebaut werden müssen. Die in Abb. 1 gezeigte Meßzelle besteht daher aus einem 200 mm langen KPG-Rohr (Geräteglas; Innendurchmesser und Wandstärke je 3 mm), das am oberen Ende den Kathodenraum trägt und am unteren Ende mit einem als Anode dienenden Cadmium-Blech (5 × 5 × 2 mm; Reinheitsgrad: 99,9%, Fa. Degussa) verschlossen ist. Die Kalibrierung des KPG-Rohres, in dem die Grenzschichtwanderung stattfindet, erfolgte nach dem unter beschriebenen Verfahren[31] und ergibt einen relativen Fehler des Meßstreckenvolumens von $\pm 0{,}02_5$%.

Der mit einer Schliffhülse (NS 14,5) versehene Kathodenraum von 80 mm Länge und 19 mm

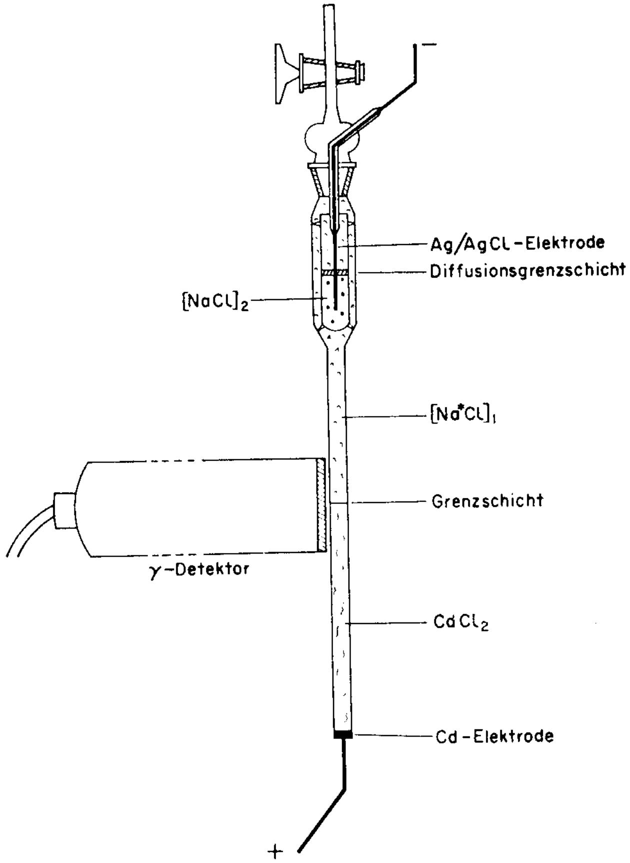

ABB. 1.—Autogene Zellefür Na^+—Überführungsmessungen.

Breitebesitzt einen 60 mm langen und 12 mm breiten Einsatz, in den während der Messung eine Ag/AgCl-Elektrode (Reinheitsgrad des Ag: 99,99%, Fa. Degussa) taucht.[31] Die Grenzschicht $NaCl/CdCl_2$ bildet sich nun bei Stromfluß an dem Cadmium-Blech selbständig aus.

Schwierigkeiten bereitete die Anbringung des Cadmium-Bleches an das KPG-Rohr. Das Cadmium-Blech wurde zuerst mit einem Gießharz (Araldit; F. Ciba, Basel) an das KPG-Rohr plan angekittet. Es zeigte sich aber, daß Araldit in Methanol etwas löslich ist, was anfangs zu zahlreichen fehlerhaften Messungen führte. Schließlich wurde in Palatal (Fa. BASF) der geeignete, gegen Methanol resistente Kleber gefunden.

Strahlungsmeßapparatur, Elektrolysestromkreis und Strommeßanordnung

Die Strahlungsmeßapparatur ist prinzipiell analog der in Ref. 31 beschriebenen aufgebaut. Als Detektor für die γ-Strahlung des ^{24}Na dient der γ-Szintillationszähler FH 439 mit dem quaderförmigen NaJ-Kristall von 8 mm Höhe, 25 mm Breite und 2 mm Stärke. Der Detektor ist mit einer Präzisionsspindel zwecks Positionswechsel verbunden.

Als Strahlenmeßgerät dient ein Ratemeter (Fa. Siemens; Typ GSDMZ; Zollnorm; Dämpfung: 0,5%; Verstärkung: 500–800 fach).

Die gewählte Diskriminatorhöhe von 30 V gestattet, daß einerseits der höher energetische Teil des Comptonkontinuums noch zur Messung herangezogen werden kann, andererseits aber Störeffekte kleiner Impulshöhe ausgeschaltet werden.

Als Registriergerät wird ein Potentiometerschreiber (Fa. Siemens; Typ MZ-A501) mit einer gewählten Papiervorschubgeschwindigkeit von 150 $mm.h^{-1}$ benutzt, deren Genauigkeit $\pm 3.10^{-2}\%$ beträgt.

Einige Grenzschichtdurchgänge der obigen Messungen wurden nicht analog sondern digital registriert.

Dazu wurde die in Ref. 33 erwähnte Methode der diskontinuierlichen Messung des Grenzschichtdurchganges herangezogen. Bei dieser Methode werden laufend Zählratenmessungen definierter Zeitvorwahl (z.B. 1 min) durchgeführt, die von einem Drucker registriert werden. Die einzelnen Zählratenmessungen erfolgen im Abstand der Druckzeit, die der Drucker zur Registrierung der Zählergebnisse benötigt. Zur Durchführung dieses Verfahrens wurde eine zweite elektronische Uhr (Fa. Siemens; Typ GS-Z/T) verwendet.

Die erste elektronische Uhr bestimmt nun die Meßzeit der einzelnen Impulsratenzählungen, die zweite die Gesamtzeit der Messung des Grenzschichtdurchganges. Aus der Differenz Gesamtzeit abzüglich Gesamtmeßzeit ist die Gesamtdruckzeit des Grenzschichtdurchganges errechenbar, woraus bei Kenntnis der Anzahl der Druckvorgänge der durchschnittliche Zeitbedarf eines einzigen Druckvorganges und somit der zeitliche Abstand zweier Zählratenmessungen ermittelt werden kann. Meßzelle und Detektor befinden sich zwecks Durchführung der Messung bei konstanter Temperatur in einem Luftthermostaten (Höhe = 540 mm; Tiefe = 570 mm; Breite = 650 mm; Temperaturkonstanz = ±0,1°), der gleichzeitig als Glovebox verwendet werden kann, so daß die eine Hälfte des Thermostaten als Arbeitsplatz, die andere zum Aufbau der Meßzelle mit Detektorapparatur dient. Seine Vorderwand besteht daher aus einer an- und abschraubbaren Plexiglasscheibe, die zwei kreisförmige Löcher mit je einem Flansch als Gummihandschuhhalterung hat.

Der Stromkreis besteht aus in Reihe geschalteten Stromkonstanthalter, Meßzelle und Strommeßgerät. Die Strommessung erfolgt mit Hilfe eines Mikroamperemeters (Fa. Marek, Bremen, Typ DX 1, Anzeigebereich in Stufen von 10^{-3} bis 10^{-6} A), dessen Genauigkeit ±0,03 % beträgt.

Herstellung der Lösungen

Wasserfreies Methanol: Käufliches Methanol (rein; Fa. Bayer, Leverkusen bzw. *p.a.*; Fa. Merck, Darmstadt) mit einem Wassergehalt von 0,1 % wurde nach dem Verfahren von Lund und Bjerrum absolutiert.[36] Die Destillation des Methanols erfolgte nach dem Umsatz mit Magnesiummethylat zuerst mit Hilfe eines Rotationsverdampfers, danach über eine Raschig-Kolonne von *ca.* 750 mm Länge. Der Wassergehalt des Destillats wurde nach dem Karl-Fischer-Verfahren zu $4 \cdot 10^{-3}$ % bestimmt. Bei allen Arbeitsoperationen wurde peinlich darauf geachtet, daß das Methanol nicht mit gefetteten Schliffen in Berührung kam.

Inaktive NaCl-Methanol-Lösung. Zur Herstellung von 100 ml einer 10^{-2}n NaCl-Methanol-Lösung wurden 58, 45 mg NaCl *p.a.* (Fa. E. Merck, Darmstadt), das mehrere Tage bei 150° getrocknet worden war, auf einer Mikrowaage unter Berücksichtigung des Luftauftriebes abgewogen. Die Einwaage wurde quantitativ in einen Jodzahlkolben überführt. Im geschlossenen Luftthermostaten wurden in trockener Luftatmosphäre bei einer Temperature von 25,0° ± 0,1° fünfmal je 20 ml Methanol aus einer geeichten Kolbenbürette in den Jodzahlkolben gegeben. Die Eichung der Kolbenbürette zeigt eine Abweichung von —0,33 ml bei einem Gesamtbürettenvolumen von 100 ml. Diese Abweichung wurde bei der Konzentrationsberechnung der Lösung berücksichtigt. Die Reproduzierbarkeit der Volumenabmessung beträgt $\pm 7{,}5 \cdot 10^{-3}$ %, die Genauigkeit der Konzentration der hergestellten Lösung $\pm 3 \cdot 10^{-2}$ %.

Radioaktive ^{24}*NaCl-Methanol-Lösung.* Das radioaktive ^{24}NaCl für die aktive 10^{-2} n Meßlösung wurde aufgrund der Kernreaktion $^{23}\text{Na}(n, \gamma)^{24}\text{Na}$ durch zwölfstündige Bestrahlung von 58,45 mg Natriumchlorid mit thermischen Neutronen (Fluß = $5{,}1 \cdot 10^{9}$ n.mm^{-2}.sec^{-1}) im BER-Kernreaktor des Hahn-Meitner-Instituts für Kernforschung in Berlin-Wannsee erzeugt. Wie die Berechnung zeigt,[37] beträgt die ^{24}Na-Aktivität ($t_{1/2}$ = 15,05 h) nach einer derartigen Bestrahlung 1800 μCi, diejenige des radioaktiven ^{38}Cl ($t_{1/2}$ = 37,5 min), das aufgrund der Kernreaktion $^{37}\text{Cl}(n, \gamma)^{38}\text{Cl}$ entstanden ist, 1064 μCi. Nach einer Wartezeit von 15 h ist die ^{38}Cl-Aktivität auf 53 pCi, also auf den *ca.* $10^{7\text{-ten}}$ Teil abgeklungen, so daß die Strahlung des radioaktiven Chlors die Messung nicht mehr stören kann. Die ^{24}Na-Aktivität beträgt nach einer Wartezeit von 15 h 900 μCi, so daß sich die Aktivitätskonzentration der zu messenden Lösung bei 100 ml Gesamtvolumen zu 9 μCi/ml ergibt. Diese aktive Lösung kann vier Tage lang (~6 Halbwertszeiten) für Messungen verwendet werden, da noch Lösungen einer Aktivitätskonzentration von 0,1 μCi/ml mit Hilfe des γ-Radioisotopenverfahrens gemessen werden können.

Um Substanzverluste auszuschließen, wurde das radioaktive ^{24}NaCl zusammen mit seinem geöffneten Bestrahlungsbehälter in vorgelegte, exakt abgemessene 100 ml wasserfreien Methanols gegeben und durch Rühren mit einem Magnetrührer über Nacht in Lösung gebracht. Als Strahlungsbehälter wurden Quarzampullen verwendet, die zum Schutz zusätzlich in eine Bestrahlungsdose aus Polyäthylen mit Quarzwolle verpackt wurden.

Strahlenschutzmaßnahmen. Die Gesamtdosisleistung von 1 mCi ^{24}Na in 1 m Abstand beträgt 42 mrad/h. Da allgemein in einer Entfernung von 0,5 m vom Präparat gearbeitet wurde, wo also eine Dosisleistung von 168 mrad/h herrschte, waren Abschirm-Maßnahmen erforderlich (Maximal zulässige Dosisleistung- 2,5 mrem/h). Alle Abfülloperationen wurden daher hinter einer 5-cm starken Bleiwand unter Verwendung von Manipulatoren durchgeführt. Die Berechnung der Dosisleistung für einen 10 cm von der Quelle entfernten Aufenthaltsort, der sich hinter dem Bleiabsorber befinden möge, ergibt unter Berücksichtigung des Massenschwächungskoeffizienten von 0,0432 den Wert 34 mr/h (Build up-Faktor: 2). Die maximale Reichweite der β-Strahlung des ^{24}Na beträgt in Luft 465 cm, in Methanol dagegen 7,5 mm und in Glas 2 mm. Befindet sich also das ^{24}NaCl in Methanol gelöst, so ist die β-Strahlung des ^{24}Na hinreichend abgeschirmt.

Durchführung der Messungen und Auswertung der Meßergebnisse

Zuerst wird die Elektrolysezelle im Luftthermostaten in mit P_2O_5 getrockneter Atmosphäre mit radioaktiver ^{24}NaCl-Methanol-Lösung bis zu einer Füllhöhe von 200 mm gefüllt. Unter Berücksichtigung des Innendurchmessers der Meßstrecke (3 mm) beträgt das Füllvolumen somit 1,4 ml an Aktiv-Lösung mit einer Gesamtaktivität von höchstens 13 μCi.

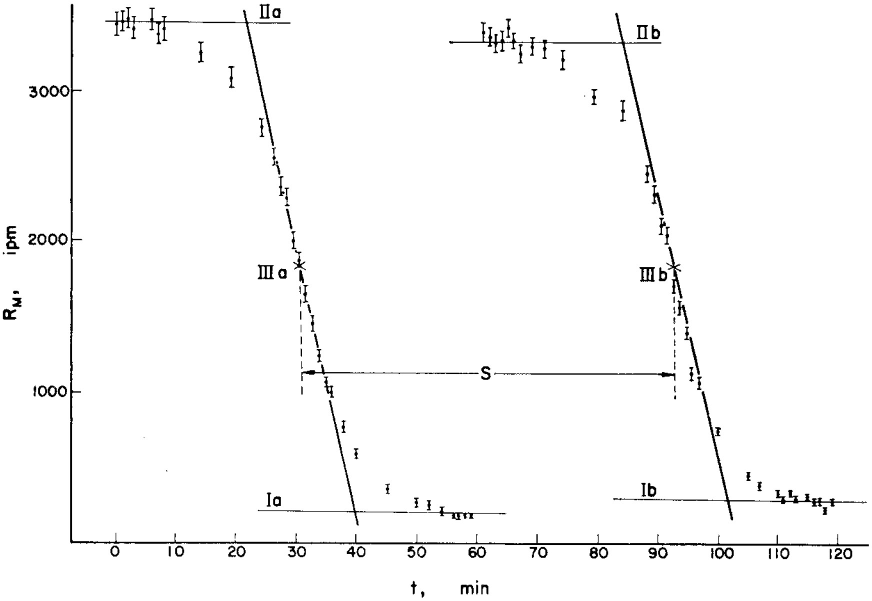

ABB. 2.—Zeitlicher Verlauf des Grenzschichtdurchganges

Der übrige Teil der Elektrolysezelle wird mit inaktiver NaCl-Methanol-Lösung gleicher Konzentration gefüllt. Diese Füllung ist mit Vorsicht und unter Beachtung völliger Konzentrationsgleichheit der verwendeten Lösungen durchzuführen, um eine Vermischung von Aktiv und Inaktivlösung zu verhindern. Eine Füllung der gesamten Elektrolysezelle mit Aktiv-Lösung ist wegen des dadurch bedingten hohen Strahlenuntergrundes ungünstig. Der möglichst gering zu haltende Strahlenuntergrund muß während der Messung konstant sein, um seinen Einfluß auf die Meßergebnisse ausschließen zu können. Jegliche Bleiabschirmungen sind zu vermeiden, da sie eine Erhöhung des Strahlenuntergrundes durch Rückstreuung bewirken.

Nach der Füllung wird die Zelle mit Hilfe eines Lotes senkrecht ausgerichtet und der Detektor im rechten Winkel an die Meßstrecke herangebracht so daß Meßstrecken- und Spindelachse zueinander parallel sind. Bei dieser Position kreuzt die Meßstreckenachse genau die Mitte der Detektorfront. Die Entfernung Detektor–KPG-Rohr ist folglich über den gesamten Bereich der Meßstrecke konstant. Nach Anbringung der Elektroden Temperierung der Meßzelle und Wahl des entsprechenden Ratemeter- und Schreiberbereiches wird die Messung durch Schließung des Stromkreises gestartet und wie schon beschrieben[31] durchgeführt.

Erfolgt die Registrierung des Grenzschichtdurchganges am Detektor mit Hilfe eines Schreibers, so erfolgt die Kurvenauswertung wie in Ref. 31 ausgeführt worden ist. Dient dagegen ein Drucker zur Registrierung, so wird die Auswertung wie folgt durchgeführt[33] (s. Abb. 2): Aus der in Abb. 2 gezeigten Punktfolge, die den zeitlichen Verlauf der Meßrate zweier Grenzschichtdurchgänge darstellt, werden mit Hilfe der Ausgleichsrechnung die Lagen je dreier Geraden I, II und III und ihrer gemeinsamen Schnittpunkte analytisch ermittelt. Zwei dieser Geraden sind Parallelen zur Abszisse, die dritte durchläuft den Wendepunkt der Punktfolge eines Grenzschichtdurchganges. Die Lage des Wendepunktes der Punktfolge, der auch bei diesem Auswertungsverfahren Bezugspunkt des Grenzschichtdurchganges ist, ergibt sich aus dem arithmetischen Mittel der Abszissenwerte der Schnittpunkte der Geraden III mit den Parallelen zur Abszisse. Die Zeit t, die die Grenzschicht zur Durchwanderung des Meßstreckenvolumens zwischen den beiden Detektorpositionen braucht, läßt sich aus der Entfernung der Wendepunkte der beiden Punktfolgen errechnen, die sich aus zwei Grenzschichtdurchgängen während einer Messung ergeben. Da auch die Konzentration c_{NaCl} der ^{24}NaCl-Methanol-Lösung und das Meßstreckenvolumen V bekannt sind, ferner die Stromstärke I während der Messung laufend ermittelt wird, sind unter Berücksichtigung der Faradayschen Konstanten F sämtliche Daten gegeben, um die Überführungszahl der Na-Ionenkomponente in wasserfreier NaCl-Methanol-Lösung aus der Bestimmungsgleichung

$$T_{\mathrm{Na(25^\circ C)}}^{\mathrm{NaCl-CH_3OH}} = \frac{c_{\mathrm{NaCl}} \cdot F \cdot V}{I \cdot t} \tag{1}$$

zu errechnen.

ZUSAMMENSTELLUNG UND DISKUSSION DER ERGEBNISSE

Tabelle I zeigt die Ergebnisse der Überführungszahlmessungen der Na-Ionenkomponente in wasserfreier 0,01n NaCl-Methanol-Lösung bei 25°. Aus diesen Meßergebnissen ergibt sich der Mittelwert für die unkorrigierte Überführungszahl der Na-Ionenkomponente zu $0{,}4582 \pm 0{,}0004$. Der auf Eigenleitfähigkeit des Lösungsmittels

$$\left(\frac{\chi_0}{\chi} = \frac{3 \cdot 10^{-7}\,\Omega^{-1}\,\mathrm{cm}^{-1}}{7{,}7 \cdot 10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}} = 4 \cdot 10^{-4}\right)$$

korrigierte Mittelwert[34] der Na-Überführungszahl beträgt 0,4584. Die Volumenkorrektur[14,24] ist im vorliegenden Fall nur $\pm 3 \cdot 10^{-6}$ und kann daher vernachlässigt werden.

Der aus den einzelnen Überführungszahlbestimmungen errechnete relative mittlere Fehler der Einzelmessung beträgt $\pm 0{,}08\,\%$, was im obigen Falle einem Absolutfehler von $\pm 4 \cdot 10^{-4}$ entspricht. Der relative mittlere Fehler des Mittelwertes ist $\pm 0{,}03\,\%$. Diese Fehler kennzeichnen die Reproduzierbarkeit der Messungen. Um ein Maß für die Genauigkeit der Messungen zu erhalten, wurde der relative Fehler der Überführungszahl nach dem Fehlerfortpflanzungsgesetz errechnet.

TABELLE I.—ZUSAMMENSTELLUNG DER ERGEBNISSE DER ÜBERFÜHRUNGSZAHLMESSUNGEN DER Na-IONENKOMPONENTE IN WASSERFREIER 0,01n NaCl-METHANOL-LÖSUNG

Nr.	$c \cdot 10^{+2}$ *mol/l.*	I, *mA*	V, *ml*	t, *sec*	S, *µCi/ml*	$T_{\mathrm{Na}}^{\mathrm{CH_3OH}}$	$T_{\mathrm{Na_{korr.}}}^{\mathrm{CH_3OH}}$
1	1,0033	0,4001	0,70686	3732	1,3	0,4583	0,4585
2	1,0033	0,4002	0,70686	3729	0,3	0,4586	0,4588
3	1,0014	0,4005	0,70686	3721	2,5	0,4583	0,4585
4	1,0018	0,4003	0,70686	3721	3,0	0,4586	0,4588
5	1,0018	0,4003	0,70686	3730	2,5	0,4576	0,4578
6	1,0018	0,4005	0,70686	3726	1,3	0,4579	0,4581

$F = 96493\ \mathrm{Cb_{abs}}$

Gordon:

$\bar{T}_{\mathrm{Na}}^{\mathrm{CH_3OH}} = 0{,}4583 \pm 0{,}0001$

$\bar{T}_{\mathrm{Na_{korr.}}}^{\mathrm{CH_3OH}} = 0{,}4585 \pm 0{,}0001$

Mittelwert dieser Messungen

$\bar{T}_{\mathrm{Na}}^{\mathrm{CH_3OH}} = 0{,}4582 \pm 0{,}0004$

$\bar{T}_{\mathrm{Na_{korr.}}}^{\mathrm{CH_3OH}} = 0{,}4584 \pm 0{,}0004$

Rel. mittlerer Fehler der Einzelmessung: $\pm 0{,}08\,\%$
Rel. mittlerer Fehler des Mittelwertes: $\pm 0{,}03\,\%$.

Aufgrund von Gleichung (1) lautet das Fehlerfortpflanzungsgesetz für die T_{Na}-Bestimmung:

$$(\Delta T_{\mathrm{Na}})_{\mathrm{rel}} = \pm\sqrt{(\Delta c_{\mathrm{NaCl}})^2_{\mathrm{rel}} + (\Delta F)^2_{\mathrm{rel}} + (\Delta V)^2_{\mathrm{rel}}\,(\Delta I)^2_{\mathrm{rel}} + (\Delta t)^2_{\mathrm{rel}}} \tag{2}$$

Zum vorliegenden Falle betragen $(\Delta F)_{\mathrm{rel}} = \pm 1 \cdot 10^{-5}$;[38] $(\Delta I)_{\mathrm{rel}} = \pm 3 \cdot 10^{-4}$;[39] $(\Delta V)_{\mathrm{rel}} = \pm 3 \cdot 10^{-4}$; $(\Delta t)_{\mathrm{rel}} = \pm 6 \cdot 10^{-4}$ und $(\Delta c_{\mathrm{NaCl}})_{\mathrm{rel}} = \pm 3{,}5 \cdot 10^{-4}$, so daß sich aus (2) der Fehler der Einzelmessung zu $\pm 0{,}08\,\%$, derjenige des Mittelwertes zu $\pm 0{,}05\,\%$ ergibt.

Gordon gibt in seiner Arbeit nur den unkorrigierten Wert für die Überführungszahl der Na-Ionenkomponente an, da er sowohl die Volumen- als auch die Leitfähigkeitskorrektur vernachlässigt. Wie aus Tabelle I ersichtlich ist, stimmen die obigen Meßergebnisse innerhalb der Fehlergrenze mit dem Wert von Gordon überein, womit die Anwendbarkeit des Radioisotopenverfahrens für Überführungsmessungen in nichtwässrigen Medien gezeigt ist. Gordon gibt als Maß für die Reproduzierbarkeit den "wahrscheinlichen Fehler" (Probable Error) an, der nur *ca.* $\frac{2}{3}$ der Standardabweichung beträgt und von den amerikanischen Autoren allgemein bevorzugt wird. Die Umrechnung vom Probable Error auf die Standardabweichung ergibt im obigen Falle an Stelle von $\pm 1 \cdot 10^{-4}$ den Wert $\pm 1{,}5 \cdot 10^{-4} \sim 2 \cdot 10^{-4}$.

Weitere Überführungszahlmessungen in niederen aliphatischen Alkoholen sind notwendig, um Aussagen über den Lösungszustand von Alkalihalogeniden in diesen Lösungsmitteln zu erhalten. Vor allem erscheint die Untersuchung von Butanol als Lösungsmittel wegen seiner Bedeutung in der Chromatographie interessant. Über derartige Messungen wird in einer späteren Arbeit berichtet werden.

Wir möchten Herrn Professor Dr. W. Schulze für sein Interesse an dieser Arbeit und für zahlreiche, wertvolle Diskussionen danken. Dem Institutsdirektor, Herrn Professor Dr. K. F. Jahr, sind wir für die Überlassung von Arbeitsmitteln zu großem Dank verpflichtet. Die Durchführung der Arbeit wurde ferner durch Arbeitsmittel des Fonds der Chemischen Industrie wesentlich gefördert, wofür hier besonders gedankt sei.

Summary—The use of radioisotopes for the determination of transport numbers by the moving boundary method has been shown to be applicable in non-aqueous media. The transport number of the sodium ion in 0·01*M* sodium chloride in dry methanol was determined using γ-emitter ^{24}Na, and the results are in good agreement with those obtained by other means. The accuracy of the technique and its advantages over optical methods are discussed.

Résumé—On montre que l'emploi de radioisotopes pour la détermination des nombres de transport par la méthode de la surface de séparation mobile est applicable en milieux non aqueux. Le nombre de transport de l'ion sodium dans le chlorure de sodium 0,01*M* en méthanol sec a été déterminé en utilisant l'émetteur γ ^{24}Na, et les résultats sont en bon accord avec ceux obtenus par d'autres moyens. On discute de la précision de la technique et de ses avantages sur les méthodes optiques.

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NOVEL APPLICATIONS OF DIPICRYLAMINE AS AN EXTRACTANT IN THE DETERMINATION OF ALKALI METALS

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Summary—A ten-stage mixer-settler type extraction procedure has been used for the preparation of rubidium-free caesium salts. A nitrobenzene solution of 0·11*M* CsDPA flows counter to a purified aqueous solution of 0·05*M* CsCl and $10^{-3}M$ Cs_4(EDTA), which removes Rb, K, Na and most other metals from the organic phase. An extraction colorimetric titration procedure for 0·2–2 mg of caesium is described, and also an indirect method for determination of potassium and sodium in admixture, based upon the difference in the ability of the two ions to replace $^{137}Cs^+$ in a nitrobenzene solution of dipicrylaminate.

THE salts of dipicrylamine (HDPA) have been used as precipitants for the gravimetric determination of heavy alkali metals,[1,2] radiochemical separation of caesium,[3] extractive separation of caesium from multivalent cations[4] and from rubidium,[5] concentration of trace amounts of caesium from large volumes of water,[6] determination of caesium by the method of concentration-dependent distribution using ^{137}Cs as radiotracer,[7] indirect determination of caesium by complexometric titration of calcium released during the extraction of calcium dipicrylaminate into nitrobenzene,[8] and for substoichiometric isolation of fission-product caesium-137 from a solution of irradiated uranium.[9] In this paper three novel applications of the dipicrylamine extraction with nitrobenzene in the determination of alkali metals are reported. They are the preparation of rubidium-free caesium salts, the colorimetric extraction titration of caesium and the indirect determination of sodium and potassium in admixture.

EXPERIMENTAL

Reagent-grade chemicals were used throughout. Nitrobenzene was purified by distillation under reduced pressure, water (for the preparation of pure caesium salts) was distilled and passed through a mixed ion-exchanger bed, and EDTA was recrystallized twice from water. The preparation of LiDPA (lithium dipicrylaminate) and of $Ca(DPA)_2$, and the technique of radiometric measurements of ^{137}Cs, have been described elsewhere.[10] The anion-exchangers were converted into the OH-form with 0·2*M* sodium hydroxide and subsequently washed thoroughly with demineralized water until a negative test for sodium was obtained.

The preparation of rubidium-free caesium salt

The initial caesium chloride contained 1·5% of rubidium. It was converted into the hydroxide by passage through a strongly basic anion-exchanger Dowex 2-X8 in the OH-form. An aqueous slurry of 0·11*M* caesium hydroxide and an equivalent amount of HDPA was shaken with an equal volume of nitrobenzene to produce solution 1 (Fig. 1.).

The rubidium–caesium separation was performed in a set of 10 polyethylene vessels, the volumes of each phase being 40 ml. The two phases were agitated with a motor-driven polyethylene stirrer for 2 min, and allowed to stand for 3 min to allow the phases to separate. The aqueous phase was transferred in a polyethylene pipette into the vessel X_{a-1}, the lower phase to the vessel X_{a+1}. The final organic phase was stripped with 0·125M hydrochloric acid and half of this extract was evaporated in a platinum vessel. The rest was made alkaline by passage through a small column of basic anion-exchanger Zerolit FF in OH-form and returned to the extraction system for recycling. The calculated amount of purified EDTA was added, the solution diluted with demineralized water to 0·05M in caesium chloride and taken as solution 2.

Until the battery reaches equilibrium, it is useful to return all the final strippings so that at this stage of the extraction procedure the concentration of the caesium salts is 0·11M in both phases.

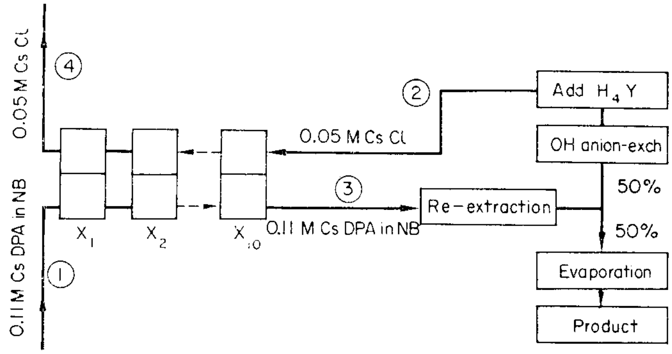

FIG. 1.—Flow-sheet of the purification procedure.
1—incoming raw caesium solution; 2—pure aqueous solution, pH 11, $10^{-3}M$ $Cs_4(EDTA)$; 3—purified rubidium-free solution in nitrobenzene; 4—waste solution, containing rubidium, potassium *etc*.

Extractive colorimetric titration

To the sample containing 0·2–2 mg of caesium as a neutral salt add 1 ml of $3 \times 10^{-3}M$ lithium hydroxide, dilute to 3 ml with water and add 3 ml of nitrobenzene. Titrate with $10^{-2}M$ LiDPA, stirring vigorously for 1 min after each addition. After phase separation measure the absorbance of the aqueous phase. Construct the titration curve by plotting the equilibrium aqueous concentration of dipicrylaminate against volume of titrant added. Prepare a calibration curve. Use a standard caesium salt to standardize the titrant. If a sufficient amount of sample is available, each point of the titration curve may be determined by a separate extraction experiment.

If CsDPA precipitates, each point of the titration curve should be determined by a separate experiment (30-min shaking after precipitation, then centrifugation).

Indirect determination of potassium and sodium

Determine the total concentration of both elements (*e.g.*, weight of sulphates or chlorides, or total molarity found by conversion of the salts into the acid by a cation-exchanger in H-form).

Construct a calibration curve D_{Cs} (distribution ratio of ^{137}Cs) *vs.* G_K/G_{Na} (ratio of amounts of K^+ and Na^+) keeping constant the total concentration of the two ions. For this, to the mixtures containing precisely the same total quantity (~90 μmole) of the two salts in varying proportions, add 1 ml of $3 \times 10^{-3}M$ calcium hydroxide and about 10^4 cpm of ^{137}Cs, dilute to 3 ml, add 3 ml of $1{\cdot}5 \times 10^{-4}M$ $Ca(DPA)_2$ in nitrobenzene and equilibrate. Count aliquots[3] of both phases and plot the distribution ratio of caesium against the ratio of G_K/G_{Na} in the initial solution.

If the G_K/G_{Na} ratio in the sample is between 3×10^{-5} and 3×10^{-2} modify the procedure as follows. Make the samples (containing exactly 9·0 mmole of the two salts in varying proportions) $10^{-3}M$ in sodium hydroxide in a 3-ml volume and extract with 3 ml of $1{\cdot}5 \times 10^{-2}M$ $Ca(DPA)_2$. Potassium is extracted preferentially. Discard the aqueous phase. Strip with 3 ml of 0·1M nitric acid, evaporate to dryness, take up in 3 ml of $10^{-3}N$ calcium hydroxide containing ^{137}Cs and extract with $1{\cdot}5 \times 10^{-4}M$ $Ca(DPA)_2$. Continue the procedure given for determination without enrichment.

RESULTS AND DISCUSSION

The preparation of rubidium-free caesium salts

Such salts were required in our laboratory as standards for the flame-photometric determination of traces of rubidium in standard caesium salts.[11]

The purification process is based on the extractability of caesium being higher than that of rubidium[10] ($D_{Cs}/D_{Rb} = 5$) from aqueous solution by nitrobenzene. The purification involved a ten-stage countercurrent (mixer-settler type) extraction process, during which the aqueous phase was enriched with rubidium and the organic phase freed from it. At the same time all lighter alkali metals and all elements undergoing masking with EDTA were removed.

The flow-sheet of the process is shown in Fig. 1. The theoretical overall decontamination factor from rubidium was calculated by the stage-to-stage method to be $1{\cdot}3 \times 10^4$. Ten g of caesium chloride were prepared by the described method, and found to be spectroscopically free from rubidium.

The advantages of this procedure are the possibility of performing the multistage continuous purification process, the easy purification of chemicals used, the possibility of obtaining easily the desired caesium salt by choosing the appropriate acid for stripping, and the large number of cations and anions removed simultaneously.

The colorimetric extraction titration of caesium

Several determinations of heavy alkali metals based on the formation of the dipicrylaminate precipitate and the colorimetric determination of the excess of reagent have been described.[1] Theoretical considerations show that by replacing the precipitation step by a nitrobenzene extraction the sensitivity can be enhanced, as in the first method it is limited by the solubility product of CsDPA. Precipitation and extraction–titration curves, both calculated and experimental, are shown in Fig. 2. The superiority of the extraction procedure is obvious. The calculations for precipitation are based on the solubility product of caesium dipicrylaminate, $S_{CsPDA} = 9{\cdot}5 \times 10^{-8}$; those for the extraction titration are dealt with in the Appendix.

Typical extraction colorimetric curves are shown in Fig. 3. It is evident that the use of lithium hydroxide and LiDPA leads to sharper breaks on the extraction curves than does the use of calcium salts. The lower limit of determination is approximately $5 \times 10^{-4}M$. The interference from other alkali metals increases from lithium to rubidium. The concentrations tolerable depend on the concentration of caesium in the solution being titrated. Curve 1 shows that a concentration of lithium about equal to that of caesium can be tolerated even at low concentrations of caesium. The tolerable concentrations of alkali metals are expected[11] to be Li:Na:K:Rb = 2500:300:10:1. The practical error of the end-point determination by the graphical method is 0·5–2% depending on the concentration range used. The theoretical titration error calculated (see Appendix) for $\Delta[\text{DPA}^-]_{aq}/[\text{DPA}^-]_{aq} = 0{\cdot}3$ is 0·75% for 0·01*M* caesium chloride and 0·8% for 0·003*M*.

The titration curves for rubidium and potassium exhibit no distinct breaks and the titration of these metals is not to be recommended. Rubidium, potassium or sodium may be determined in pure solutions by means of a calibration curve given by the dependence of the absorbance of the equilibrium aqueous phase on the concentration of the salts present. In these curves the amount of LiDPA and lithium hydroxide is constant and the use of standard conditions of extraction is more critical. Such a transition from a titration procedure to one depending on a calibration curve is quite familiar in radiometric titration[12,13] and in one-phase spectrophotometric methods. Typical calibration curves and the accuracy attainable at certain concentration levels are given in Fig. 4.

The advantages of this determination are simplicity of the apparatus required, rapidity of procedure and relatively high sensitivity. The main drawback is the rather low selectivity.

The indirect determination of potassium and sodium

In the indirect determinations of potassium and sodium described,[1] use is made of the dependence of a certain property of the mixture on the relative abundance of both elements. Our method is based on the differing ability of sodium and potassium to displace caesium from the organic phase.[11] These are in a ratio of about 100 which is much higher than for any other property so far used, and is responsible for the comparatively high accuracy of the method. Curve 1 in Fig. 5 shows the dependence on the initial ratio of the metals of the distribution ratio of tracer ^{137}Cs in extraction experiments where the original aqueous phase was 0·03M (Na, K) Cl. If very small K/Na ratios are to be determined it is possible to enrich the mixture in K first by a dipicrylamine extraction with a substoichiometric amount of $Ca(DPA)_2$.

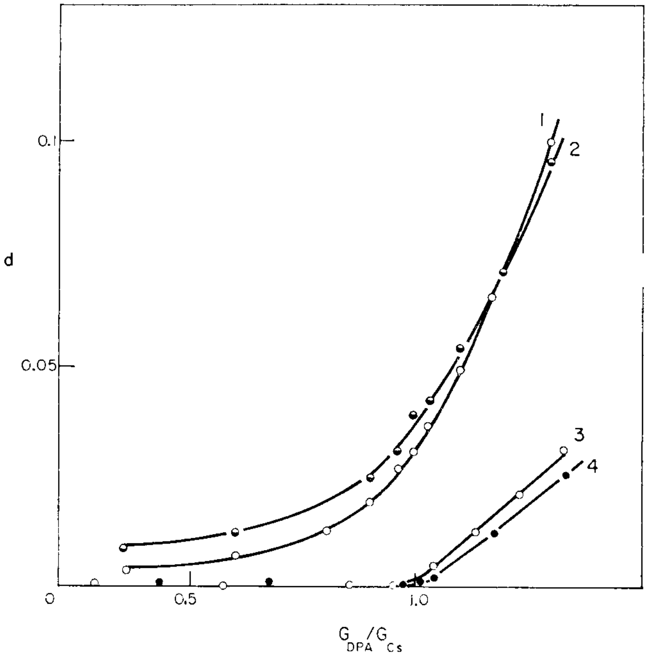

FIG. 2.—Precipitation and extraction colorimetric titration of caesium salts with dipicrylaminate.
3 × $10^{-3}M$ CsCl, d = aqueous equilibrium concentration of dipicrylaminate (mole/l.); G_{DPA} = amount of the titrant added (mole); G_{Cs} = amount of caesium salt present (mole).
1—precipitation, theoretical curve; 2—precipitation, experimental curve; 3—extraction experimental curve; 4—extraction, theoretical curve.

It seemed of interest to compare the calibration curve obtained experimentally with that expected on the basis of the extraction mechanism involved. The construction of the theoretical curve is mathematically rather complicated and an analogue

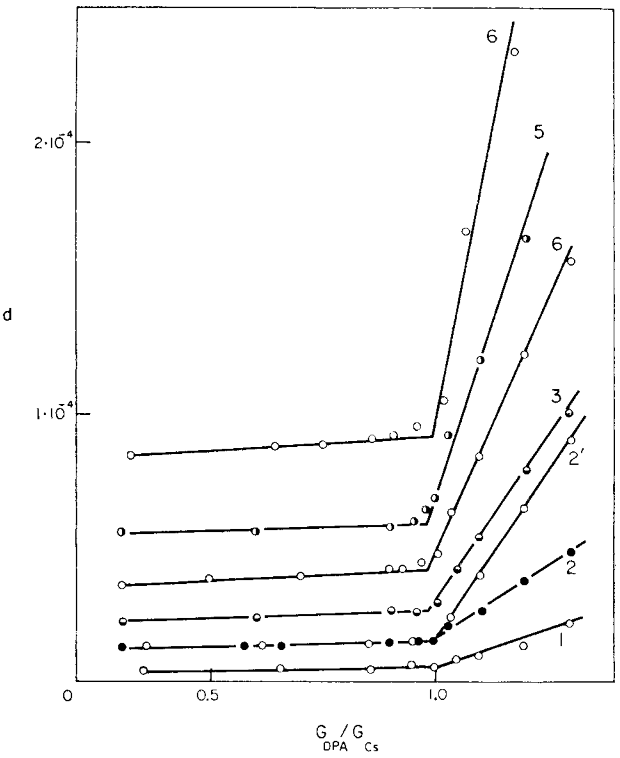

FIG. 3.—Typical extraction titration curves.

For *d*, *G* see Fig. 2. For greater clarity, the curves *3–6* are shifted vertically to increase the distances between them (the values of *d* for curves *3–6* and for $G_{DPA}/G_{Cs} = 0 \cdot 5$ should lie between 1 and $2 \times 10^{-5}M$). 1—$5 \times 10^{-4}M$ CaCl, titrant LiDPA; 2—$10^{-3}M$ CsCl, titrant Ca(DPA)$_2$; 2′—$10^{-3}M$ CsCl, titrant LiDPA; 3—$2 \times 10^{-3}M$ CsCl, titrant Ca(DPA)$_2$; 4—$3 \times 10^{-3}M$ Ca(DPA)$_2$; 5—$4 \times 10^{-3}M$ Ca(DPA)$_2$; 6—$6 \times 10^{-3}M$ Ca(DPA)$_2$.

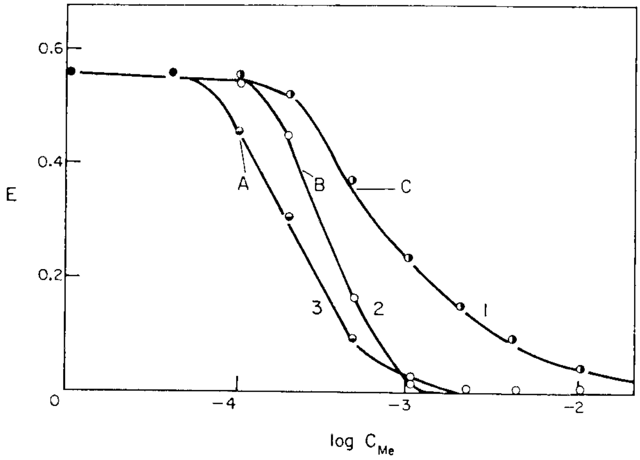

FIG. 4.—Calibration curves for indirect colorimetric extraction determination of Rb, K and Na.

E—absorbance, C_{Me}—colar concentration of the metal to be determined in the original aqueous phase, $10^{-3}M$ LiDPA; $5 \times 10^{-4}M$ LiOH; 1—NaCl; 2—KCl; 3—RbCl. Relative standard deviation *A*—3%, *B*—5%, *C*—7%.

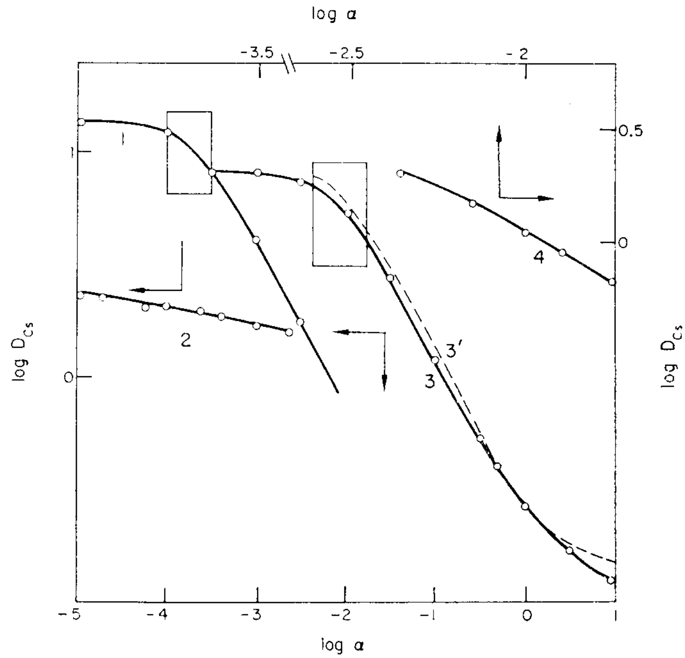

Fig. 5.—Indirect extraction radiometric determination of Na and K in a mixture. α—ratio of the concentration of potassium to the concentration of sodium, D_{Cs}—distribution ratio of tracer ^{137}Cs in the system. 1—after pre-concentration; 2—part (marked in Fig.) of curve 1 in detailed investigation, average error of ±9%; 3—without preconcentration (3′—theoretical curve); 4—part of curve 3 in detailed investigation, error ±1·3%; the arrows indicate which scales are valid for the curve in question.

computer has been used for performing the calculations.[15] The theoretical curve fits the experimental one very closely.

The accuracy found by repeated identical determinations using different points of the calibration curve is given in Fig. 5.

Acknowledgement—The authors wish to thank Dr. R. Tlalka and Dr. L. Hájek for performing the spectrophotometric determinations.

Zusammenfassung—Zur Herssellung rubidiumfreier Caesiumsalze wurde ein zehnstufiges Extraktionsverfahren vom Misch-Trenn-Typ verwendet. Eine Nitrobenzollösung von 0,11*M* CsDPA fließt im Gegenstrom zu einer gereinigten wäßrigen Lösung von 0,05*M* CsCl und $10^{-3}M$ $Cs_4(EDTA)$, das Rb, K, Na und die meisten anderen Metalle aus der organischen Phase entfernt. Ein kolorimetrisches Extraktions-Titrationsverfahren für 0,2–2 mg Caesium wird beschrieben sowie eine indirekte Methode, beigemischtes Kalium und Natrium zu bestimmen, das auf dem interschied zwischen den beiden Ionen beruht, $^{137}Cs^+$ in einer Nitrobenzollösung von Dipikrylaminat verdrängen zu können.

Résumé—On a utilisé une technique d'extraction en dix temps du type mélangeur-décanteur pour la préparation de rubidium exempt de sels de caesium. Une solution de CsDPA 0,11*M* dans le nitrobenzène s'écoule à contre-courant d'une solution aqueuse purifiée de CsCl 0,05*M* et de $Cs_4(EDTA)$ $10^{-3}M$, qui élimine Rb, K, Na et la plupart des autres métaux de la phase organique. On décrit une technique de titrage colorimétrique par extraction pour 0,2–2 mg de caesium, et aussi une methode indirecte pour le dosage du potassium et du sodium en mélange, basée sur la différence d'aptitude des deux ions à remplacer $^{137}Cs^+$ dans une solution en nitrobenzène de dipicrylaminate.

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APPENDIX

The formula for calculating the theoretical extraction-titration curve was derived assuming that the only species present in water are Li^+, Cs^+, DPA^-, Cl^-, and in the nitrobenzene phase, Li^+, Cs^+, DPA^-. The volume changes of the two phases ($v_{aq} = v_{org}$) during titration can be neglected.

The following equilibria[10] are involved:

$$[Cs^+]_{org}[Li^+]_{aq}/[Cs^+]_{aq}[Li^+]_{org} = A = 10^4;$$

$$[Cs^+]_{org}[DPA^-]_{org}/[Cs^+]_{aq}[DPA^-]_{aq} = B = 10^{4.41}.$$

Combining these equations with the mass-balance and electroneutrality conditions the following relationship for $[DPA^-]_{aq} = d$ is obtained:

$$a_3d^3 + a_2d^2 + a_1d + a_0 = 0$$

where $a_3 = A - K - B + 1$; $a_2 = 3K\lambda - 2A\lambda + A\lambda\gamma - B\lambda^\circ + \lambda^\circ - B\lambda - \lambda$;

$$a_1 = A\lambda^2 - 3K\lambda^2 - A\lambda\gamma - \lambda^\circ;\ a_0 = K\lambda^3.$$

In this expression $K = A/B$; λ = amount of titrant (LiDPA) added per 1. of the organic phase (mole/1.); λ° = concentration of LiOH (constant); γ = initial concentration of the caesium salt (mole/1.).

The derivation of the formula for the precipitation titration is much simpler, yielding $d^2 + d(\gamma - \lambda) - 9{\cdot}5 \times 10^{-8} = 0$.

The titration error $\Delta\lambda$ was calculated from the evident relationship for the point of equivalence: $\Delta\lambda = (\partial\lambda/\partial d).\Delta d$. The function $(\partial\lambda/\partial d) = f(\lambda, d\ldots)_{\lambda^\circ A,B,\gamma}$ can be easily found by differentiating the cubic equation above.

An alternative procedure is based on measuring the distribution of DPA^- instead of ^{137}Cs. The latter procedure is more accurate but it cannot be used over such a wide range of K/Na ratios as the method described here, because after the enrichment step no useful colorimetric calibration curves can be obtained.

Instead of dipicrylaminate, lithium tetraphenylborate can be used in the radiometric method. Our experiments show that the usefulness of both reagents is practically the same.

No indirect method has been found in the literature for the determination of sodium and potassium in mixtures covering as wide a concentration range as by the method described.

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ANION-EXCHANGE BEHAVIOUR OF SEVERAL ELEMENTS IN HYDROBROMIC ACID-ORGANIC SOLVENT MEDIA

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Summary—The anion-exchange behaviour of 19 elements in hydrobromic acid–organic solvent media has been investigated. The batch distribution coefficients of the metal ions were determined in these systems employing the strongly basic anion-exchange resin Dowex 1, × 8. Organic solvents used were methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetone, tetrahydrofuran and acetic acid. The most suitable conditions for some quantitative separations based on these equilibrium studies are indicated and discussed.

PREVIOUS investigations have shown[1,2] that in hydrobromic acid–organic solvent media several unique separation possibilities exist for metal ions on both anion[1]- and cation[2]-exchange resins of the strongly basic and strongly acidic types respectively. While the cation-exchange behaviour on Dowex 50 of numerous elements has been studied in these systems,[2] relatively little information is available on the exchange characteristics of elements on Dowex 1.[1] The work presented in this paper is an attempt to investigate systematically the adsorption behaviour on Dowex 1 of inorganic ions in mixed hydrobromic acid–organic solvent media. The data obtained in these media and shown in Tables I–XVI can readily be compared with the distribution coefficients measured in media containing hydrochloric acid and organic solvents.[3]

EXPERIMENTAL

Reagents

Ion-exchange resin. The strongly basic anion-exchanger Dowex 1, X8 (bromide form; 100–200 mesh) was used for the batch and the separation experiments. The preparation of the bromide form of this exchanger from the commercially available chloride form has been described earlier.[1]

Standard solutions. Exactly weighed amounts of UO_2(II), Th, Ce(III), Mo(VI), V(V)†, Fe(III), Al, In, Bi, Mg, Ca, Sr, Pb, Zn, Cd, Cu(II), Mn(II), Co(II) and Ni as bromides, oxides, carbonates or hydroxides were dissolved in 1·5, 3, 6 and 9*M* hydrobromic acid to give solutions containing 5 mg of the element per ml.

Solvents. The following reagent-grade organic solvents were used: methanol, ethanol, n-propanol, isopropanol, methyl glycol (monomethyl ether of ethylene glycol, CH_3—O—CH_2—CH_2OH), glacial acetic acid, tetrahydrofuran and acetone.

Determination of the various elements

Most of the elements investigated were determined titrimetrically, by suitable chelatometric methods with EDTA (disodium salt) as the titrant. Molybdenum was determined by titration with standard lead nitrate, PAR [4-(pyridyl-2-azo)resorcinol] being used as indicator.

Determination of distribution coefficients

The weight distribution coefficients (K_d values) of all elements were determined by using the batch equilibrium method described in an earlier publication.[4]

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† In the presence of bromide and organic solvents vanadium is readily reduced to the quadrivalent state.

TABLE I.—DISTRIBUTION COEFFICIENTS IN AQUEOUS METHANOLIC 0·6*M* HYDROBROMIC ACID

Ion	Methanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	<1	<1	6
Th(IV)	<1	<1	<1	<1	<1	<1
Ce(III)	<1	<1	<1	<1	<1	<1
Mo(VI)	21	19	17	9	5	5
V(IV)	<1	<1	<1	<1	<1	<1
Fe(III)	<1	<1	2	5	19	133
Al(III)	<1	<1	<1	<1	<1	<1
In(III)	9	14	25	49	240	$>10^3$
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mg(II)	<1	<1	<1	<1	<1	<1
Ca(II)	<1	<1	<1	<1	<1	<1
Sr(II)	<1	<1	<1	<1	<1	<1
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	25	57	150	290	290	340
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	2	3	4	8	116	620
Mn(II)	<1	<1	<1	<1	<1	<1
Co(II)	<1	<1	<1	<1	<1	1
Ni(II)	<1	<1	<1	<1	<1	<1

TABLE II.—DISTRIBUTION COEFFICIENTS IN AQUEOUS ETHANOLIC 0·6*M* HYDROBROMIC ACID

Ion	Ethanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	<1	1	1·2
Th(IV)	<1	<1	<1	<1	2	3
Ce(III)	<1	<1	<1	<1	3	7
Mo(VI)	21	21	22	24	25	27
V(IV)	<1	<1	<1	<1	1	2
Fe(III)	<1	<1	2	3	20	112
Al(III)	<1	<1	<1	<1	<1	<1
In(III)	9	19	41	110	10^3	$>10^3$
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mg(II)	<1	<1	<1	<1	2	2
Ca(II)	<1	<1	<1	<1	3	4
Sr(II)	<1	<1	<1	2	5	7
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	25	100	310	650	660	650
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	2	3	4	11	16	560
Mn(II)	<1	<1	<1	<1	1	3
Co(II)	<1	<1	<1	<1	1	5
Ni(II)	<1	<1	<1	<1	2	3

RESULTS AND DISCUSSION

Aliphatic Alcohol Media

In Tables I–IV and IX–XII, the distribution coefficients measured in hydrobromic acid–aliphatic alcohol mixtures are listed.

Uranium(VI), thorium and cerium(III)

In 0·6*M* hydrobromic acid media of varying concentrations of methanol and ethanol (Tables I and II) the adsorption coefficients of uranium, thorium and cerium

TABLE III.—DISTRIBUTION COEFFICIENTS IN AQUEOUS n-PROPANOLIC 0·6*M* HYDROBROMIC ACID

Ion	n-Propanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	<1	7	13
Th(IV)	<1	<1	<1	2	11	11
Ce(III)	<1	<1	<1	2	14	38
Mo(VI)	21	7	8	10	13	21
V(IV)	<1	<1	<1	1	4	6
Fe(III)	<1	<1	<1	<1	<1	75
Al(III)	<1	<1	<1	<1	4	4
In(III)	9	17	32	75	130	600
Bi(III)	$>10^3$	$<10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mg(II)	<1	<1	<1	<1	6	8
Ca(II)	<1	<1	<1	1	8	16
Sr(II)	<1	<1	<1	2	15	42
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	25	69	110	163	200	$>10^3$
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	2	11	15	15	132	274
Mn(II)	<1	<1	<1	<1	5	12
Co(II)	<1	<1	<1	1	6	16
Ni(II)	<1	<1	<1	<1	6	11

TABLE IV.—DISTRIBUTION COEFFICIENTS IN AQUEOUS ISOPROPANOLIC 0·6*M* HYDROBROMIC ACID

Ion	Isopropanol concentration, %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	<1	6	34
Th(IV)	<1	<1	<1	<1	9	10
Ce(III)	<1	<1	<1	2	16	58
Mo(VI)	21	26	44	53	110	145
V(IV)	<1	<1	<1	1	6	9
Fe(III)	<1	<1	1	4	60	56
Al(III)	<1	<1	<1	<1	4	3
In(III)	9	22	62	190	250	220
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	64
Mg(II)	<1	<1	<1	1	5	12
Ca(II)	<1	<1	<1	2	8	24
Sr(II)	<1	<1	<1	3	19	71
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	25	680	305	310	171	$>10^3$
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	2	13	16	29	195	195
Mn(II)	<1	<1	<1	<1	7	24
Co(II)	<1	<1	<1	<1	7	38
Ni(II)	<1	<1	<1	1	8	23

are extremely low; however, the adsorption reaches a maximum when the alcohol concentration increases to 90%. Slight adsorption increase is observed also with increasing hydrobromic acid concentration (Tables IX and X). This increase is more pronounced in 60–90% n-propanolic and isopropanolic media (Tables III and IV). An increase of the hydrobromic acid concentration in 90% n-propanol and isopropanol (Tables XI and XII) increases the adsorption of uranium, thorium and especially of cerium to a larger extent than that in methanolic or ethanolic media. However, low adsorption of the three elements in the entire concentration range is due to the

TABLE V.—DISTRIBUTION COEFFICIENTS IN 0·6M HYDROBROMIC ACID IN AQUEOUS METHYL GLYCOL SOLUTION

Ion	Methyl glycol concentration, %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	<1	1	15
Th(IV)	<1	<1	<1	<1	<1	<1
Ce(III)	<1	<1	<1	<1	<1	<1
Mo(VI)	21	25	19	12	5	<1
V(IV)	<1	<1	<1	<1	<1	<1
Fe(III)	<1	1	2	4	13	5
Al(III)	<1	<1	<1	<1	<1	<1
In(III)	9	12	25	38	14	6
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mg(II)	<1	<1	<1	<1	<1	<1
Ca(II)	<1	<1	<1	<1	<1	<1
Sr(II)	<1	<1	<1	<1	<1	<1
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	25	63	245	407	300	$>10^3$
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	2	60	500	185	75	70
Mn(II)	<1	<1	<1	<1	<1	3
Co(II)	<1	<1	<1	<1	<1	20
Ni(II)	<1	<1	<1	<1	<1	<1

TABLE VI.—DISTRIBUTION COEFFICIENTS IN 0·6M HYDROBROMIC ACID IN AQUEOUS ACETIC ACID

Ion	Acetic acid concentration, %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	4	150	250
Th(IV)	<1	<1	<1	<1	5	18
Ce(III)	<1	<1	<1	<1	6	8
Mo(VI)	21	10	11	42	150	$>10^3$
V(IV)	<1	26	36	49	71	70
Fe(III)	<1	1	5	450	$>10^3$	500
Al(III)	<1	<1	<1	<1	6	12
In(III)	9	17	44	$>10^3$	$>10^3$	$>10^3$
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mg(II)	<1	<1	<1	<1	4	7
Ca(II)	<1	<1	<1	<1	2	3
Sr(II)	<1	<1	<1	<1	1	1
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	ppt	ppt
Zn(II)	25	160	900	880	850	850
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	2	50	50	350	$>10^3$	$>10^3$
Mn(II)	<1	<1	<1	13	17	$>10^3$
Co(II)	<1	<1	<1	2	130	$>10^3$
Ni(II)	<1	<1	<1	<1	9	11

low tendency to form negatively charged bromide complexes in these systems. In analogous hydrochloric acid media similar behaviour of thorium and cerium was observed[3] but uranium was strongly retained, so effective separations were achieved. In hydrobromic acid media no such separations are possible.

Molybdenum(VI) and vanadium(IV)

In alcoholic 0·6M hydrobromic acid the retention of molybdenum is invariably higher than that of vanadium (Tables I–IV). While in methanol, ethanol and

TABLE VII.—DISTRIBUTION COEFFICIENTS IN 0·6*M* HYDROBROMIC ACID IN AQUEOUS TETRAHYDROFURAN

Ion	Tetrahydrofuran concentration, %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	<1	<1	3
Th(IV)	<1	<1	<1	<1	7	10
Ce(III)	<1	<1	<1	<1	8	24
Mo(VI)	21	35	22	12	7	<1
V(IV)	<1	<1	<1	2	3	5
Fe(III)	<1	<1	<1	<1	<1	<1
Al(III)	<1	<1	<1	<1	<1	<1
In(III)	9	19	11	<1	<1	<1
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	500
Mg(II)	<1	<1	<1	<1	3	8
Ca(II)	<1	<1	<1	<1	7	20
Sr(II)	<1	<1	<1	2	14	35
Pb(II)	$>10^3$	$>10^3$	$>10^3$	620	190	190
Zn(II)	25	88	167	55	20	28
Cd(II)	$>10^3$	$>10^3$	$>10^3$	796	200	180
Cu(II)	2	13	5	5	3	3
Mn(II)	<1	<1	<1	<1	2	4
Co(II)	<1	<1	<1	<1	6	26
Ni(II)	<1	<1	<1	<1	3	5

TABLE VIII.—DISTRIBUTION COEFFICIENTS IN 0·6*M* HYDROBROMIC ACID IN AQUEOUS ACETONE

Ion	Acetone concentration, %					
	0	20	40	60	80	90
UO_2(II)	<1	<1	<1	<1	10	35
Th(IV)	<1	<1	<1	<1	13	34
Ce(III)	<1	<1	<1	<1	11	35
Mo(VI)	21	13	14	19	36	<1
V(IV)	<1	<1	<1	1	5	11
Fe(III)	<1	7	12	27	2	<1
Al(III)	<1	<1	<1	<1	<1	5
In(III)	9	19	36	24	<1	<1
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	900
Mg(II)	<1	<1	<1	<1	6	14
Ca(II)	<1	<1	<1	<1	6	14
Sr(II)	<1	<1	<1	1	9	14
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	25	80	32	150	80	110
Cd(II)	$>10^3$	$>10^3$	$>10^3$	950	240	160
Cu(II)	2	21	18	51	13	8
Mn(II)	<1	<1	<1	<1	6	57
Co(II)	<1	<1	<1	<1	12	100
Ni(II)	<1	<1	<1	<1	7	17

n-propanol media the difference in the distribution coefficients is too low to allow clean-cut separations, media containing >40% isopropanol can be used for separation purposes. Similar adsorption of the two elements is observed in aqueous hydrobromic acid media (Table XVII).

The adsorption of molybdenum from methanol and ethanol media decreases rapidly when the molarity of hydrobromic acid is increased (Tables IX and X). On

TABLE IX.—DISTRIBUTION COEFFICIENTS IN 90% METHANOL MIXTURES CONTAINING 10% OF HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO$_2$(II)	<1	<1	5·7	8·2
Th(IV)	<1	<1	<1	<1
Ce(III)	<1	<1	<1	<1
Mo(VI)	$>10^3$	11	5	16
V(IV)	<1	<1	<1	<1
Fe(III)	24	37	133	300
Al(III)	<1	<1	<1	<1
In(III)	320	$>10^3$	$>10^3$	$>10^3$
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mg(II)	<1	<1	<1	<1
Ca(II)	<1	<1	<1	<1
Sr(II)	<1	<1	<1	<1
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	300	300	340	190
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	320	600	620	$>10^3$
Mn(II)	<1	<1	<1	<1
Co(II)	<1	<1	1	3
Ni(II)	<1	<1	<1	<1

TABLE X.—DISTRIBUTION COEFFICIENTS IN 90% ETHANOL MIXTURES CONTAINING 10% OF HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO$_2$(II)	<1	<1	1·2	1·4
Th(IV)	<1	2	3	4
Ce(III)	3	5	7	8
Mo(VI)	$>10^3$	630	27	45
V(IV)	<1	1	2	2
Fe(III)	35	81	112	124
Al(III)	<1	<1	<1	<1
In(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Bi(III)	10^3	10^3	$>10^3$	$>10^3$
Mg(II)	<1	<1	2	3
Ca(II)	<1	2	3	4
Sr(II)	3	4	7	10
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	620	620	650	650
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	380	450	560	$>10^3$
Mn(II)	<1	1	3	5
Co(II)	1	2	5	16
Ni(II)	1	2	3	3

the other hand neither an increase nor a maximum is observed in the case of a vanadium which shows invariably low distribution coefficients. In spite of the very high separation factors for Mo/V ($>10^3$) in media containing 0·15M hydrobromic acid in 90% methanol) separations could not be achieved. This may be due to partial reduction of molybdenum to a lower valency state (or formation of different complexes) which is less retained by the resin than molybdenum(VI).

TABLE XI.—DISTRIBUTION COEFFICIENTS IN 90% n-PROPANOL MIXTURES CONTAINING 10% OF HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, M			
	0·15	0·3	0·6	0·9
UO_2(II)	6	10	13	14
Th(IV)	9	10	11	12
Ce(III)	26	35	38	39
Mo(VI)	38	25	21	41
V(IV)	5	6	6	7
Fe(III)	84	77	75	60
Al(III)	4	4	4	3
In(III)	$>10^3$	$>10^3$	600	260
Bi(III)	$>10^3$	$>10^3$	$>10^3$	160
Mg(II)	6	7	8	9
Ca(II)	10	11	16	16
Sr(II)	25	33	42	43
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	$>10^3$	390	$>10^3$	407
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	340	234	274	320
Mn(II)	8	9	12	15
Co(II)	10	12	16	34
Ni(II)	8	10	11	11

TABLE XII.—DISTRIBUTION COEFFICIENTS IN 90% ISOPROPANOL MIXTURES CONTAINING 10% OF HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, M			
	0·15	0·3	0·6	0·9
UO_2(II)	16	25	34	22
Th(IV)	9	10	10	10
Ce(III)	34	42	58	60
Mo(VI)	70	49	145	230
V(IV)	<1	<1	9	10
Fe(III)	400	102	56	30
Al(III)	5	5	3	3
In(III)	$>10^3$	900	220	78
Bi(III)	$>10^3$	$>10^3$	64	26
Mg(II)	8	10	12	14
Ca(II)	19	23	24	23
Sr(II)	41	55	71	76
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	$>10^3$	$>10^3$	$>10^3$	427
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	348	212	195	282
Mn(II)	13	17	24	41
Co(II)	15	20	38	67
Ni(II)	15	19	23	29

Iron(III), aluminium, indium and bismuth

In 0·6M hydrobromic acid media (Tables I–IV) the adsorption of iron increases slightly with an increase of the concentration of organic solvent, while the retention of aluminium is slight in the entire concentration range. In 90% alcohol media a separation of these two elements should be possible.

An increase of hydrobromic acid concentration (Tables IX–XII) in media containing 90% alcohol increases the retention of iron while the adsorption of aluminium is

TABLE XIII.—DISTRIBUTION COEFFICIENTS IN 90% METHYL GLYCOL MIXTURES CONTAINING 10% OF HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	4	8	15	120
Th(IV)	<1	<1	<1	<1
Ce(III)	<1	<1	<1	2
Mo(VI)	7	2	<1	2
V(IV)	<1	<1	<1	<1
Fe(III)	12	9	5	5
Al(III)	<1	<1	<1	<1
In(III)	16	9	6	4
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mg(II)	<1	<1	<1	<1
Ca(II)	<1	<1	<1	<1
Sr(II)	<1	<1	<1	<1
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	$>10^3$	$>10^3$	$>10^3$	830
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	140	90	70	60
Mn(II)	<1	1	3	10
Co(II)	3	6	20	68
Ni(II)	<1	<1	<1	1

TABLE XIV.—DISTRIBUTION COEFFICIENTS IN 90% ACETIC ACID MIXTURES CONTAINING 10% OF HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	300	270	250	220
Th(IV)	15	21	18	13
Ce(III)	26	18	8	4
Mo(VI)	$>10_3$	$>10^3$	$>10^3$	$>10^3$
V(IV)	96	84	70	48
Fe(III)	$>10^3$	$>10^3$	500	180
Al(III)	20	18	12	8
In(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mg(II)	13	10	7	5
Cd(II)	6	5	3	1
Sr(II)	3	2	1	<1
Pb(II)	ppt	ppt	ppt	ppt
Zn(II)	850	850	850	870
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mn(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Co(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Ni(II)	20	15	11	11

invariably low. Thus, very effective separations of iron from aluminium can be achieved in methanolic or ethanolic systems which are 0·6–0·9*M* in hydrobromic acid or in n-propanolic systems with lower acid concentration.

Over the entire range of aqueous hydrobromic acid media (Table XVII) the distribution coefficients of iron and aluminium are <1. Indium also shows low adsorption values while bismuth is strongly adsorbed in all cases ($K_d > 10^3$). For that reason

Table XV.—Distribution coefficients in 90% tetrahydrofuran mixtures containing 10% of hydrobromic acid of varied molarity

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	1	1·3	3	8
Th(IV)	42	30	10	6
Ce(III)	42	42	24	16
Mo(VI)	47	10	<1	<1
V(IV)	31	8	5	3
Fe(III)	<1	<1	<1	<1
Al(III)	<1	<1	<1	<1
In(III)	<1	<1	<1	<1
Bi(III)	$>10^3$	$>10^3$	500	150
Mg(II)	12	11	8	5
Ca(II)	24	23	20	15
Sr(II)	66	64	35	22
Pb(II)	190	190	190	190
Zn(II)	28	31	28	37
Cd(II)	295	226	180	143
Cu(II)	3	3	3	3
Mn(II)	10	10	4	17
Co(II)	17	17	26	56
Ni(II)	15	13	5	2

Table XVI.—Distribution coefficients in 90% acetone mixtures containing 10% of hydrobromic acid of varied molarity

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	33	34	35	46
Th(IV)	125	82	34	15
Ce(III)	91	73	35	16
Mo(VI)	$>10^3$	85	<1	<1
V(IV)	21	18	11	8
Fe(III)	<1	<1	<1	<1
Al(III)	22	19	5	8
In(III)	<1	<1	<1	<1
Bi(III)	$>10^3$	$>10^3$	900	$>10^3$
Mg(II)	17	16	14	8
Ca(II)	24	23	14	6
Sr(II)	46	35	14	5
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	110	120	110	200
Cd(II)	270	400	160	141
Cu(II)	8	8	8	7
Mn(II)	22	27	57	61
Co(II)	45	67	100	115
Ni(II)	29	23	17	12

bismuth can be separated readily from iron, aluminium and indium in aqueous hydrobromic acid.

An increase of the alcohol concentration increases the adsorption of indium rather regularly, with maximum K_d values of $>10^3$. In media containing more than 60% of aliphatic alcohol indium can be separated from iron and aluminium. A similar behaviour is shown by gallium, as was observed earlier.[1]

TABLE XVII.—DISTRIBUTION COEFFICIENTS IN HYDROBROMIC ACID OF VARIED MOLARITY

Ion	Final HBr concentration, *M*			
	0·15	0·3	0·6	0·9
UO_2(II)	<1	<1	<1	<1
Th(IV)	<1	<1	<1	<1
Ce(III)	<1	<1	<1	<1
Mo(VI)	54	47	21	14
V(IV)	<1	<1	<1	<1
Fe(III)	<1	<1	<1	<1
Al(III)	<1	<1	<1	<1
In(III)	2	4	9	17
Bi(III)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Mg(II)	<1	<1	<1	<1
Ca(II)	<1	<1	<1	<1
Sr(II)	<1	<1	<1	<1
Pb(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Zn(II)	3	8	25	80
Cd(II)	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cu(II)	<1	5	2	2
Mn(II)	<1	<1	<1	<1
Co(II)	<1	<1	<1	<1
Ni(II)	<1	<1	<1	<1

Bismuth is the most strongly adsorbed of these four metals and its distribution coefficients at various concentrations of aliphatic alcohol and hydrobromic acid are in most cases $>10^3$. Separations of bismuth from indium can be achieved in 0·6*M* hydrobromic acid media containing 20–40% alcohol. A separation of bismuth from iron and aluminium is possible in most of the alcoholic media investigated.

It should be mentioned here that a separation of bismuth from iron, aluminium and indium can also be achieved in aqueous 0·15–0·9*M* hydrobromic acid systems. Similar separation possibilities for aluminium and indium were observed in 6*M* hydrochloric acid media containing 90% aliphatic alcohol.[3] Iron can be separated from uranium (Table XVIII).

Magnesium, calcium, strontium and lead

Low adsorption of magnesium, calcium and strontium is shown in alcoholic 0·6*M* hydrobromic acid media (Tables I–IV), the distribution coefficients being mostly <1, except for 80 and 90% ethanol, n-propanol and isopropanol.

TABLE XVIII.—SEPARATION CHARACTERISTICS OF METAL IONS IN HYDROBROMIC ACID–ORGANIC SOLVENT MEDIA

Metal ion, *mg*	Composition of eluant	Breakthrough volume, *ml*	Elution volume, *ml*	Batch-K_d
		(on 1-g column)		
Mn(II) 2	90% methanol–0·9*M* HBr	0	18	<1
Cu(II) 2·5		$\gg 40$	$>10^3$	$>10^3$
Fe(III) 2·9*	90% acetone–0·6*M* HBr	2	16	<1
U(VI) 2·5		>24	$\gg 24$	35

* This separation of iron from uranium was carried out on a 5-g column of Dowex 1.

A decrease of the hydrobromic acid concentration in 90% aliphatic alcohol (Tables IX–XII) slightly increases the adsorption values, an effect most pronounced in the case of strontium. In 90% isopropanol (hydrobromic acid 0·9*M*) a separation of strontium from magnesium should be possible.

Lead shows the same distribution coefficient of $>10^3$ at all concentrations of aliphatic alcohols and hydrobromic acid. Separations of lead from magnesium, calcium and strontium can be achieved. These elements are also separable in aqueous hydrobromic acid.

Zinc and cadmium

The adsorption of zinc increases when the concentration of the organic component in the mixtures is increased (Tables I–IV). Maximum adsorption is reached in 90% n-propanol and isopropanol ($K_d > 10^3$). On the other hand cadmium shows a distribution coefficient which is invariably $>10^3$ at all concentrations of aliphatic alcohols. In the entire range of alcohol concentrations the adsorption values of zinc are too high to allow a rapid separation of zinc and cadmium. A similar behaviour of zinc and cadmium is observed in 90% aliphatic alcohol media containing 10% of hydrobromic acid of varying molarity (Tables IX–XII). Conditions are also unfavourable in 0·6–0·9*M* aqueous hydrobromic acid (Table XVII). However, the separability of the two elements is greater when the acidity is decreased to 0·15*M*; here the separation factor ($K_{d_{Cd}}/K_{d_{Zn}}$) is >300.

In hydrochloric acid–aliphatic alcohol systems[3] a simple separation of these two elements is also not possible, because of the similarity of the distribution coefficients.

Copper(II) and manganese(II)

The adsorption of copper increases with increase in the concentration of aliphatic alcohols (Tables I–IV). Unlike copper, manganese shows only low adsorption values. At higher alcohol concentration (80 or 90% alcohol) copper can be separated from manganese. Similar separation possibilities exist with aliphatic alcohols containing varying concentration of hydrobromic acid (Tables IX–XII). An effective separation in 90% methanol medium (0·9*M* hydrobromic acid) was achieved (Table XVIII).

A separation of copper from manganese is not possible in aqueous hydrobromic acid media (Table XVII) but separations can be achieved in 6*M* hydrochloric acid systems containing 90% methanol or ethanol.[3]

Cobalt(II) and nickel

In virtually all cases cobalt and nickel show a similar adsorption pattern, *i.e.*, their distribution coefficients are very low and increase slightly at 80–90% ethanol, n-propanol and isopropanol (Tables I–IV). The adsorption of nickel is somewhat lower than that of cobalt but the distribution coefficients are not sufficiently different for separation purposes. However, both elements can be separated from cadmium, lead, bismuth and zinc. Similar separation possibilities exist with aliphatic alcohol systems containing varying concentrations of hydrobromic acid (Tables IX–XII) as well as in aqueous hydrobromic acid media of low acidity (Table XVII).

In contrast to hydrobromic acid systems, separations of cobalt from nickel can be effected in hydrochloric acid media.[3]

Methyl Glycol Media

The results of measurements of the distribution coefficients of the elements in hydrobromic acid–methyl glycol media are shown in Tables V and XIII.

Uranium(VI), thorium and cerium(III)

The behaviour of these three elements in media containing varying concentration of methyl glycol and hydrobromic acid is virtually the same as that observed in the hydrobromic acid–aliphatic alcohol mixtures. However, the adsorption of uranium increases at higher hydrobromic acid concentration, its distribution coefficient reaching a value of 120 in 0·9*M* hydrobromic acid, suggesting separability in this medium. Similar separation possibilities exist with hydrochloric acid–methyl glycol media.[3]

Molybdenum(VI) and vanadium(IV)

These two elements show adsorption characteristics similar to those observed in aliphatic alcohol media. While the adsorption of vanadium is invariably low, the retention of molybdenum decreases at high methyl glycol and hydrobromic acid concentrations. Nevertheless the difference in their adsorption values is too small to allow a separation.

Iron(III), aluminium, indium and bismuth

Iron is only very slightly adsorbed on the anion-exchange resin from mixtures of all concentrations of hydrobromic acid and methyl glycol, tetrahydrofuran or acetone as organic solvents. On the strongly acidic cation-exchanger Dowex 50, iron is also not retained.[2] Consequently this behaviour of iron in methyl glycol and also in acetic acid, acetone and tetrahydrofuran media (Tables VI–VIII and XIV–XVI) is due to an extraction effect which prevents the adsorption of iron on both exchangers. This effect, which is observed also with other elements and in several other mineral acid–organic solvent systems, has amply been demonstrated in previous publications.[2,5–7] Separations based on this principle have been termed CIESE (Combined Ion-Exchange–Solvent Extraction).[5–7] In the case of hydrobromic acid–methyl glycol media this non-adsorbability of iron allows its separation from bismuth, lead, zinc and cadmium. Aluminium is not adsorbed at any concentration of methyl glycol and hydrobromic acid and for that reason separations of aluminium from these elements are also possible.

In hydrobromic acid–methyl glycol media the adsorbability of indium is very low and since a similar low adsorption is observed on Dowex 50 this may also be due to an extraction effect. Therefore the separability is similar to that of iron and aluminium.

Bismuth is strongly adsorbed at all concentrations of methyl glycol and hydrobromic acid. This allows its separation from various other elements.

Magnesium, calcium, strontium and lead

In hydrobromic acid–methyl glycol media these elements show a similar behaviour to that observed in aliphatic alcohol systems. At all concentrations of methyl glycol and hydrobromic acid separations of magnesium, calcium and strontium from lead are possible.

Zinc and cadmium

Both elements show the same high adsorption at all hydrobromic acid concentrations (Table XIII) so that separation is not possible. This behaviour is similar to that observed in hydrochloric acid–methyl glycol media.[3]

Copper(II) and manganese(II)

Maximum adsorption of copper is observed in media containing 40% methyl glycol. In media containing 90% methyl glycol the distribution coefficient of copper was found to decrease with an increase in the molarity of hydrobromic acid.

Manganese is only very slightly retained at all concentrations of hydrobromic acid. Separations of copper from manganese can be effected at all methyl glycol concentrations which are 0·6*M* in hydrobromic acid.

Cobalt(II) and nickel

Cobalt and nickel in hydrobromic acid–methyl glycol media show a behaviour which is similar to that observed in aliphatic alcohols. The low adsorbability of the two elements allows their separation from bismuth, lead, zinc and cadmium.

Acetone and Tetrahydrofuran Media

In Tables VII, VIII, XV and XVI are shown the results of determinations of the distribution coefficients of the various metal ions in acetone and tetrahydrofuran media containing hydrobromic acid. The elements show a similar behaviour in both organic solvents, except for uranium, which is considerably less strongly retained from tetrahydrofuran media than from the corresponding acetone systems.

The extraction effect mentioned above (under methyl glycol media) is observed with iron and indium and was used to separate iron from uranium in acetone media containing hydrobromic acid. Data concerning this separation are recorded in Table XVIII.

Acetic Acid Media

The results of measurements of distribution coefficients of the elements in acetic acid media containing hydrobromic acid are shown in Tables VI and XIV. The solubility of lead bromide in some of the systems has been found to be very low so that a determination of the distribution coefficients in these media was not possible. In these instances the Tables do not list the distribution coefficient; instead the abbreviation "ppt" (for precipitation) has been put.

When the concentration of acetic acid increases from 0 to 90% the retention of molybdenum, indium, copper, manganese and cobalt increases to give distribution coefficients of $>10^3$ in the presence of 90% acetic acid in the entire concentration range of hydrobromic acid from 0·15 to 0·9*M*. This means that ready separation not only of these elements but also of iron, bismuth, zinc and cadmium from magnesium, calcium and strontium can be achieved in media containing high concentrations of acetic acid.

Aqueous Media

In Table XVII the behaviour of the elements in pure aqueous solutions containing varying concentrations of hydrobromic acid is shown. Possible separations in these systems include bismuth and lead from uranium, thorium, cerium, vanadium, iron, aluminium, magnesium, calcium, strontium, manganese, copper, cobalt and nickel in 0·15–0·9*M* hydrobromic acid and separations of zinc from cadmium in 0·15–0·3*M* hydrobromic acid. Thus, in these systems fewer possibilities exist for the separation of the various metal ions from one another than in media containing organic solvents.

Résumé—On a étudié le comportement à l'échange anionique de 19 éléments en milieux acide bromhydrique–solvant organique. On a déterminé les coefficients de partage des ions métalliques dans ces systèmes en utilisant la résine échangeuse d'anions fortement basique Dowex 1 × 8. Les solvants organiques utilisés sont: méthanol, éthanol, *n*-propanol; isopropanol, méthylglycol, acétone, tétrahydrofuran et acide acétique. On indique les conditions les plus convenables pour quelques séparations quantitatives basées sur ces études d'équilibre et en discute.

Zusammenfassung—Das Anionenaustauschverhalten von 19 Elementen in Medien aus Bromwasserstoffsäure und organischen Lösungsmitteln wurde untersucht. Die Verteilungskoeffizienten der Metallionen in diesen Systemen wurden mit dem stark basischen Anionenaustauschharz Dowex 1 × 8 bestimmt. Als organische Lösungsmittel wurden Methanol, Äthanol, n-Propanol, Isopropanol, Methylglykol, Aceton, Tetrahydrofuran und Essigsäure verwendet. Die auf Grund dieser Gleichgewichtsuntersuchungen ermittelten optimalen Bedingungen für einige quantitative Trennungen werden angegeben und diskutiert.

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POLAROGRAPHY OF ARSENIC

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Summary—The polarographic behaviour of arsenic in various media is reviewed with particular emphasis on the mechanisms of the electrode reactions and on the use of polarographic methods for the determination of the element.

IN MOST supporting electrolytes the reduction of arsenic gives rise to complicated waves unsuitable for analytical work. There are, however, a few media in which well defined, well behaved polarographic waves are produced. Further study of such systems is desirable as the polarographic reduction of arsenic is not, in general, subject to interference due to antimony, so the conventional separation due to antimony, so the conventional separation step (usually reductive distillation) common to most methods for the determination of arsenic may frequently be omitted from polarographic procedures. The more refined high-resolution, high-sensitivity techniques (*e.g.*, cathode-ray polarography or square-wave polarography) may be used to advantage in the determination of trace quantities of arsenic.

In acidic solution, the stepwise reduction of arsenic(V) through arsenic(III) to the element and thence to arsine is possible in whole or in part, depending on the nature of the supporting electrolyte:

$$As^{5+} + 2e \rightarrow As^{3+}$$

$$As^{3+} + 3e \rightarrow As$$

$$3H^+ + As + 3e \rightarrow AsH_3$$

Although this sequence certainly represents the successive changes in oxidation number undergone by the arsenic species during polarography, the actual arsenic polarograms are more complex. Double maxima may appear on the waves, and pH exerts an unexpected influence. Adsorption of elemental arsenic undoubtedly occurs, and it seems probable that catalysed hydrogen evolution may play a part in the formation of the maxima. The nature of the various arsenic species present in acid solution has been determined only recently, and tentative suggestions have been advanced regarding the detailed course of the reduction mechanism corresponding to the first part of the arsenic(II) polarogram. In general the most complicated and irreversible polarograms occur in non-complexing acid media (*e.g.*, hydrochloric acid, sulphuric acid, nitric acid; Fig. 1 is typical), whereas in the presence of such complexing agents as tartaric acid, citric acid or pyrogallol, simpler waves are produced.

In alkaline media, anodic (oxidation) waves for arsenic(III) have been obtained, but cathodic reduction waves have been reported only in complexing media, or in solutions of lithium compounds.

REDUCTION IN ACIDIC MEDIA

In this section the behaviour of arsenic is considered in the absence of complexing agents.

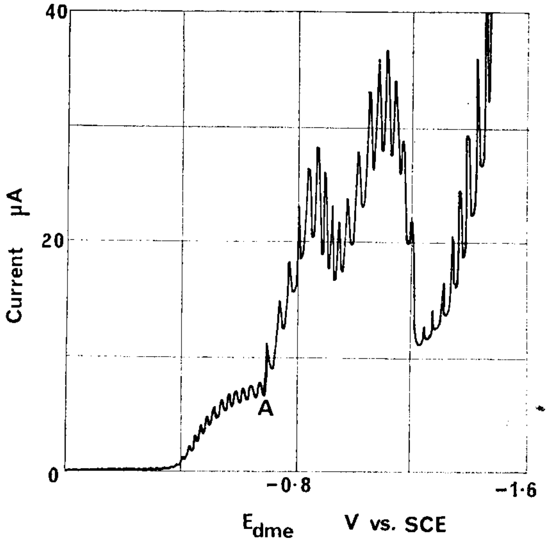

FIG. 1.—Normal polarogram of Arsenic(III) (50 μg/ml) in $1N$ hydrochloric acid.

The nature of the acid

In dilute acids (0·1 to $3M$) tervalent arsenic gives a complicated polarogram in two parts.[1–10] The half-wave potential and the definition of the first wave depend on the concentration of the acid. The second part of the polarogram consists of a double maximum superimposed upon what appears to be a single wave. The nature of this double maximum depends on the nature of any surface-active agents present in solution, on the drop-time and (to a smaller extent) on the concentration of the acid. The reduction of quinquevalent arsenic is possible in a few non-complexing acidic electrolytes (*e.g.*, $11{\cdot}5M$ hydrochloric acid[1] and 100% phosphoric acid[11]).

In the absence of maximum suppressors, polarograms of arsenic(III) in $0{\cdot}1M$ hydrochloric, nitric, sulphuric, or perchloric acid are similar in appearance.[7] At very low concentrations of arsenic (in the range 1–2 × $10^{-4}M$) the waves are of equal height, but above 2 × $10^{-4}M$ the second wave begins to exhibit its characteristic double maximum. The limiting current of the first wave, and the height of the maxima, do not increase linearly with arsenic concentration; the plateau of the first wave reaches a limiting value above 2–3 × $10^{-3}M$ arsenic(III). However, the height of the "minimum" (Fig. 1) seen just before the final hydrogen discharge wave varies approximately linearly with arsenic concentration, but is too near the hydrogen discharge wave to permit accurate measurement. With increasing concentration of arsenic(III), the point on the plateau of the first wave at which the first sharp increase of current begins (A), and the positions of the peaks of the maxima, move to more negative potentials; values of potential at A are −0·70, −0·72, and −0·75 V (*vs.* S.C.E.), as arsenic(III) concentrations of 1·02 × $10^{-3}M$, 2·04 × $10^{-3}M$ and 4·08 × $10^{-3}M$ respectively in $0{\cdot}1M$ hydrochloric acid. The polarograms in these acids are unsuitable for analytical work.

Increasing the concentrations of acid in the supporting electrolyte to $1M$ produces minor differences in the positions of the components of the arsenic(III) polarograms, but the overall appearance is unaltered.[1,3,4,6] Again, these is a minimum concentrations of arsenic(III), (*e.g.*,[1] 5 × $10^{-3}M$ for $1M$ hydrochloric acid below which two fairly well defined waves of equal height are obtained. Above this concentration, the second wave exhibits the characteristic double maximum. At concentrations of arsenic(III) between 1 and 4 × $10^{-3}M$, the height of the first wave becomes independent of the arsenic concentration.[1,3] This behaviour is not affected by changes in temperature[1] (between 18° and 32°) or by hydrochloric acid concentration[1] (up to $2{\cdot}0M$).

The half-wave potential of the first wave in $1M$ hydrochloric acid is given as −0·428 ± 0·005 V (*vs.* S.C.E.),[1] and begins at about −0·3 V (*vs.* S.C.E.).[3] The second arsenic wave (having the double maximum) begins at about −0·7 V,[1] or −0·6 V,[3] *vs.* S.C.E. The heights of the maxima increase disproportionately as the arsenic concentration increases.[3]

In solutions of yet greater acidity, the first wave becomes more positive. An expression for the half-wave potential of the first wave in hydrochloric acid has been derived:[1]

$$E_{1/2} = -0{\cdot}427 + 0{\cdot}135 \log[\mathrm{HCl}].$$

The error in $E_{1/2}$ is ±2 mV and this equation is applicable in the acid concentration range 0·1–2*M*. In the supporting electrolytes so far considered, the arsenic reduction waves are unsatisfactory for analytical application in the absence of maximum suppressors (on account of the large maxima), but one report appears in the literature[2] claiming that two well defined waves for arsenic(III) were obtained in 1–3*M* hydrochloric acid. The diffusion current of the first wave was reported to be proportional to the arsenic concentrations over the range from 10^{-3} to $2 \times 10^{-3}M$, and the wave was stated to be suitable for analytical applications.

In hydrochloric acid more concentrated than 4*M* mercury is spontaneously oxidised to form mercury(I) chloride. In 11·5*M* hydrochloric acid[1] the height of the first wave is directly proportional to the concentration of arsenic(III) up to at least $4 \times 10^{-3}M$. The half-wave potential of the second wave is about −0·55 V (*vs.* S.C.E.), but is so poorly defined that neigher the half-wave potential nor the diffusion current can be measured accurately.

The nature of the reduction of arsenic(III) in hydrochloric acid has been studied by a.c. polarography.[12,13] The irreversibility of the reduction was shown by a comparison of the a.c. potential, current constant and peak half-width with the d.c. half-wave potential.[12] It was further shown[13] that the electrical double layer capacity was decreased in the presence of arsenic(III).

Arsenic(V) has been found to yield reduction waves in concentrated acids. In 100% phosphoric acid (prepared by heating a 50% solution to a final temperature of 265°) the half-wave potential is −0·75 V,[11] and the reduction is irreversible. In 11·5*M* hydrochloric acid, arsenic(V) yields a polarogram consisting of two parts.[1] The first wave merges with the anodic wave due to the dissolution of mercury. The second wave, which is irreversible, has a half-wave potential of −0·52 ± 0·02 V. At concentrations of arsenic(V) above about $4 \times 10^{-4}M$, especially with short drop-times, the relative height of the second wave increases rapidly; with $2{\cdot}5 \times 10^{-3}M$ arsenic(V) the total height is several times the expected value. At the same time, the polarograms became much more complex as additional waves appear.

Surfactants

Several substances have been proposed for use as maximum suppressors, especially gelatine,[14–18] although this has several disadvantages. Peptone,[19] glucose,[15] thymolphthalein,[20] sodium Methyl Red,[7] Fuchsine,[17] Methylene Blue,[6,7,21–23] and "Triton-X"[24] have also been tried. The use of polyvinylpyrrolidone has been suggested,[25] and the properties of dodecyltrimethylammonium chloride[26] have been investigated. These maximum suppressors are of use only with solutions of arsenic(III), as no maximum suppressor for arsenic(V) has been reported which suppresses the maxima without causing a severe distortion of the whole polarogram.

Gelatine has used as maximum suppressor for solutions of arsenic(III) in 0·1*M*,[7] 1*M*,[1,4,17] and 3*M* hydrochloric acid,[8] 0·5*M* sulphuric acid[4,5,17] and 1*M* nitric acid.[4] In 0·1*M* hydrochloric acid, containing $1{\cdot}02 \times 10^{-3}M$ arsenic(III), concentrations of gelatine of 0·001, 0·003, 0·006, and 0·009% were employed.[7] Although suppression of the double maximum on the second wave was complete with 0·009% gelatine, this concentration of maximum suppressor markedly reduced the wave height, and a general deterioration in the definition of the polarogram was observed. Even in the presence of as little as 0·003% gelatine, the point at which the "minimum" (Fig. 1) occurred became too indistinct for its height to be measured at all. The polarographic waves were unsuitable for analytical work.

A similar state of affairs is seen for solutions of arsenic(III) in 1*M* hydrochloric acid containing 0·01% gelatine. The unsuitability of this maximum suppressor is evidenced by the absence of a well defined plateau on the second wave, and the first wave is shifted to potentials so negative that the two waves almost coalesce.[1] The polarogram was said to exhibit waves beginning at about −0·4 and −0·9 V and an ill-defined plateau at −0·8 V, with height proportional to the concentration of arsenic.[4] Polarograms taken in 0·5*M* sulphuric acid and 1*M* nitric acid containing 0·01% of gelatine are almost identical with those in hydrochloric acid,[4] but somewhat better defined. The wave-heights are stated to be proportional to the arsenic concentration.

Methylene Blue has proved to be far more satisfactory than gelatine. Concentrations of $0{\cdot}5$–$10 \times 10^{-4}\%$ have been used in solutions of arsenic(III) in 0·1*M* hydrochloric acid,[7] and $0{\cdot}43$–$3{\cdot}00 \times 10^{-4}\%$ in solutions of 1*M* hydrochloric acid.[1] In 1*M* hydrochloric acid $1{\cdot}5 \times 10^{-4}M$ in Methylene Blue the plateau of the second wave is quite well defined, and the total diffusion current constant for the double wave is almost exactly twice the value for the first wave alone.[1] Increasing the concentration of Methylene Blue to $10^{-3}M$ still effectively removes the maxima on the second wave without decreasing the wave-height[7] ($10^{-3}M$ arsenic(III) in 0·1*M* hydrochloric acid). However, solutions of arsenic(III) in 0·1*M* nitric acid in the presence of Methylene Blue give only poorly defined waves unsuitable for analysis.[7] In 0·1*M* perchloric acid the addition of Methylene Blue gave rise to a scarlet precipitate which caused erratic flow from the dropping mercury electrode.[7]

Other substances used as maximum suppressors have not been so thoroughly investigated. The addition of 0·001% of sodium Methyl Red had little effect on the overall height of the wave in 0·1*M* hydrochloric acid [10^{-3}*M* arsenic(III)], but did not completely eliminate the first maximum or the subsequent "dip" in the diffusion current.[7] Increasing the concentration to 0·0015% caused deterioration of the polarogram. The waves were considered to be unfit for analytical work. Polyvinylpyrrolidone in a concentration of 0·01% almost completely eliminated the double maximum on the second wave in a solution of arsenic(III) (50 μg/ml) in 2*M* hydrochloric acid.[25] Unfortunately, the height of the first wave was diminished considerably.

Cyclohexanone and a number of its derivatives produce an abrupt decrease in the diffusion current at certain potentials in the arsenic(III) polarogram.[27] This "cut-out" effect occurs at about −1·2 V (*vs.* S.C.E.), and may be seen in a solution of arsenic(III) in 1*M* hydrochloric acid that is 0·005*M* in cyclohexanone. It is not observed in neutral or alkaline media. 2-Methylcyclohexanone, 4-methylcyclohexanone, 1-isopropyl-4-methylcyclohexanone, 1-methyl-4-isopropylcyclohexanone, and 1,1-dimethyl-3, 5-cyclohexanedione also give the "cut-out" effect. Only those alkylcyclohexanones which may exist in the chair conformation are effective (those held in the boat form are not). This effect is attributed, in part, to chemisorption at the electrode.

Effect of neutral salts

The effect of neutral salts on the polarogram of arsenic(III) in 0·5*M* sulphuric acid has been studied by several workers. The combination 0·5*M* sulphuric acid/1*M* manganese sulphate/0·01% gelatine yields a two-part arsenic(III) polarogram with half-wave potentials of −0·54 and −0·69 V (*vs.* S.C.E.)[9] (with half-wave potentials of −0·7 and −1·0 V in the absence of manganese sulphate), but these values depend on the interpretation of the waves. The same combination with no maximum suppressor gives a two-part trace having a drawn-out, ill-defined first wave between about −0·6 and −0·8 V (*vs.* S.C.E.) and a clearly defined second wave with a half-wave potential of −0·97 V (*vs.* S.C.E.).[17]

In the latter case,[17] an increase of sulphuric acid concentration (between 0·8*N* and 4*N*), with manganese sulphate concentration kept constant at 1*M*, made no perceptible difference to the wave-height (although it is not specified exactly where this was measured). Similarly, an increase in concentration of manganese sulphate (0·6–1·5*M*), and the addition of small quantities of nitric acid (final concentration 0·1–0·4*M*) caused no perceptible difference in the wave height. However, in the former case,[9] an increase in sulphuric acid concentration caused an increase in the height of the first wave, and a decrease in the height of the second. The first wave was not suitable for quantitative analysis, but the second wave could be so used, being proportional to arsenic concentration over the range 0·5–5 × 10^{-4}*M*.

With 1*N* sulphuric acid/0·5*M* potassium chloride/10^{-5}*M* Methylene Blue, a very similar result is obtained. Two waves are obtained, with half-wave potentials of −0·42 and 0·65 V (*vs.* S.C.E.).[21] The first wave is not proportional to the arsenic concentration, but the second is, and is thus suitable for analytical applications.

The reduction of arsenic(III) in a supporting electrolyte of 0·1–1·0*M* potassium iodide, between pH 2·1 and 2·5 (hydrochloric acid) has been studied.[26] In 0·1*M* potassium iodide containing 0·001% dodecyltrimethylammonium chloride as maximum suppressor, the polarogram of arsenic(III) consisted of two parts. The first part comprised a well defined wave at concentrations of arsenic(III) of less than 8 × 10^{-4}*M*. With concentrations of arsenic(III) greater than 10^{-3}*M*, the plateau became markedly convex. The second wave was well defined with this concentration of maximum suppressor. However, in the absence of a maximum suppressor, a double maximum very similar to that observed in dilute mineral acids[1,2,7] was obtained.

The effects of the pH of this supporting electrolyte on the half-wave potentials and diffusion currents were studied.[26] Below pH 1·9, the starting potential of the first wave was so close to the anodic mercury dissolution wave that measurements of the wave height were very difficult. The height of the first wave decreased with increasing pH in the range 1·90–2·50, but the total height remained constant. Above pH 3·00, the wave height apparently decreased with increasing pH. These results were taken to indicate that the reduction of arsenic(III) decreased with a decrease in hydrogen ion concentration.

The half-wave potentials of the first and second waves shifted to more negative potentials with increasing pH, the second wave farther than the first.[26] With 10^{-3}*M* arsenic(III) in 0·1*M* potassium iodide, for example, the half-wave potential of the first wave shifted from −0·57 V at pH 2·0 to −0·63 V at pH 2·5. The half-wave potential of the second wave shifted from −0·85 V at pH 2·0 to −0·93 V at pH 2·5. In 1·0*M* potassium iodide containing the same concentration of arsenic(III), the corresponding shifts were: first wave, −0·52 V at pH 1·7 to −0·63 V at pH 2·7; second wave, −0·78 V at pH 1·7 to −0·93 V at pH 2·7 (all voltages *vs.* S.C.E.).

The reduction of arsenic(III) in a supporting electrolyte of potassium chloride adjusted to various pH values with hydrochloric acid has been studied.[8,10] Recently, work has been carried out with a rapid dropping mercury electrode (RDME), with mechanical detachment of the drops at the rate of about 4/sec.[10] It was found that below pH 0·5 in potassium chloride/hydrochloric acid solutions (containing no maximum suppressors) the reduction of arsenic(III) occurs in three distinct steps. The waves tend to merge at pH 1·0, and at appreciably higher pH values only two waves are produced. Comparison of these results with normal polarograms observed on the same solutions indicates that the two maxima reported previously are due to the second and third reduction steps. The second wave disappears as neutrality is approached, and is presumably due to proton participation in the reduction mechanism.

The appearance and nature of the characteristic double maximum on the second wave of the arsenic(III) polarogram observed in the absence of maximum suppressors is highly dependent on the presence of traces of metal ions in the supporting electrolyte. This is so even in cases where the presence of these ions has no effect on the position and character of the rest of the polarogram. It has been claimed that polarographic reduction of arsenic(III) does not occur in neutral solutions of very pure salts such as sodium, potassium, ammonium or magnesium sulphate, but if a weak acid is present (formic, acetic, monochloracetic, oxalic, malonic, succinic, benzoic or phosphoric), and impurities are present in the supporting electrolyte, reduction occurs and maxima appear on the polarogram.[15,28] The maximum appearing directly before the final hydrogen discharge (usually between −1·2 and −1·5 V in electrolytes such as those mentioned above) is proportional to the arsenic concentration, and occurs when cobalt, iron or nickel ions are present in solution.[15,27] The effect of cobalt and iron salts in the reduction of arsenic is considered to be analogous to the catalytic effects of cobalt in the reduction of cysteine and dimethylformamide, since in the potential range in which the maxima occur catalysed hydrogen evolution is observed. Simple salts such as cobalt sulphate, chloride and acetate, iron(III) chloride, iron(II) sulphate and iron(II) ammonium sulphate are effective in producing the catalytic action, while complex salts such as potassium ferrocyanide and ferricyanide are not. The presence of surface-active agents decreases the maxima in these solutions in the usual way, but a $10^{-4}M$ solution of Methylene Blue increases the height of the maxima in the presence of formic, acetic, monochloracetic, malonic or benzoic acid.[28]

Attempts have been made to correlate the appearance of the arsenic(III) maxima with movements of the supporting electrolyte or the emerging mercury drops. In the supporting electrolyte of 0·2–0·4*M* magnesium or sodium sulphate, 0·015*M* acetic acid, 0·015*M* cobalt sulphate [containing $10^{-5}M$ arsenic(III)] it is found that a maximum is not necessarily accompanied by significant movement of the electrolyte or mercury.[29] (These movements were made visible by including in the solution indifferent powders such as talc, mica and purified charcoal, and filming under 10–20 × magnification.) The effect of drop-time is complex, drop-times of 1·8–2·5 sec producing intense movements in both the electrolyte and the mercury, but these are not uniform, and vary with the geometrical characteristics of the capillary. Shorter drop-times cause a decrease in the height of the maxima. This sensitivity of the height of the maxima to drop-time has been noted elsewhere.[10] When a long drop-time, *e.g.*, 5–6·5 sec, was used, no movement could be observed even when prominent maxima were formed, but there is no simple relationship between the appearance of a maximum and flow phenomena round the dropping mercury electrode.

Observations of turbulence have also been made in relatively simple electrolytes having no deliberately added catalytic component such as the cobalt ion. In 0·1*N* hydrochloric, nitric, sulphuric or perchloric acids, turbulence could definitely be seen to occur at potentials at and between those at which the two maxima are seen (Fig. 1). When this occurred, the movement of the liquid was directed upwards towards the drop, causing a swirling motion around the electrode. At all other points on the polarogram only the normal movement of the liquid, due to the passage of the mercury drop, was observed. Attempts to view the turbulence in the presence of maximum suppressors were unsuccessful because the added suppressors were adsorbed by the finely divided powders (talc, charcoal, graphite) used to make the movements visible. The effect of drop-time was not studied.

Arsenic species in solution

Arsenious oxide, As_2O_3, is sparingly soluble in water, yielding a solution containing the weak arsenious acid, H_3AsO_3.[30] The production of silver orthoarsenite Ag_3AsO_3 provides some evidence for the existence of the ion AsO_3^{3-} in solution.[30] Since the polarograms of arsenic(III) in dilute (0·1–1*N*) solutions of hydrochloric, sulphuric, nitric and perchloric acids (in the absence of maximum suppressors) are very similar,[7] the arsenic is no doubt largely present in the same form in all these solutions. In $\sim 4M$ hydrochloric acid media, marked changes appear in the polarogram and have been attributed[7] to the formation of chloro-complex anions such as $AsCl_4^-$. Such ions have been considered to be present in very concentrated (11·5 *M*) hydrochloric acid, where, for the reduction of arsenic(V), a very high activity of both hydrogen and chloride ions is required.[1]

However, only recently has an attempt been made to determine the nature of all the arsenic species present in aqueous solutions at different pH values. The work is confined to solutions of hydrochloric acid, hence no further comment can be made here upon species existing in moderately concentrated or very concentrated solutions of the other acids mentioned. Calculations based on the distribution and solubility data of arsenic(III) complexes extracted from aqueous acidic solution into 2,2′-dichlorodiethyl ether are found to be consistent with the existence of the following species[31] in hydrochloric acid solutions:

$$AsCl_3,\ As(OH)Cl_2,\ As(OH)_2Cl,\ As(OH)_2^+,\ H_3AsO_3$$

In 12M hydrochloric acid, the only species present in significant amount is $AsCl_3$; in 9M hydrochloric acid the predominent species are $AsCl_3$ and $As(OH)Cl_2$; in ~5M hydrochloric acid all five of the species are present. It would be expected that this applies to less concentrated solutions as well and formation constants for these species are given (Table I).[31] Although hydroxychlorides have not been isolated, the compound $AsOCl{\cdot}H_2O$ has been prepared.[32]

TABLE I

$As(OH)_2^+$	$K_1 = 0{\cdot}5$
$As(OH)_2Cl$	$K_2 = 0{\cdot}085$
$As(OH)Cl_2$	$K_3 = 3{\cdot}4 \times 10^{-4}$
$AsCl_3$	$K_4 = 6.25 \times 10^{-5}$

Mechanism of the reduction

In general the polarograms of arsenic(III) consist of two main parts corresponding to reduction to the element, and then to arsine[1,3,4,7] (Fig. 1). These reaction products have been confirmed in the case of 0·1N solutions of hydrochloric, sulphuric, nitric and perchloric acids.[7] Elementary arsenic was seen at potentials corresponding to the first reduction wave. A modified Gutzeit method was used to detect arsine at potentials beyond that corresponding to the highest point on the first maximum. The first wave (corresponding to reduction to elementary arsenic) reaches a constant height above an arsenic(III) concentration of 2–3 × $10^{-3}M$ and this is attributed to the formation of a film of adsorbed elementary arsenic on the surface of the mercury drop.

The height of the "minimum" on the polarogram just before the final hydrogen discharge wave is not affected by non-distorting maximum suppressors such as Methylene Blue, and was considered to represent the true diffusion current for the reduction to arsine ($n = 6$).[7] The mean value of the diffusion current constant for this point in 0·1M hydrochloric acid/0·001 % Methylene Blue is 12·6, and the corresponding value for 0·05M sulphuric acid/0·001 % Methylene Blue is 12·8, for a range of arsenic(III) concentrations from 0·76 to 1·76 × $10^{-3}M$. This value is approximately twice the value of that for the first wave, as expected. The irreversible nature of the arsenic(III) reduction is indicated by the negative shift of the potentials of the various sections of the wave as the arsenic concentration is increased, and also by the slope (0·11) of the plot of E *vs.* $\log i/(i_d - i)$ for waves in the arsenic concentration range 1–2 × $10^{-4}M$, *i.e.*, at arsenic concentrations at which relatively simple waves are obtained.

In 1M hydrochloric acid the diffusion current constant of the first wave (no maximum suppressor needed) is 6·04 ± 0·03 (mean of 17 determinations),[1] and that of the total double wave (0·15 × $10^{-4}M$ Methylene Blue present) is 12·00 ± 0·04.[1] These values confirm that the reduction of arsenic(III) in hydrochloric acid solutions proceeds by two successive three-electron steps. The irreversibility of the first wave is indicated by the value of $E_{3/4} - E_{1/4}$ (*viz.* −35 ± 5 mV in 0·05–3·5M acid): the expected value for a thermodynamically reversible three-electron reduction is −18·8 mV. In 11·5*M* hydrochloric acid, the diffusion current constant of the first wave is 3·94 ± 0·07,[1] only 65% of its value in the 1*M* acid. The second wave is so poorly defined that its diffusion current constant cannot be measured.

If the method of rapid polarography is used (about 4 drops/sec), with a supporting electrolyte of hydrochloric acid or hydrochloric acid/potassium chloride, at pH 0·1–0·5, arsenic(III) yields a polarogram consisting of three waves.[10] The diffusion current constants of these waves are 5·51, 2·90, and 6·09. The similarity of the first and last values to that for the first wave in 1*M* hydrochloric acid obtained by normal polarography has led to the conclusion that these waves represent reduction to arsine *via* elementary arsenic as usual. The "middle" wave is attributed to proton participation.

The presence of gelatine gives rise to gross distortion and considerable changes in diffusion current. In 1*M* hydrochloric acid containing 0·01% gelatine, the diffusion current of the first wave was 8·6 (8·4 for sulphuric acid, 8·8 for nitric acid).[4]

The adsorption of elemental arsenic on the growing mercury drop is typical of that of adsorption waves in general,[33] and the first wave reaches a limiting height when a monolayer of adsorbed arsenic is present on the drop. Similar behaviour is found in the polarographic reductions of selenium(IV) and tellurium(IV),[34] and in that of germanium(II).[35] In each case, analogous explanations were advanced. In the case of arsenic polarography the effects were originally attributed to adsorption of arsenious oxide.[3] The adsorption phenomenon has been used to derive a value for the radius of the arsenic atom.[1] In 1*M* hydrochloric acid containing arsenic(III)[1] the first wave reaches a constant height at an arsenic concentration of 0·9 × $10^{-3}M$. Using a capillary delivering drops of known mass (9·02 ± 0·02 mg) it is found that the product $i_d t$ remains constant and equal to 58·5 ± 2·0 μc as the drop-time is varied from 1·7 to 5·1 sec. It is then assumed that the arsenic produced by this quantity of electrical energy just suffices to cover the exposed area of the drop at the end of its life. Assuming that the drop is spherical, the arsenic radius is calculated to be 0·098 nm. (The Goldschmidt value is 0·116 nm for a symmetrical atom in a symmetrical electrical field.)

Confirmation that the arsenic phenomenon is the result of an adsorption process has been given by workers who applied an adsorption isotherm type of analysis to the waves. In a supporting electrolyte of 0·1*M* potassium iodide, adjusted to pH 2·0–2·4 with hydrochloric acid, the wave-height is proportional to arsenic(III) concentration up to about $10^{-3}M$.[26] Above this value, the relationship becomes non-linear and the wave-height reaches a limiting value at an arsenic(III) concentration of about 4 × $10^{-3}M$. In this region of non-linearity, values of observed wave-height (i_m), the corresponding current value when extrapolated to a linear relation (i_c), and the difference between these two (i_a) were obtained. Then, from the general equation of isothermal adsorption $i_c - i_m = i_a = aC^{1/n}$, where C is the concentration of arsenic(III), and n is a constant (current in μA).

Therefore:

$$\log i_a = \log a + \frac{1}{n} \log C.$$

The plots of log i_a *vs.* log C showed a linear relationship, consequently a non-linear relationship between the reduction wave-height and the concentration of arsenic(III) can be attributed to adsorption.[26]

Although a reduction mechanism for the first, comparatively well-behaved, wave has been suggested,[36] the second wave has proved more difficult to explain in detail.

In this scheme,[36] from the knowledge of the arsenic species in solution (stated previously) and the effects of the changes in the concentration of chloride and hydrogen ion on the half-wave potentials, electron transfer to $As(OH)Cl_2$ is deduced to be the slow step in the reduction of arsenic(III) to arsenic(O) in acidic chloride media.

Two possible types of reaction mechanism are in accord with the experimental data:

Mechanism I

$$As(OH)Cl_2 + 2\ (\text{or } 3)e^- \xrightarrow{\text{slow}} As(I)\ (\text{or } As)$$

Mechanism II

$$\begin{aligned}
As(OH)_xCl_y^{3-x-y} + e^- &\xrightarrow{\text{fast}} As(OH)_xCl_y^{2-x-y}\\
As(OH)_xCl_y^{2-x-y} + (2-y)Cl^- &\xrightarrow{\text{fast}} As(OH)Cl_2^- + (x-1)OH^-\\
As(OH)Cl_2^- + 1\ (\text{or } 2)e^- &\xrightarrow{\text{slow}} As(I)\ (\text{or } As).
\end{aligned}$$

Preference is given to the latter mechanism because it suggests the possibility of an ion-bridge mechanism of a type known for some redox reactions in solution. Such a mechanism might proceed:

$$\begin{aligned}
As(OH)_2^+ + Cl^- + e^- &\xrightarrow{\text{fast}} As(OH)Cl + OH^-\\
As(OH)Cl + Cl^- + e^- &\xrightarrow{\text{slow}} As(I)\\
As(I) + e^- &\xrightarrow{\text{fast}} As
\end{aligned}$$

The chloride ions are assumed to come from the tightly bound double layer at the dropping mercury electrode, and to act as a bridge between the electrode and the arsenic ion.

In the case of arsenic(V), the diffusion current constant for the total double wave in 11·5M hydrochloric acid is 10·7,[1] almost exactly $\frac{8}{3}$ of that for the three-electron reduction of arsenic(III) in this medium. The reduction is therefore considered to proceed to the arsine stage, with the first wave representing reduction to elemental arsenic, although the height is somewhat less than the expected $\frac{5}{8}$ of the total wave-height. Again, no suggestions for the detailed course of the reduction mechanism are available.

REDUCTIONS IN NEUTRAL OR ALKALINE MEDIA

Comparatively few references appear in the literature relating to the reduction of arsenic in an alkaline medium. The influence of complexing agents will be considered in the next section.

Cathodic reductions

Although the use of neutral electrolytes will be mentioned it has been claimed that arsenic(III) is not reduced in neutral solutions of very pure salts such as sodium, potassium, ammonium, and magnesium sulphate.[15,28]

It has not proved possible to obtain a cathodic reduction wave of arsenic(III) in 1M sodium hydroxide,[37] or in 1M hydrazine/1M sodium hydroxide,[24] although a shift in the wave of the supporting electrolyte revealed some activity due to the arsenite ions.[38] In a further study of this phenomenon polarograms obtained with a solution of arsenite ion ($3{\cdot}76 \times 10^{-4}M$ As(III) in 0·1M sodium chloride/0·01M sodium hydroxide), differed from a polarogram of the supporting electrolyte alone;[39] the decomposition potential of the solution containing the arsenite ion was lower (*e.g.*, current values were 2 and 0·4 μA respectively, at 1·9 V *vs.* silver/silver chloride electrode). This was taken to indicate that, although the arsenite ions were reduced in the 0·1*M* sodium chloride/0·01*M* sodium hydroxide medium, the polarographic wave was obscured by that of the sodium ions. Confirmation of this theory was obtained by the production of a well defined wave due to arsenite ion in a 0·1*M* lithium chloride/0·01*M* lithium hydroxide supporting electrolyte. (Lithium ions are not reduced until a potential of −2·1 V *vs.* the silver/silver chloride electrode is reached.) The height of this (irreversible) wave was proportional to arsenic concentration in the range 1–6 × $10^{-4}M$. Its half-wave potential was −1·88 V *vs.* the silver/silver chloride electrode at pH 12·0. Under these conditions, the diffusion current constant was 14·4. From comparison with the diffusion current constant for the six-electron reductions of arsenic(III) to arsenic(−III) (12·0),[1] it was concluded that the wave in the lithium chloride/hydroxide media represented the six-electron reduction to arsine.

In further work[40] on the same electrolyte (0·1*M* lithium chloride/0·01*M* lithium hydroxide) the height of the polarographic arsenic wave was found to be directly proportional to arsenic concentration over the range 6–20 × $10^{-4}M$ arsenic(III). The production of cathodic reduction waves of arsenic(III) has been observed in several electrolytes other than simple alkaline solutions. The data obtained from this work are summarized in Table II. The table refers only to arsenic(III), since arsenic(V) is not reducible in any supporting electrolyte mentioned in this section. Data on some similar solutions containing hydrochloric acid are included for comparison.

Anodic waves

Anodic (oxidation) waves for arsenic(III) have been reported in alkaline solutions of various concentrations[6,24,42,43] The waves are accompanied by maxima which may be removed by gelatine. In 0·5*M* potassium hydroxide, the height of the wave is found to be proportional to the arsenic concentration in the range 0·9–4 × $10^{-3}M$.[43] The diffusion current constant is 3·82 ± 0·02 at 25°. The half-wave potential is −0·26 V (*vs.* S.C.E.), and is independent of concentration. Other concentrations of alkali (sodium hydroxide) which have been employed are 1*M*, giving a wave at −0·31 V (*vs.* N.C.E.),[6] and 10*M*, giving a wave at −0·337 V (*vs.* S.C.E.).[24] In all three cases, the wave was attributed to oxidation to arsenic(V).

REDUCTIONS IN COMPLEXING MEDIA

Many reports dealing with the polarographic behaviour of metals in complexing media include work on arsenic, but detail is often lacking.

Acidic complexing electrolytes

The perchloric acid/pyrogallal supporting electrolyte is of particular interest, since it is one of the few in which arsenic(V) is easily reducible. In a mixture of 2*M* perchloric acid/0·5*M* pyrogallol three well-defined waves are obtained.[44] The half-wave potentials, which are unaffected by the arsenic concentration in the range studied (0·5–2·0 × $10^{-3}M$), are −0·11, −0·46, and −0·72 V (*vs.* S.C.E.). These values are unaffected by perchloric acid concentration in the range 1–3*M*. (At perchloric acid concentrations less than 1*M* the second and third waves become less well-defined: above 3*M* acid, the third wave develops a maximum.) The relative wave-heights suggest the stepwise reduction scheme:

$$\mathrm{As(V)} \xrightarrow{2e} \mathrm{As(III)} \xrightarrow{3e} \mathrm{As} \xrightarrow{3e} \mathrm{AsH_3}$$

The corresponding values of $E_{3/4} - E_{1/4}$ are 0·096, 0·052, and 0·020. The diffusion coefficient of the arsenic(V) complex with pyrogallol (1·7 × 10^{-5} mm^2 . sec^{-1}) suggests a rather bulky and slow-moving complex.

The range of arsenic concentration over which proportionality exists may be compared to that in 11·5*M* hydrochloric acid, where only two waves occur and in which the waves became too complex to be useful above an arsenic(V) concentration of 0·4 × $10^{-3}M$.[1] The perchloric acid/pyrogallol medium will doubtless prove very valuable for analytical applications. As expected, the reduction of arsenic(III) in this medium gives only two waves.[44] With an arsenic(III) concentration of 0·5 × $10^{-3}M$, the half-wave potentials are −0·460 and −0·740 V (*vs.* S.C.E.). Half-wave potentials are the same in the presence and absence of pyrogallol, and the diffusion coefficient of arsenic(III) in the pyrogallol medium is much greater, *i.e.*, 1·0 × 10^{-3} mm^2.sec^{-1}.

A number of carboxylic acids have been employed (*e.g.*, acetic, tartaric, oxalic, citric, lactic and salicylic) and complexing mixtures which include hydrochloric acid with, *e.g.*, tartaric acid[45–47] or acetic acid[7,10,15,28] have been reported. The reduction of arsenic(III) in 1*M* tartaric acid/1*M* hydrochloric acid gives two well defined waves.[45–47] The half-wave potentials of these are about −0·4 and

TABLE II

Supporting electrolyte	Reduction scheme	$E_{1/2}$, *V vs.* SCE or NCE	Remarks	Ref.
0·25*M* Ammonia/0·25*M* ammonium chloride	As(III) → AsH$_3$	−1·72*	Well defined; wave-height ∝ [As].	6
1*M* Hydrazine/1*M* ammonia/1*M* ammonium chloride	As(III) → As (film?) → As (?)	−1·11† −1·35$_6$†	Small pre-wave, small max., fairly well-defined. Final current increase (actually max. of next wave) begins at about −1·5 V.	24
0·5*M* Potassium iodide	As(III) → AsH$_3$	—	Wave merges with electrolysis wave of supporting electrolyte.	6
0·5*M* Potassium chloride	As(III) → AsH$_3$	*ca.* −1·7*	as above	6
0·5*M* Calcium chloride	As(III) → AsH$_3$	−1·57*	as above	6
0·5*M* Sodium perchlorate	As(III) → AsH$_3$	*ca.* −1·7*	as above	6
0·5*M* Potassium thiocyanate	As(III) → As	−0·70*		6
	As → AsH$_3$	*ca.* −1·2*	Height of wave not measurable.	
1*M* Potassium thiocyanate/0·001*M* hydrochloric acid§	As(III) → As (film?)	−0·68†	Fairly well defined, irreversible.	24
	→ AsH$_3$ (?)	−1·09†	Ill-defined, irreversible.	
	(?)	−1·56†	Very ill-defined.	
1*M* Potassium thiocyanate/0·002% "Triton-X"/0·001*M* hydrochloric acid§	As(III) → As (film?)	−0·70†	Well-defined, height halved by Triton X.	24
		−0·13†	Fairly well defined, irreversible.	
		−1·61†	Ill-defined, wave height unchanged by Triton-X.	
10*M* Potassium thiocyanate/0·001*M* hydrochloric acid§	As(III) → As (film?)	−0·69†	Well defined, irreversible.	24
	→ AsH$_3$ (?)	−1·50†	Very well defined, nearly irreversible.	
Saturated hydrazine hydrochloride	As(III) → As (film?)	−0·192†	Well defined, irreversible.	24
		−0·575†	Fairly well defined, abnormally steep.	
0·5*M* Ammonium oxalate	As(III) → AsH$_3$	−1·72†		6
0·1*M* Sodium bicarbonate	As(III) → AsH$_3$	−1·74†	Wave height ∝ [As] up to $1{\cdot}5 \times 10^{-3}M$. [Recommended supporting electrolyte for determination of arsenic(III).]	41

* V *vs.* N.C.E.

† V *vs.* S.C.E.

§ Included for comparison.

$-0{\cdot}7$ V (both *vs.* S.C.E.) respectively. These waves are attributed to reduction to arsine *via* elementary arsenic.

The first wave was proportional in height to the concentration of arsenic, and was suitable for analysis[45] (diffusion current constant, 4·32). The second wave decreased in size when the solution was left in contact with mercury for several hours, or in the presence of silver nitrate. In these circumstances an initial current was obtained at 0 V, indicating the presence of silver or mercury ions in solution. Since these metals form relatively insoluble arsenides, it was inferred that at potentials at which arsenic would normally form, the metals reacted with the deposited arsenic to form the arsenides. In a detailed study of this phenomenon, a distinct change in the polarographic characteristics of the system was observed when the concentration of arsenides formed exceeded a certain value. This transition occurred at an arsenic(III) concentration of $3{\cdot}75 \times 11^{-4}M$. Taking this point to represent the solubility limit of arsine, a value of $1{\cdot}13 \times 10^{-4}M$ was derived for this. A second similar determination gave $1{\cdot}0 \times 10^{-4}M$ (at 30°).

Arsenic(III), at a concentration of $10^{-4}M$, produces a series of relatively simple polarograms in sodium acetate/hydrochloric acid solutions of different pH.[7] As the pH increases, the wave-height decreases (from 4 μA at pH 1·4 to 3·6 μA at pH 2·6), while the half-wave potentials shift to more negative values, *i.e.*, $-0{\cdot}765$ V (*vs.* S.C.E.) at pH 1·4 to $-0{\cdot}905$ V (*vs.* S.C.E.) at pH 2·6. Above pH 2·6 accurate measurement becomes impossible owing to interference with the hydrogen wave, while above pH 4·2 the arsenic wave completely merges with that of hydrogen. At a higher concentration of arsenic(III) ($0{\cdot}66 \times 10^{-3}M$) the polarographic waves exhibit large maxima,[10] similar to those appearing in hydrochloric acid alone. A similar shift in half-wave potential with pH is found, indicating the formation of arsenic–acetate complexes. A mole-ratio of 1:3 for arsenic:acetic acid for such a complex has been found[15,28] but the composition of the complex species probably depends on the conditions. Solutions of arsenic(III) ($0{\cdot}66 \times 10^{-3}M$) in hydrochloric acid/sodium acetate have also been examined by the technique of the rapid dropping mercury electrode (4·1 drops/sec).[10] In a solution at pH 1·1, three waves are obtained. The negative shift of half-wave potentials (relative to those in hydrochloric acid alone) is again evident. In solutions of pH between 1·9 and 4·9 only one wave appears. The change in half-wave potential is from $-1{\cdot}1$ V at pH 1·9 to $-1{\cdot}6$ V (*vs.* S.C.E.) at pH 4·9.

In an acetic acid (0·25*M*)/sodium acetate (0·5*M*) buffer, arsenic(III) gives a polarographic wave with a half-wave potential of $-1{\cdot}25$ V (*vs.* N.C.E.),[6] but the wave-height is not measurable. Arsenic(III) is not reduced in a 1*M* ammonium acetate/1*M* acetic acid solution, but in 2*M* ammonium acetate/2*M* acetic acid it gives a poorly defined wave, with half-wave potential $-0{\cdot}92$ V.[48] In a 1:4 mixture of saturated aqueous calcium hydroxide and 0·1*M* citric acid, arsenic(III) gives a well defined wave suitable for analysis.[49] The wave is separated from that of antimony, and it is possible to determine arsenic in an antimony/arsenic mixture in which the antimony is in a 60-fold excess.

Arsenic(III) is also reducible in a 0·1*M* ammonium oxalate/0·1*M* oxalic acid solution.[50] This is primarily of interest from an analytical point of view, since arsenic may be determined in this electrolyte in the presence of antimony(III) and tin(IV), but not with good accuracy. With derivative polarography, the arsenic(III) peak currents show a logarithmic proportionality to concentration. Arsenic(III) may also be determined in a supporting electrolyte of 2*N* sulphuric acid/0·0075*N* potassium iodate and 0·0037*M* ceric sulphate, made 0·01*M* in tartaric acid immediately before polarography.[51]

Arsenic(III) is readily reduced in solutions of 0·5*N* ascorbic acid adjusted to various pH values.[19] Two well defined waves are observed in highly acid solutions, but as the acidity decreases the second wave becomes distorted. The half-wave potentials (*vs.* S.C.E. at 20°) are as follows. In the original work, gelatine in concentrations of 0·005–0·01 % was used to eliminate the maxima appearing on the waves.

pH	1·0	2·0	3·0	4·0	5·0	6·0
$E_{1/2}$, 1st wave, *V*	−0·78	−0·82	−0·85	−0·88	−0·91	−0·95
$E_{1/2}$, 2nd wave, *V*	−1·1	−1·1	—	—	—	—

Neutral and alkaline complexing media

In neutral ascorbic acid solution, arsenic(III) does not give a reduction wave, although in alkaline solutions two well-defined waves are formed;[19] the half-wave potentials are as follows. These waves are suitable for analysis, with height proportional to the concentration of arsenic(III) over the range 0·1–0·2 mg/ml. Again, the maxima may be suppressed by gelatine provided its concentration does not exceed 0·01 % (when a negative shift in the half-wave potentials occurs).

Other complexing agents used include lactates, malates and salicylates,[52] 1*M* ammonium fluoride adjusted to pH 7,[53] and 0·1 and 1·0*M* solutions of the following amines: 1-amino-3-propanol, bis(2-hydroxypropyl)-2-hydroxyethylamine, and bis(2-hydroxybutyl)-2-hydroxyethylamine.[54] In a supporting electrolyte of EDTA/potassium cyanide no reduction wave for arsenic(III) is observed,[55] but in 0·1*M* EDTA in the pH range 3–10, a wave has been reported,[56] the half-wave potential varying from −0·85 to −1·75 V (*vs.* S.C.E.). A solution at pH 7·3, containing 0·0001% of gelatine, is recommended for the determination of arsenic [wave-height proportional to concentration from 0 to $1{\cdot}2 \times 10^{-3}M$ arsenic (III)]. In 0·5*M* ammonium oxalate, arsenic(III) gives a wave with a half-wave potential of −1·72 V (*vs.* N.C.E.)[6] representing reduction to arsine. In 0·1*M* pyridine/0·1*M* pyridinium chloride solution, arsenic(III) yields two ill-defined waves, with half-wave potentials −0·90 and −1·05 V (*vs.* S.C.E.).[24] A supporting electrolyte consisting of 0·2*M* tetramethylammonium bromide/0·02*M* tetramethylammonium hydroxide has been suggested for the determination of arsenic(III).[40]

There are examples of the use of sodium hydroxide solution containing complexing agents; the waves produced in these solutions are anodic. Thus, in a 1*M* pyridine/1*M* sodium hydroxide electrolyte, arsenic(III) produces a single fairly well defined wave, half-wave potential −0·235 V (*vs.* S.C.E.),[24] representing oxidation to arsenic(V). Arsenic(III) gives a clearly defined anodic wave in 5*M* sodium hydroxide containing 60 g of mannitol per litre.[20,57] The half-wave potential is 0·29 V and the wave-height is proportional to the concentration of arsenic. No interference was found from cadmium, lead, zinc, bismuth, molybdenum, vanadium, tungsten, chromium, aluminium, calcium, barium, potassium, sodium, iron(III), tin(IV), arsenic(V), antimony(III), sulphate, carbonate, phosphate or fluoride.

ANALYTICAL APPLICATIONS

In most polarographic methods for the determination of arsenic, three steps may be distinguished. Initially, oxidative attack is used to produce an aqueous solution of arsenic(V). Secondly, the arsenic in solution is reduced to the tervalent form which is finally measured polarographically. Many of the methods described include the separation of a volatile compound of arsenic(III) and its absorption in a supporting electrolyte before polarography.

The initial attack is frequently carried out with sulphuric acid, usually in association with nitric acid. Other oxidizing agents (*e.g.*, perchloric acid) have been used. Hydrazine sulphate is the favoured reducing agent although it is scarcely soluble enough in some cases. Other reducing agents employed include sulphur dioxide and potassium iodide. Excess of sulphur dioxide must be removed by boiling the solution. Unfortunately, iodine (formed from potassium iodide) reacts with mercury and may interfere with the electrodes.

Metallurgical methods

Silicates have been decomposed with a mixture of hydrofluoric and sulphuric acids,[21] in a method for the determination of both arsenic and antimony. After evaporation until fumes of sulphuric acid appeared, the residue was dissolved in distilled water and transferred to a distillation vessel. Arsenic(V) was reduced to arsenic(III) by the addition of potassium bromide, concentrated sulphuric acid, concentrated hydrochloric acid, and hydrazine sulphate. The distillation vessel was heated to 80° in a glycerol bath and further quantities of potassium bromide and sulphuric acid were added. When the temperature was raised to 200°, arsenic and antimony trichlorides distilled over and were collected in dilute nitric acid. After further treatment of this distillate with sulphuric acid and hydrazine sulphate the residue was dissolved in a supporting electrolyte of 1*N* sulphuric acid/0·5*M* potassium chloride/$10^{-5}M$ Methylene Blue. Polarographic waves of antimony, $E_{1/2} = -0{\cdot}14$ V, and arsenic, $E_{1/2} = -0{\cdot}42$ and −0·65 V (*vs.* S.C.E.) were obtained. By use of a calibration curve 1 μg of arsenic could be determined in the presence of 50 μg of antimony (and *vice versa*), the second arsenic wave being used.

If the procedure was altered somewhat, arsenic trichloride alone could be distilled.[22] The sample was decomposed with a mixture of hydrofluoric, sulphuric and nitric acids, evaporated to fumes of sulphuric acid, and diluted with water; hydrazine sulphate was then added and the solution heated to 140°. A slow current of carbon dioxide was passed through the solution and a solution of potassium chloride added dropwise. Arsenic trichloride distilled over and was collected in a solution of 1*M* ammonium sulphate/0·5*M* potassium chloride/$10^{-5}M$ Methylene Blue before polarography.

Metals are usually dissolved in nitric acid before determination of arsenic. Iron or steel have been dissolved in hot nitric acid and the arsenic separated from iron by co-precipitation with manganese dioxide.[16] The washed precipitate was dissolved in dilute sulphuric acid/hydrogen peroxide and the solution heated until fumes of sulphuric acid appeared. Concentrated hydrochloric acid, hydrazine sulphate and hypophosphorous acid were added, and the mixture was heated in a stream of carbon dioxide. Arsenic trichloride distilled and was collected in cold water. After the addition of tartaric acid and gelatine the arsenic was determined polarographically. The method is suitable for iron, steel and iron ore, but the nitric acid concentration needs careful control (to about $0{\cdot}5M$) to ensure complete co-precipitation of arsenic.

Other polarographic methods for the determination of arsenic in iron ores have been employed. Samples have been decomposed with 1:1 nitric acid or sulphuric acid,[58] and the arsenic(V) formed has been reduced with 3:2 hydrochloric acid and iron(II) sulphate. The volatile arsenic trichloride was originally distilled and estimated by amperometric titration. Alternatively,[59] the arsenic has been precipitated as arsenious sulphide (As_2S_3) after distillation from the sample. The sulphide was converted into the complex $(NH_4)_3AsS_3$ with aqueous ammonia, and a known excess of cadmium sulphate solution was added. After separation of the cadmium sulphide, the excess of cadmium ion in the ammonia solution was determined polarographically. To determine arsenic in ores containing up to 5% arsenic and 3% antimony, but no mercury, the material was treated with sulphuric and nitric acids in the usual way and, after separation of the insoluble residue, arsenic was co-precipitated with iron by aqueous ammonia.[20] The precipitate was dissolved in sulphuric acid and, after reduction of arsenic(V) with hydrazine sulphate, arsenic(III) was determined polarographically in a supporting electrolyte of sodium hydroxide containing mannitol, thymolphthalein and sodium sulphite.[57]

For the determination of arsenic in copper,[23] the sample was dissolved in nitric acid. Sulphuric acid was added and the solution evaporated gently to remove the nitric acid. After cooling, the solution was made $6M$ in hydrochloric acid, and elemental arsenic was precipitated with sodium hypophosphite. The precipitated arsenic was filtered off and dissolved in concentrated nitric acid. Concentrated sulphuric acid was then added and the mixture evaporated until fumes of sulphuric acid appeared. After boiling with hydrazine sulphate the solution was made $1N$ in sulphuric acid, Methylene Blue was added, and the polarogram recorded. The recovery was incomplete (93%) and the polarogram consisted of two poorly separated waves. The method may be used to determine 0·02–1·0 mg of arsenic, corresponding to a minimum of 0·0004% in a 5-g sample. For quantities of arsenic between 0·10 and 1·0 mg a reproducibility of ±3% is possible, but for quantities of the element below 0·10 mg the reproducibility and accuracy deteriorate seriously. Tellurium interferes and must be separated.

In the determination of arsenic in lead,[17] sulphuric acid was added to a nitric acid solution of the sample to precipitate lead sulphate. The precipitate was washed and the filtrate and washings evaporated until fumes of sulphuric acid appeared. The arsenic was reduced by hydrazine sulphate and the resulting solution either mixed with alcohol, acetic acid and gelatine, or adjusted to $1N$ in sulphuric acid and $1M$ in manganese sulphate before polarography. Arsenic (0·003–0·6%) could be determined in lead metal. In the former supporting electrolyte, no interference was found from the following (in quantities less than 10 μg/ml): iron(III), bismuth(III), antimony(III), tin(IV), copper(II) and zinc(II). In the latter electrolyte, no interference was found from the same ions in quantities less than 50 μg/ml.

Arsenic (in amounts of 0·1–0·0001%) has been determined in zinc by a co-precipitation technique.[18] A suitable weight of sample was dissolved in nitric acid and diluted. The solution was boiled and arsenic co-precipitated with iron(III) hydroxide. The precipitate was filtered off, washed and then suspended in water while sulphur dioxide was passed through, to reduce arsenic to the tervalent state. The excess of sulphur dioxide was removed by boiling and the solution cooled. After addition of $5N$ sulphuric acid and dilution to an acidity of $1N$, the solution was polarographed (with gelatine as maximum suppressor). By this method, results within the range 0·1–0·001% arsenic showed a mean relative deviation of ±2%. The accuracy of the method diminishes as the arsenic content approaches 0.0001%, at which concentration the relative error is 20%. In the determination of arsenic in the residuals arising from the production of zinc and sulphide ores, cadmium is present and must be separated if present in amounts greater than 0·1%.

Biological Materials

Few polarographic methods have been reported for the estimation of arsenic in biological materials. Care must be taken when dry-ashing or wet-oxidizing biological matter, to ensure that losses of volatile arsenic compounds do not occur. A polarographic method based on dry-ashing and dissolving the residue (after reduction and distillation) in 11M potassium hydroxide has been reported[60] but most workers prefer wet-oxidation procedures. Sulphuric acid is used with nitric acid. Attempts have been made to substitute 50% hydrogen peroxide for the latter, but losses of arsenic occurred under the conditions examined.[61] If nitric acid is employed it must be completely removed before polarography is begun.

In one method,[62] the biological materials were oxidized with sulphuric and nitric acids, and the arsenic(V) reduced with potassium iodide. The iodine produced was destroyed by sodium thiosulphate and both arsenic and antimony were extracted into carbon tetrachloride as the xanthates. The organic solution was evaporated to dryness and the residue decomposed by sulphuric, nitric and perchloric acids. The resulting solution was reduced to give arsine and stibine which were absorbed on filter paper impregnated with silver nitrate. This paper was extracted with a hydrochloric acid (1M)/tartaric acid (1M) solution. When this solution was polarographed, three waves were observed, the first due to antimony, and the second and third due to arsenic. The arsenic wave at $-0{\cdot}43$ V was suitable for quantitative application, but that at $-0{\cdot}67$ V could be used only to confirm the presence of arsenic. This procedure (absorption in silver nitrate and extraction with hydrochloric/tartaric acids) has been found to be specific, sensitive (1 μg) and precise. Arsenic may be recovered at 75 ± 4% of the quantity used.[63]

In an alternative method, the sample was wet-ashed, and oxides of nitrogen were removed by treatment with a saturated solution of ammonium oxalate.[64] The prepared sample, in a solution of sulphuric acid, was mixed with hydrochloric acid and diluted. Potassium iodide and tin(II) chloride solutions and zinc rods were added. Arsine, hydrogen and some hydrogen sulphide (removed by absorption in lead acetate solution), were evolved, and the gases were passed into mercury(II) chloride solution to give mercury(II) arsenide. This was heated with excess of mercury(II) chloride over a steam-bath to produce arsenic(III) oxide and mercury(I) chloride. After concentration of the solution, hydroxylamine sulphate solution was added, followed by aqueous ammonia (dropwise) until the mercury was precipitated. The mixture was heated until no further nitrogen was evolved, and then cooled. Hydrochloric acid was added to the clear supernatant solution and, after degassing, the solution was polarographed. The half-wave potential was $-0{\cdot}35$ V (*vs.* S.C.E.) in 1·5M hydrochloric acid, and $-0{\cdot}5$ V (*vs.* S.C.E.) in 0·5M hydrochloric acid. Antimony did not interfere, and arsenic could be determined in the range 1–1000 μg.

Oscillopolarography has been used to develop a method for the detection and determination of arsenic, antimony and tin in the presence of each other, in electrolytes containing hydrochloric acid and the chlorides of alkali metals.[65] With a supporting electrolyte of 1M hydrochloric acid containing arsenic(III) in the concentration range $1\text{–}5 \times 10^{-4}M$, characteristic cut-ins were noted on the oscillopolarographic waves $\mathrm{d}V/\mathrm{d}t = f(V)$, these being suitable for quantitative purposes. By this method, arsenic may be determined in biological materials after suitable decomposition and preparation of the sample. Oscillopolarographic methods for the determination of arsenic and other contaminants in foodstuffs have been reviewed.[66]

Other materials

Microgram quantities of arsenic have been determined in white phosphorus by an interesting application of square-wave polarography.[67] The phosphorus samples were prepared by the following methods: distillation of white phosphorus; distillation of red phosphorus after melting with lead; vacuum distillation of white phosphorus after melting with indium. The prepared samples were dissolved in nitric acid by warming on a water-bath, and excess of nitric acid was expelled from the solution by continued heating. After the addition of sulphuric acid and hydrazine sulphate, the mixture was dissolved in hydrochloric acid and the polarogram recorded. The arsenic content of the samples was also determined by the Gutzeit method, and good agreement was obtained.

The square-wave polarograms were found to be best defined in hydrochloric acid solutions. In $2M$ hydrochloric acid, the two arsenic peaks were clearly separated, appearing at $-0{\cdot}42$ and $-0{\cdot}63$ V (*vs.* S.C.E.) respectively, although the shape of the second was better than that of the first. The calibration curve was found to be linear over the range $2\text{–}16 \times 10^{-6}M$ arsenic(III). In view of the fact that a good polarogram may be obtained from a dilute solution of hydrochloric acid as the supporting electrolyte to d.c. polarography, it would be interesting to see whether the workable range for arsenic could be increased, and to apply the method to the determination of arsenic in other materials.

Arsenic may be determined in sulphuric acid itself by neutralizing with sodium carbonate (to Methyl Orange), and recording the polarogram after adding a slight excess of potassium tartrate.[68] The application of polarography to the determination of arsenic (and lead) in phosphoric acid, and the influence of phosphoric acid concentration and common impurities have also been discussed.[6]

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Zusammenfassung—Es wird eine Übersicht über das polarographische Verhalten von Arsen in verschiedenen Medien gegeben. Besonderer Nachdruck wird auf die Mechanismen der Elektrodenreaktionen und auf polarographische Verfahren zur Bestimmung des Elements gelegt.

Résumé—On passe en revue le comportement polarographique de l'arsenic en divers milieux en mettant en particulier l'accent sur les mécanismes des réactions à l'électrode et sur l'emploi de méthodes polarographiques pour le dosage de cet élément.

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SHORT COMMUNICATIONS

Radiochemical separations by the ring-oven technique—IV.

The system $^{144}Ce/^{144}Pr$

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IN PREVIOUS papers[1-3] it has been shown that the ring-oven technique of Weisz can be successfully applied in rapid radiochemical separations. Various genetically related radionuclides, formed by fission, could be separated in such a way that the parent nuclide was fixed in the centre of the filter paper, while the daughter nuclide was milked off and concentrated in the ring zone.

Such a nuclide pair, also formed by fission, is $^{144}Ce/^{144}Pr$. Its determination is of interest for calculating reactor-fuel burn-up.[4] For selective evaluation of ^{144}Pr in a nuclide mixture (requiring its separation from ^{144}Ce) and for investigating the characteristics of short-lived isotopes of Pr and Ce,[5] rapid separation techniques would be advantageous.

It will be shown how ^{144}Pr can be separated from ^{144}Ce quite easily by the ring-oven technique, with filter paper impregnated with hydrated manganese oxide.

EXPERIMENTAL

Preparation of filter papers

Filter papers MN 2260, 55 mm in diameter (Macherey, Nagel and Co., Düren, West Germany), were immersed for 10 min in 0·4% potassium permanganate solution, blotted with "Weißband" filter paper (Schleicher u. Schüll 589[2]) and exposed to air for 4–5 min. Thereafter, each paper was immersed vertically for 25 sec in 125 ml of 1% hydrogenperoxide solution in a tall, narrow glass tank (80 × 30 × 80 mm). To ensure uniform impregnation, the filter paper must be dropped as quickly and completely as possible into the solution. Contact with the tank walls must be avoided, and the peroxide solution must be renewed after every second filter paper. After the immersion each paper was rinsed in distilled water and then left for 1 hr in distilled water in another container. This water was replaced by fresh water every 10 min. Finally the impregnated papers were placed on filter paper sheets and air-dried.

Procedure

A hydrochloric acid carrier-free $^{144}CeCl_3$ solution, at pH ~1, with a specific activity of 33 μCi/ml was used for this investigation; 2 μl were spotted on the centre of an impregnated filter paper, and the still moist spot was fumed with ammonia and dried with warm air. A second 2-μl portion was applied to the first spot and treated similarly. The ^{144}Pr was separated from the ^{144}Ce and concentrated in the ring by washing with six 20-μl portions of 0·06–0·07M trichloracetic acid by the customary method on a ring-oven. After the third portion had been added, a stop-watch was started (time $t = 0$ of the separation). A final wash was given with 20 μl of distilled water, and the filter paper was fumed over ammonia and dried with warm air. Immediately, a 19-mm diameter disc was cut out of the centre of the filter paper (^{144}Ce). The rest of the filter paper was covered with aluminium (2·15 mg/mm^2) and the decay of the ^{144}Pr was followed by β-measurement, starting approx. 4 min after the time $t = 0$.

About 3 hr after the first separation (*ca.* 10 half-lives of ^{144}Pr) another portion of ^{144}Pr could be milked from the cut out disc. For this purpose, it was trimmed to 17-mm diameter, pressed onto the centre of another impregnated filter paper[1,6] and washed with eight 20-μl portions of trichloracetic acid, followed by 20μl of distilled water, on the ring-oven (the stop-watch was started after addition of the fifth portion of acid). As soon as the separation was complete, filter-paper and disc were fumed over ammonia and dried with warm air. Again a 19-mm disc was cut out of the centre of the filter paper before the ^{144}Pr-activity in the ring was determined. Thus the interfering ^{144}Ce-activity, that passed into the underlying filter paper (2–5% of the total ^{144}Ce) could be eliminated (*cf.* refs. 1–3).

To calculate the ^{144}Pr yield, the activity R_0 in the ring at time $t = 0$ was obtained by extrapolating the activity–time curve, and the activity R before separation was obtained by counting the spot on the paper, covered with 2·15 mg/mm^2 aluminium sheet, before washing was begun. The yield Y is given by $Y = 100\,R_0F/R$ where F is the geometry factor (experimentally determined). The decontamination factor D was determined from the β-measurement of the uncovered disc (counting rate R_d) and ring (rate R_r) 3–4 hr after the separation; $D = R_d \,.\, Y/100\,\mathrm{R}_rF$.

RESULTS AND DISCUSSION

After numerous trials with various exchange materials, the filter papers prepared as described above, were found to exhibit the most suitable properties for the ^{144}Ce–^{144}Pr separation. With 0·06–0·07M trichloracetic acid as wash solution, ^{144}Pr-yields of 80–90%, with decontamination factors $>10^3$, were obtained. When considering these values, it must be borne in mind that the separation was achieved over a relatively short distance (the diameter of the ring is 22 mm) and was completed within about 3 min. The yield could be increased to $>96\%$ by using 0·07–0·08M trichloracetic acid or by extracting the daughter nuclide with a larger volume of wash solution, but then the decontamination factor decreases to 10^2–10^3.

The decay of the ^{144}Pr in the ring was followed and the half-life calculated by the least-squares method for a few decay-curves as well as by the so-called "quotient method" (see, *e.g.*, Böhler[7]). From 14 results a mean half-life of 17·60 ± 0·05 min was obtained.

Various parameters that affect the separation were thoroughly investigated, such as type and concentration of wash solution (nitric and hydrochloric acids were also used) and, above all, the preparation of the impregnated filter paper. It was found that the exchange properties of the hydrated manganese oxide depended mainly on the method of preparation.

The following methods were tried: (*a*) air oxidation of manganese(II) hydroxide, (*b*) reaction between Mn(II) and permanganate, (*c*) reduction of permanganate with excess of hydrogen peroxide.

The impregnated filter papers prepared by methods (*a*) and (*b*) gave poor yields of ^{144}Pr as well as very low decontamination factors. Bigliocca and co-workers[8] investigated the sorption properties of a hydrated manganese oxide (average composition $MnO_{1.88}$), prepared by method (*b*) and found that cerium was sorbed but that praseodymium was only partially sorbed.

In preparation of the impregnated filter paper by method (*c*), the permanganate and hydrogen peroxide concentrations and the reduction time were all important: too high a permanganate concentration resulted in low ^{144}Pr-yields; too low permanganate and peroxide concentrations as well as a short reduction time gave unsatisfactory decontamination factors.

An unexpected result was obtained when the quantity of manganese on the filter papers was determined. The oxidation equivalent (iodometrically) and the manganese content (chelatometrically) were determined for every filter paper. It was concluded from these titrations that the manganese (average 2·3 mg per filter) had an average oxidation number of +3. Similar compounds were prepared by Feitknecht and Marti,[9] by oxidation of an ammoniacal solution of manganese(II), with hydrogen peroxide. To call products, prepared by method (c), "manganese dioxide" would be erroneous. The "manganese dioxide" filter papers used in the ^{99}Mo–^{99m}Tc separation[2] were also most probably papers with hydrated manganese oxide having an average oxidation state of +3. Filter papers that had been prepared by method (*b*) definitely had better exchange properties after a final immersion in hydrogen peroxide solution. From this, it can be deduced that the hydrogen peroxide can reduce the permanganate further than to the MnO_2 stage.

Kolařik and Krtil[10] describe the separation of various fission products by "manganese(IV) hydroxide". Their column material was also produced by reduction of permanganate with hydrogen peroxide, but apparently an excess of reductant was avoided.

A purified filter paper, *e.g.*, "Weißband", was used to blot the filter papers after immersion in the permanganate solution. If qualitative paper was used, an uncontrollable partial reduction of permanganate took place. The impregnated filter papers prepared by method (*c*) should be air-dried for one day and used within 10–14 days. This precaution is necessary because of chemical and physical changes that the precipitate undergoes with longer periods of time.

The reason that cerium and praseodymium behave differently on the exchange material used, may be that Ce(III) is oxidized to Ce(IV) by the higher oxidation-state manganese oxide hydrates.[11] The separation described was developed by using carrier-free ^{144}Ce/^{144}Pr solution; the results were distinctly influenced by small additions of cerium(III) carrier. With a carrier concentration of 5 μg/ml varying but definitely lower ^{144}Pr-yields were obtained; with carrier at the 50 μg/ml level, the "capacity" of the exchange material was evidently exceeded, as a large portion of the ^{144}Ce was found in the ring.

To investigate the possibility of determining ^{144}Ce/^{144}Pr in a mixture of fission products, the behaviour of ^{137}Cs, ^{90}Sr/^{90}Y and ^{106}Ru was studied under the same conditions: more than 99·5% of the ^{137}Cs, 99% of the ^{90}Sr and 95–98% of the ^{90}Y were washed into the ring. With carrier-free ^{106}Ru (in 1M nitric acid) difficulties were encountered; 80% of this nuclide remained in the centre of the filter paper, whereas 80% were washed into the ring after a formaldehyde treatment of the nitric acid solution.[11]

The results show that the method described is not only useful for the parent–daughter separation but also—after suitable modification—for solving other analytical radiochemical problems.

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Summary—By using filter papers impregnated with a manganese oxide hydrate having an average oxidation number of +3, it is possible to separate ^{144}Pr from ^{144}Ce rapidly by the ring-oven technique. With 0·06–0·07M trichloracetic acid as wash-solution, the daughter nuclide can be concentrated in the ring zone with 80–90% yield and decontamination factors $>10^3$. The half-life of the separated ^{144}Pr was found to be 17·60 ± 0·05 min. The behaviour of other fission nuclides under the same conditions was also investigated.

Zusammenfassung—Auf Filterpapieren, die mit einemMangan oxidhydrat der mittleren Oxidationszahl +3 imprägniert sind, kann man mit Hilfe der Ringofenmethode ^{144}Pr schnell von ^{144}Ce trennen. Mit 0,06–0,07 M Trichloressigsäure als Waschlösung kann das Tochternuklid in der Ringzone mit 80–90% Ausbeute und Dekontaminationsfaktoren über 10^3 angereichert werden. Die Halbwertszeit des abgetrennten ^{144}Pr wurde zu 17,60 ± 0,05 min gefunden. Das Verhalten anderer Spaltnuklide unter denselben Bedingungen wurde ebenfalls untersucht.

Résumé—En utilisant des papiers filtres imprégnés d'un hydrate d'oxyde de manganèse ayant un niveau d'oxydation moyen de 3, il est possible de séparer rapidement ^{144}Pr de ^{144}Ce par la technique du four annulaire. Avec de l'acide trichloracétique 0,06–0,07M comme solution de lavage, on peut concentrer le nucléïde-fille dans la zone annulaire avec un rendement de 80–90% et un facteur de décontamination $>10^3$. On a trouvé que la demi-vie du ^{144}Pr séparé est de 17,60 ± 0,05 mn. On a également étudié le comportement d'autres nucléïdes de fission dans les mêmes conditions.

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Zero-current bipotentiometric indication using two differently pretreated electrodes

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CONSIDERATION of the parameters which govern the kinetics of a single electrochemical reaction, leads to a general expression for the electrode potential E,

$$E = (C, i, A, \delta, \alpha, k_s) \tag{1}$$

where C is the concentration of the potential-determining species at the surface of the electrode, i the current, A the surface areas of the electrode, δ the thickness of the Nernst diffusion layer, α the electrochemical transfer coefficient and k_s the heterogeneous rate constant of the electrochemical reaction. The explicit form of this function is not known, but a function of this kind enables us to predict that two indicator electrodes immersed in a solution of constant composition will exhibit the same potential only if all the parameters involved have the same value for both electrodes. If there exist differences in one or more of the parameters in function (1), these differences will cause the otherwise identical indicator electrodes to respond at different rates to the changes in solution, that is, a potential difference will be set up between them during a titration.[1] This potential difference will show a sudden change at the end-point thus permitting location of it (bipotentiometric technique).

Differences in the following potential-determining parameters have been exploited for bipotentiometric indication.

(*a*) Concentration (C): differential titration according to Cox, with differently retarded electrode systems.[2]

(*b*) Surface area (A): achieved with two electrodes of different apparent geometric area,[3,4] or different effective surface area.[5]

(*c*) Overvoltage: constant current potentiometry, bipotentiometry or differential electrolytic potentiometry.[6]

(*d*) Thickness of the diffusion layer (δ): obtained either by very fast stirring or by vibrating one of the indicator electrodes.[1]

This paper describes a new bipotentiometric indication technique based on differences in the kinetic parameters (α, k_s) which affect the reversibility of an electrochemical reaction on two differently pretreated platinum indicator electrodes.[7,8] The potential differences at the end-point will be a function of time, caused by the difference in the rates with which the dissimilar electrodes approach equilibrium and such differences are therefore to be expected to appear only in those cases where at least one of the electrode reactions is initially slow. Some aspects of the nomenclature and the rational classification of different potentiometric technique are also dealt with.

EXPERIMENTAL

Zero-current bipotentiometric titrations were carried out with a conventional potentiometric assembly consisting of a 50-ml tall-form beaker, a 10-ml semimicro burette and an electromagnetic stirrer. Two identical rectangular smooth platinum indicator electrodes each with an apparent geometric area of 93 mm^2 were used. Before use, the platinum electrodes were pretreated as indicated in our previous paper.[8] A Radiometer Type TTT1 pH-meter was used for measurement of potentials, The very small current drain of the apparatus (1 pA) is negligible as far as its polarizing effect is concerned. The platinum electrodes were connected directly to the potentiometer. Titration curves of potential difference between the platinum electrodes *vs*. volume of titrant added were recorded in the usual way. The following titrations were performed: $0{\cdot}0013M$ iron(II) with $0{\cdot}01M$ cerium(IV) (case I, both systems fast electrochemically), $0{\cdot}002M$ vanadium(V) with $0{\cdot}01M$ iron(II) (case II, the first system slow) and $0{\cdot}0015N$ oxalic acid with $0{\cdot}01N$ permanganate (case III, both systems slow).

Analytical grade chemicals and doubly distilled water were used.

RESULTS AND DISCUSSION

When two identical platinum indicator electrodes subjected to the same pretreatment procedure are used bipotentiometric titration curves as shown in Fig. 1 are obtained.

As expected, the potential difference between the electrodes in this case (identical pretreatment of the electrodes) is small during the whole titration. Although as a rule ΔE should be zero during the titration, a small break is observed near the end-point owing to some differences in the parameters of equation (1), mainly in the true electrode area and in the catalytic properties of the two electrodes. The general shape of the titration curves obtained is the same when other (but identical) pretreatment procedures are used, *e.g.*, reduction, ignition of the platinum, or preparation of bare surfaces.

Dissimilar pretreatment of the electrodes results in much higher potential differences during titrations. The shape of the titration curves depends on the electrochemical reversibility of the systems involved, as well as on the influence of the pretreatment on the rate of the corresponding electrode processes (Fig. 2).

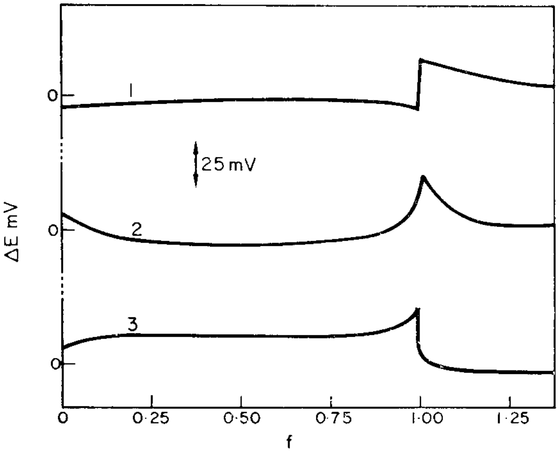

FIG. 1.—Zero-current bipotentiometric titration curves taken with identically pretreated platinum electrodes.

Treatment: electrochemical oxidation at +1·45 V (*vs.* S.C.E.). *1*—both systems fast, case (I); *2*—one system slow, case (II); *3*—both systems slow, case (III) (see text). ΔE is the potential difference observed between the electrodes, *f* is the equivalent fraction of titrant added.

The surface state of the electrodes also depends on the nature of the oxidizing or reducing agents used, as well as on the nature of the ions adsorbed.[8] Thus, electrodes oxidized in different ways yield different surfaces and consequently different titration curves (Fig. 3).

The following surfaces were investigated: oxidized (O), reduced (R), bare (B), and ignited (I), in all possible combinations in pairs, OB, OR, OI, BR, BI and RI. In each case the titration curves obtained were similar to those represented in Fig. 2 and 3, being characterized either by a sharp peak (*e.g.*, curves 2 or 3 in Fig. 2) or by a large potential jump (*e.g.*, curve 1, in Fig. 2) at the equivalence point. The potential change of each of the individual electrodes during the titration, measured against a reference electrode, is described by the usual S-shaped potentiometric curve, but owing to differences in the rates of the corresponding electrode reactions, one curve lags behind the other (Fig. 4).

It is apparent from Figs. 2 and 3 that the bipotentiometric titration curves obtained can be divided according to their form, into three categories: first-derivative curves of a usual potentiometric titration curve (curves 2, 3 in Fig. 2 and curve 2 in Fig. 3), second-derivative curves (curve 4 in Fig. 2) and some intermediate forms between these (curves 1 in Figs. 2 and 3). The first-derivative curve appears when both electrodes exhibit the same primitive curve, the only difference being that one curve lags behind the other. The second-derivative curves as well as the intermediate forms appear when the individual electrodes exhibit potentiometric curves of different shape (different potential break, different slope of the straight line portion) and/or the lag between the curves changes sign at the end-point. In each case the end-point can be easily detected, and used for automation purposes.

The rate of establishment of the electrode potential in general was rapid for ignited electrodes and slow on bare ones. The oxidized or reduced electrodes showed an intermediate position, but those oxidized with permanganate responded very slowly. The known fast systems (Fe^{3+}/Fe^{2+}, Ce^{4+}/Ce^{3+}) behaved more reversibly on all the surfaces studied than did the slow ones. Nevertheless an adequate electrode combination (*e.g.*, IO or IR) behaved satisfactorily even for the titration of oxalate with permanganate. The accuracy and precision in all cases was the same as for other electrochemical indication techniques under the same conditions. Similarly treated electrode pairs were unsatisfactory: ΔE was small and the location of the end-point was sometimes in error by more than 2%.

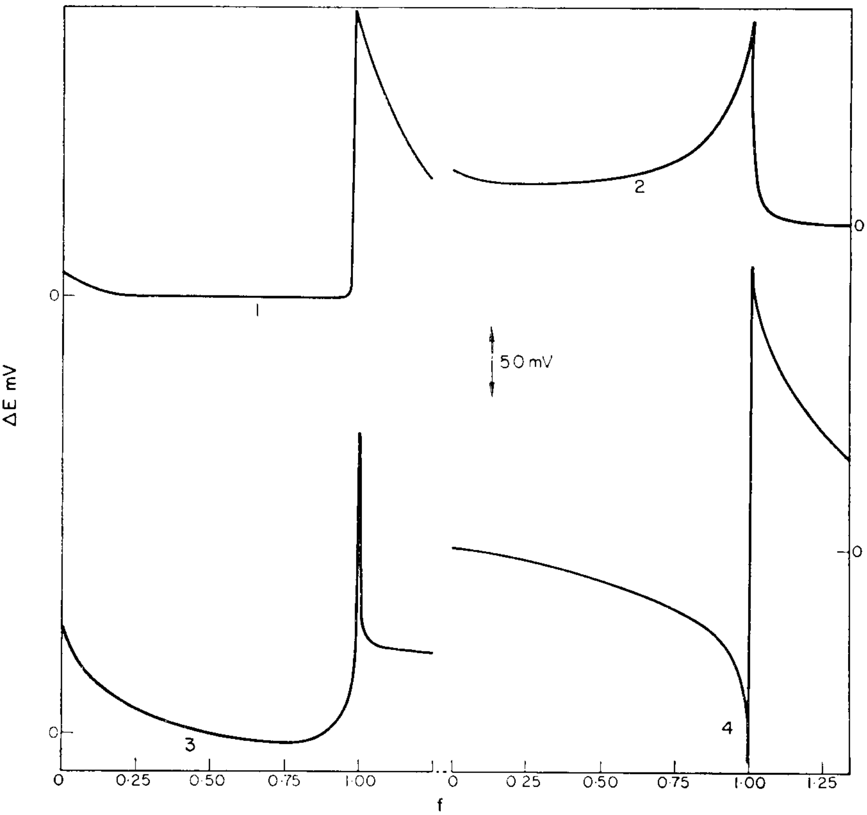

FIG. 2.—Zero-current bipotentiometric titration curves taken with dissimilarly pretreated electrodes.
1—case (I); *2*—case (II); *3*—case (III) (see text); one electrode was oxidized at +1·50 V (*vs*. S.C.E.), the other reduced at −0·300 V (*vs*. S.C.E.); *4*—case (II) but one electrode was bare, the other reduced electrochemically.

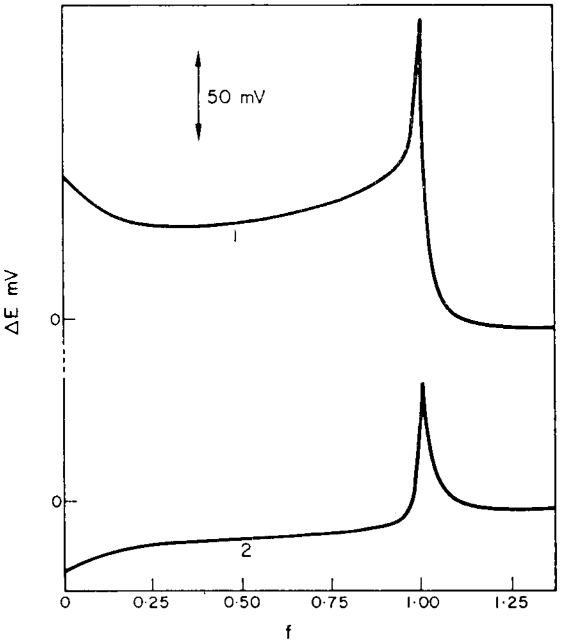

FIG. 3.—The effect of different oxidative pretreatments on the shape of zero-current bipotentiometric titration curves.
Case (II). One electrode was bare, the other oxidized: *1*—electrochemically at +1·50 V (*vs*. S.C.E.), *2*—with $KMnO_4$.

TABLE I.—SUGGESTED NOMENCLATURE AND CLASSIFICATION OF POTENTIOMETRIC TITRATION METHODS

Current	Experimental conditions in stirred solution	Response measured	Existing nomenclature	Suggested nomenclature
$i = 0$	one indicator electrode, sometimes pretreated	$E = f$ (volume of titrant)	potentiometric titration	zero-current potentiometric titration potentiometric titration
$i = 0$	two dissimilar indicator electrodes having different values for any of the parameters: $C, A, \delta, \alpha, k_s$	$\Delta E = f$ (volume of titrant) ΔE being the potential difference between the indicator electrodes	titration with twin electrodes at zero current[14]	zero-current bipotentiometric titration
$i =$ constant	one indicator electrode, sometimes pretreated	$E = f$ (volume titrant)	potentiometric titration with one polarizable electrode	constant-current potentiometric titration
$i =$ constant	two indicator electrodes, identical or dissimilar as above	$\Delta E = f$ (volume titrant)	potentiometric titrations with two polarizable electrodes, bipotentiometric titrations, differential electrolytic potentiometry, derivative polarographic titration, potentiometry at constant current, constant current potentiometry, or in German: Polarizationsspannungstitration, Polarovoltammetrie	constant-current bipotentiometric titration
$i = i_{\sim}$	one indicator electrode sometimes pretreated	$E_{\sim} = f$(volume of titrant)	not yet investigated	a.c. potentiometric titration
$i = i_{\sim}$	two indicator electrodes, identical or dissimilar as above	$\Delta E_{\sim} = f$ (volume of titrant)	polarization titration	a.c. bipotentiometric titration

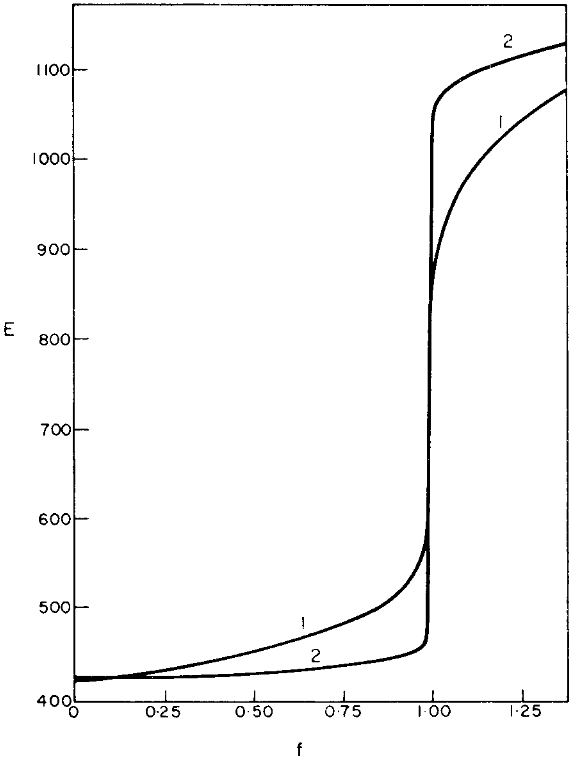

FIG. 4.—Potential–equivalent fraction of titrant added (f) relationship for individual electrodes used in the titration of V(V) with Fe(II).
One electrode was reduced (curve 1), the other bare (curve 2). The corresponding zero-current bipotentiometric titration curve is represented in Fig. 2, curve 4.

As little information is available on the effect of pretreatment of electrodes on their response in titration systems, the most suitable pretreatment must be found by trial and error for a given system. Zero current bipotentiometry based on two differently pretreated platinum electrodes is a very simple analytical procedure of general applicability, in which platinum electrodes can be used as concentration-potential transducers.

Consideration of the guiding principles of electroanalytical methods[11,12,13] as well as those discussed in the introductory part of this paper, lead us to attempt a revision of the nomenclature and classification of the many related techniques. Table I summarizes the characteristics of the possible potentiometric methods and offers suggestions concerning their nomenclature and rational classification.

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Summary—A new potentiometric technique of zero-current bipotentiometry using differently pretreated platinum electrodes is described, and its application to various redox titrations discussed. The potential across the electrodes appears to be generated by differences in kinetics of the reactions occurring on the two dissimilar electrode surfaces.

Zusammenfassung—Die stromlose Bipotentiometrie, eine neue potentiometrische Arbeitsweise, bei der verschieden vorbehandelte Platinelektroden verwendet werden, wird beschrieben und ihre Anwendung auf verschiedene Redoxtitrationen diskutiert. Die Spannung zwischen den Elektroden wird anscheinend durch die verschiedene Kinetik der Reaktionen verursacht, die sich an den beiden voneinander verschiedenen Elektrodenoberflächen abspielen.

Résumé—On décrit une nouvelle technique potentiométrique de bipotentiométrie à courant nul utilisant des électrodes de platine différemment prétraitées et discute de son application à divers titrages redox. Le potentiel à travers les électrodes se présente comme étant engendré par des différences dans les cinétiques des réactions se produisant sur les deux surfaces d'électrodes dissemblables.

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Sequential oxidimetric determination of thallium(I) and (III)

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Redox methods for the determination of thallium involve the oxidation of thallium(I) to thallium(III) either by direct titration with powerful oxidants such as potassium bromate,[1–3] potassium iodate,[4,5] chloramine,[6,7] potassium ferricyanide,[8] potassium permanganate,[5,9–12] lead tetra-acetate,[13] potassium dichromate[14] and cerium(IV) sulphate[5,15,16] or by adding excess of an oxidant such as iodine[17] in alkaline medium, filtering off the thallium(III) hydroxide and titrating the excess of iodine, after acidification, with thiosulphate. Alternatively, thallium(III) can be titrated directly with titanium(III),[2] hydrazine sulphate,[18] thiosulphate,[19] ascorbic acid,[20,21] vanadium(II),[22] chromium(II)[23] or hydroquinone,[24] or thallium(III) is allowed to react with excess of potassium iodide and the liberated iodine is titrated with thiosulphate[25–31] or arsenite.[30] All these methods involve the determination of either thallium(III) or thallium(I) alone.

It has been found necessary, in the investigation of the oxalate complexes of thallium,[32] to determine thallium and oxalic acid when present together. It was found that in the methods so far described for the oxidimetric determination of thallium, oxalic acid often interfered either by reacting with the titrant or by making the end-point less sharp.

The redox potential of the thallium(III)–thallium(I) couple does not vary much with sulphuric acid concentration,[33,34] and is ∼1·2 V, sufficiently high for oxidation of oxalic acid. The reaction between thallium(III) and oxalic acid was therefore investigated spectrophotometrically. Figure 1 shows that when thallium(III) is heated with excess of oxalic acid in 0·5*N* sulphuric acid it is reduced to thallium(I).

$$\mathrm{Tl(III)} + \mathrm{(COOH)_2} \rightarrow \mathrm{Tl(I)} + 2\mathrm{H}^+ + 2\mathrm{CO_2}$$

If conditions could be found for titration of oxalic acid in the presence of thallium(I) it would be possible to determine both thallium(I) and (III) in the same solution.

A survey of the literature[1,2,5,9–11,15,16] shows that for the titration of thallium(I) the presence of chloride is necessary, whereas oxalic acid can be titrated with either potassium permanganate or cerium(IV) sulphate even in the absence of chloride, a temperature of 70° and a 0·5–1*N* sulphuric acid medium being recommended.[35] This paper describes the investigation and application of the necessary conditions for sequential titration of oxalic acid and thallium(I).

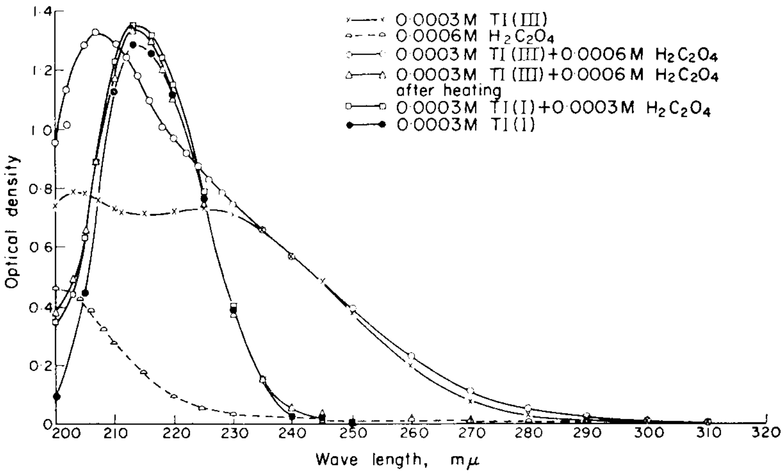

FIG. 1. Spectra in 0·5*N* sulphuric acid

EXPERIMENTAL

Reagents

Thallium(I) solutions were prepared by dissolving laboratory grade thallium(I) carbonate in sulphuric acid and standardizing by titration with cerium(IV) sulphate.

Thallium(III) solutions were prepared by oxidizing the thallium(I) solution with excess of bromine water, boiling off the excess, precipitating the hydroxide with ammonia, and dissolving it in sulphuric acid.

Oxalic acid solutions were prepared from the analytical grade reagent and standardized by permanganate titration.

Cerium(IV) sulphate solutions were standardized by titration against sodium oxalate without an indicator.[15]

Titration of oxalic acid in presence of thallium(I)

The possible interference of thallium(I) in the titration of oxalic acid in 0·5*N* sulphuric acid at 70–80° was investigated and the results are given in Table I, which shows that thallium(I) does not interfere in media containing sulphuric acid alone, but does if chloride is present. At a sufficiently high concentration of chloride both oxalic acid and thallium(I) react quantitatively.

The effect of varying the sulphate concentration was next examined, for the titration of a mixture of oxalic acid and thallium(I) in a medium consisting of 0·5*N* sulphuric acid and 0·5*M* sodium chloride (Table II). The results show that the effect of $<$0·5*M* chloride on the interference of thallium(I) could be prevented by making the titrate about 2*M* in ammonium sulphate.

Determination of thallium(III) and thallium(I)

It is clear that oxalic acid can be titrated in the presence of thallium(I) if in sulphuric acid medium, and both thallium(I) and oxalic acid should be titrated if enough chloride is added. Reduction of thallium(III) with excess of oxalic acid is quantitative in 0·5*N* sulphuric acid at the temperature of the boiling water-bath. Hence it is clear that thallium(III) could be reduced with excess of oxalic acid, the excess titrated with cerium(IV) sulphate and the amount of thallium(III) computed. On addition of enough chloride, the total thallium(I) [that produced by reduction of thallium(III) plus any originally present] could then be titrated with cerium(IV) sulphate at 80–90°, and the original thallium(I) content calculated.

Procedure

To 5 ml of a solution that is not more than 0·025*M* in thallium, add 10 ml of 2·5*M* sulphuric acid and 10 ml of 0·05*M* oxalic acid. If chloride is present add 25 g of ammonium sulphate. Dilute to 100 ml with water and heat on a boiling water-bath for 5 min (or heat just to boiling). Titrate at 70–80° with cerium(IV) sulphate until a faint yellow colour persists for about a minute. Note the consumption of titrant (x ml). Then add 5–6 ml of concentrated hydrochloric acid; the yellow colour should disappear. Continue the titration at 80–90° until a faint colour stable for one minute

TABLE I

[Chloride], *M*	Oxalic acid (0·05*M*) taken, *ml*	Thallium(I) (0·025*M*) added, *ml*	Ceric sulphate (0·05*M*) consumed, *ml*
0·0	5·00	0·00	10·00
		2·00	10·00
		5·00	10·00
		10·00	10·00
0·1 HCl	5·00	2·00	11·35
0·25 HCl			11·80
0·50 HCl			12·00
0·10 KCl	3·50	1·00	7·00
0·25 KCl			7·80
0·50 KCl			7·90
0·75 KCl			7·90
1·00 KCl			8·00
1·50 KCl			8·00
2·00 KCl			8·00
0·10 NH_4Cl	5·00	2·00	10·50
0·50 NH_4Cl			11·70
1·00 NH_4Cl			11·90
1·50 NH_4Cl			11·90
2·00 NH_4Cl			12·00
2·50 NH_4Cl			12·00
5·00 NH_4Cl			12·00

TABLE II

Concentration of ammonium sulphate, *M*	Oxalic acid (0·05*M*) taken, *ml*	Thallium(I) (0·0958*M*) taken, *ml*	Ceric sulphate (0·0532*M*) consumed, *ml*
—	5·00	—	9·40
—	—	0·50	1·80
—	5·00	0·50	11·20
0·50	5·00	0·50	11·00
1·00	5·00	0·50	9·80
1·50	5·00	0·50	9·50
2·00	5·00	0·50	9·40
2·50	5·00	0·50	9·40

TABLE III

Thallium(I) taken, *mmole*	Thallium(III) taken, *mmole*	Thallium(I) found, *mmole*	Thallium(III) found, *mmole*
0·0000	0·1250	0·0000	0·1250
0·0250	0·1000	0·0251	0·1001
0·0500	0·0750	0·0501	0·0751
0·0750	0·0500	0·0750	0·0499
0·1000	0·0250	0·1002	0·0250
0·1250	0·0000	0·1255	0·0000

is again obtained. Note the total volume of titrant added (y ml). Titrate 10 ml of the oxalic acid separately with the cerium(IV) sulphate (z ml). Then the volume of cerium(IV) sulphate equivalent to the thallium(III) present in the mixture is $(z - x)$ ml and that corresponding to the thallium(I) is $(y - x)$ ml. The amount of titrant needed to indicate the end-point is assumed to cancel. The results obtained in a typical set of experiments are given in Table III.

Interferences

Cadmium, zinc, ammonium, potassium, calcium, strontium and barium and similar ions do not interfere in the titration. Copper(II) does not interfere if its concentration is below $0{\cdot}01M$, but at higher concentrations masks the colour change at the end-point. Iron(III) does not interfere up to $0{\cdot}001M$, but above that concentration the deep yellow colour of iron(III) oxalate interferes with the detection of the end-point. Other ions oxidizable with cerium(IV) sulphate or which are strongly coloured will interfere. The interference of chloride (up to $0{\cdot}5M$) in titration of the excess of oxalic acid can be suppressed by adding enough ammonium sulphate (Table II).

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Summary—The reaction between thallium(III) and oxalic acid in sulphuric acid medium has been investigated. Spectrophotometric results show that thallium(III) can be quantitatively reduced to thallium(I) with oxalic acid in aqueous medium when heated to near boiling point. Conditions for the estimation of the excess of oxalic acid with cerium(IV) sulphate in the presence of thallium(I) and for the estimation of a mixture of thallium(I) and thallium(III) have been investigated. The method is simpler than many other redox methods reported for the determination of thallium(III) and is free from many interferences encountered in these titrations. The reagents are cheap and quite stable.

Zusammenfassung—Die Reaktion zwischen Thallium(III) und Oxalsäure in schwefelsaurem Medium wurde untersucht. Spektrophotometrische Ergebnisse zeigen, daß Thallium(III) mit Oxalsäure in wäßrigem Medium quantitativ zu Thallium(I) reduziert werden kann, wenn fast bis zum Sieden erhitzt wird. Es wurde untersucht, unter welchen Bedingungen der Überschuß an Oxalsäure in Gegenwart von Thallium(I) mt Cer(IV) sulfat bestimmt und Gemische von Thallium(I) und Thallium(III) analysiert werden können. Das Verfahren ist einfacher als viele andere für die Bestimmung von Thallium(III) angegebene Redoxmethoden und frei von vielen Störungen, die man bei diesen Titrationen antrifft. Die Reagentien sind billig und recht stabil.

Résumé—On a étudié la réaction entre le thallium(III) et l'acide oxalique en milieu acide sulfurique. Les résultats spectrophotométriques montrent que le thallium(III) peut être quantitativement réduit en thallium(I) par l'acide oxalique en milieu aqueux lorsqu'on chauffe au voisinage du point d'ébullition. On a étudié les conditions pour l'estimation de l'excès d'acide oxalique par le sulfate de cérium(IV) en la présence de thallium(I) et pour l'estimation d'un mélange de thallium(I) et thallium(III). La méthode est plus simple que de nombreuses autres méthodes redox décrites pour la détermination du thallium(III) et est exempte de nombreuses interférences rencontrées dans ces titrages. Les réactifs sont bon marché et tout à fait stables.

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PRELIMINARY COMMUNICATIONS

A simple low-power reduced-pressure microwave plasma source for emission spectroscopy

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THERE is a growing interest in sources other than flames for the determination of traces of metal ions in solution by emission spectroscopy. In particular, there has been much attention to the development of capacitatively and inductively coupled plasma sources.[1-7] Although sensitivity is frequently excellent, the apparatus is often complex and expensive and the power requirement high. There is a need for a simple, compact low-power microwave plasma source offering rapid, sensitive routine determination of traces of metal ions in aqueous solution, and conveniently usable with commercially available detection systems such as those of flame spectrophotometers. This communication describes such an apparatus which we have constructed.

EXPERIMENTAL

Apparatus

The apparatus is shown diagrammatically in Fig. 1. The power source was a Microtron 200 microwave generator (maximum output 200 W, 2450 MHz) and 214 L resonant cavity (Electro-medical Supplies Ltd., London). The detection system consisted of the grating monochromator

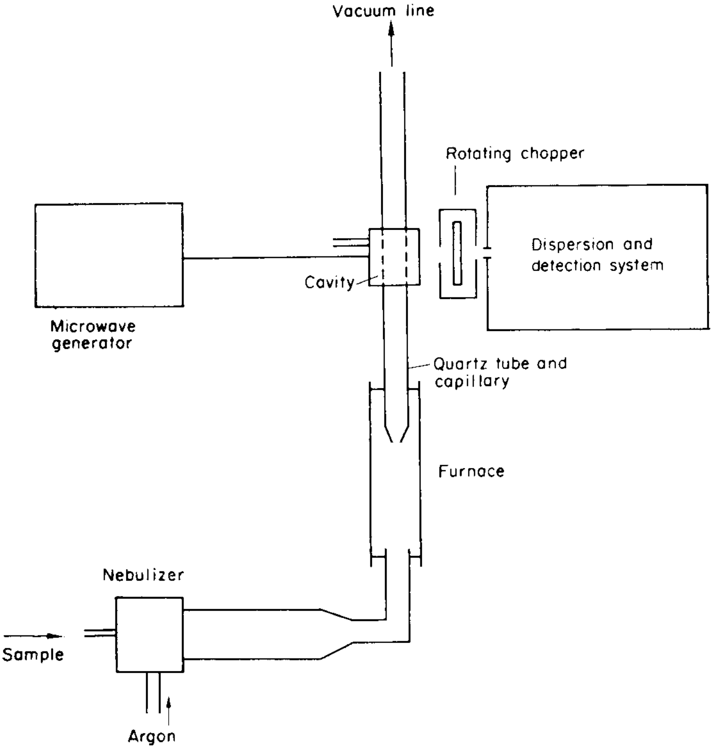

FIG. 1.—Diagrammatic representation of apparatus employed.

(f/10, reciprocal linear dispersion at exit slit 3·3 nm/mm), photomultiplier (Hamamatsu Type R213, spectral response 185–800 nm, maximum response at 430 nm) and amplification system of a Techtron AA4 flame spectrophotometer.

Method

Sample solution is introduced *via* an indirect nebulizer operated on argon (Pressure 41 kN/m^2; gas flow-rate 4·3 l./min). The sample mist is passed through a heated silica tube (15 mm diameter, 300 mm long) in an electrically heated furnace at 550° and drawn into a quartz tube 8 mm bore) *via* the capillary (cross-section 0·4 mm^2) at its end within the furnace. The quartz tube passes through the air-cooled resonant cavity, and the pressure within the tube is kept at 120 mbar by a rotary vacuum pump connected *via* a moisture trap. In this way the sample solution is nebulized at above atmospheric pressure, and the partly evaporated aerosol is sampled and the discharge maintained at reduced pressure. The radiation is focussed onto the slit of the monochromator. A rotating chopper (285 Hz) is interposed between the source and the slit so that the a.c. amplification system of the spectrophotometer can be used.

RESULTS

The effect of the argon pressure used for nebulization, on the emission intensity of the selenium 203·9 nm atomic line is shown in Fig. 2*b*. Figure 2*a* shows the effect of the microwave power on the emission intensity of the mercury 253·7 nm atomic line. Similar results are obtained for other metal ions, and power of 100 W and argon pressure of 41KN/m^2 were chosen as operating conditions.

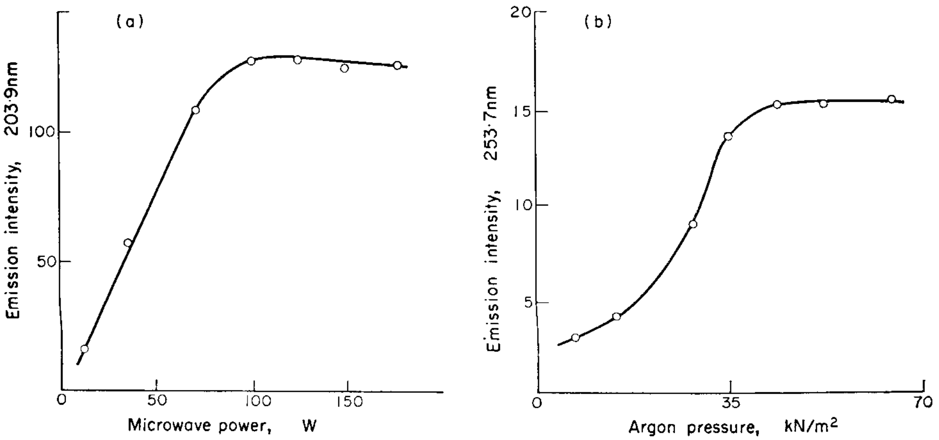

FIG. 2.—(*a*) Effect of microwave power on the emission intensity for mercury at 253·7 nm.
(*b*) Effect of argon nebulization pressure on the emission intensity for selenium at 203·9 nm.

The characteristic argon spectrum constitutes the background emission between 200 and 600 nm. When aqueous solutions are nebulized the background emission intensity from argon is reduced considerably. The water vapour present, however, contributes to the background *via* intense emission from the 306·4 nm system of OH and from H_2O itself above 550 nm. For each element tested the emission spectrum was recorded between 190 and 600 nm, and the strongest atomic line chosen for quantitative measurements. Detection limits (based on a signal-to-noise signal ratio of unity) are shown in Table I. Rectilinear calibration graphs were obtained for each of the elements investigated.

The reproducibility of the intensity measurements was initially unsatisfactory, owing to blockage of the capillary and overheating of the resonant cavity, but when the capillary is placed well within the furnace and the cavity is air-cooled, excellent reproducibility is obtained. The high emission intensities obtained enable a high resolution monochromator to be employed at narrow slit-width. This results in relative freedom from interelement effects due to the spectral overlap. The preliminary

TABLE I.—DETECTION LIMITS FOR ELEMENTS STUDIED

Element	Wavelength, *nm*	Slit-width, *μm*	Detection limit, *ppm*
Ca	422·7	75	0·02
Zn	213·9	75	0·05
Mg	383·8	75	0·1
Sn	242·9	50	4·0
Na	589·0	50	0·02
Sb	259·8	50	0·1
As	228·8	75	1·0
Te	214·3	75	0·2
Se	204·0	125	10
Fe	372·0	50	1·0
Cu	324·7	20	0·4
Cd	228·8	60	0·04
Hg	253·7	40	0·001

results suggest that this simple source offers considerable promise as an alternative to a conventional flame for emission spectroscopy.

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Summary—The construction of a simple low-power microwave plasma source for emission spectroscopy is described.

Zusammenfassung—Die Konstruktion einer einfachen Mikrowellen-Plasmaquelle niedriger Leistung für die Emissionsspektroskopie wird beschrieben.

Résumé—On décrit la construction d'une source simple de plasma à microondes, de faible puissance, pour la spectroscopie d'émission.

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Solid–liquid separation after liquid–liquid extraction

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LIQUID–LIQUID extraction of metal chelates has been widely used especially in the spectrophotometric determination of traces of metals. However, the distribution equilibrium of the chelate between both phases is sometimes not attained very quickly or the phase separation after shaking is not very clear. Here we present a new method in which liquid–liquid extraction at elevated temperature is followed by solid–liquid separation at room temperature using the spectrophotometric determination of copper as an example.

EXPERIMENTAL

Reagent pellet

Reagent-grade 8-hydroxyquinoline (5·0 g) and reagent-grade diphenyl (495 g; m.p. 70·5°) warmed on a steam-bath, melted, mixed well, cooled, and divided into 5·0 g portions.

Procedure

About 50 ml of sample solution are taken in a 100-ml round-bottomed concial flask furnished with a tightly sleeved glass stopper. The pH of the solution is adjusted to ~6·0 after addition of a small amount of ammonium acetate as buffering agent. The solution is heated on a steam-bath to above 90° a reagent pellet is added and the mixture is tightly stoppered and shaken vigorously and then let stand at room temperature. The liquid diphenyl layer dissolves the copper oxinate, and on cooling solidifies to a ball and sinks to the bottom. The aqueous layer is removed and the pellet washed with a small amount of water by decantation, and dissolved in chloroform after addition of a small amount of anhydrous sodium sulphate. The solution is then transferred quantitatively into a 25-ml volumetric flask and diluted to the mark with chloroform. The absorbance at 410 nm is measured.

RESULTS AND DISCUSSION

Beer's law holds up to 3 μg of copper per ml of original solution. Paraffins, naphthalene and its derivatives, and any suitable substances which melt between ~40 and 90° can be used as the solvent, but diphenyl has the big advantages of a high interfacial tension against water and of a specific gravity >1. The distribution equilibrium is attained very rapidly as the distribution coefficient is high enough at the temperature used.

The proposed method could also be applied to the removal of interfering major components in trace analyses and to the decontamination of radioactive elements.

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Summary—A low-melting solid is used as organic solvent for liquid-liquid extraction at elevated temperatures followed by solidification and decantation of the aqueous phase.

Zusammenfassung—Ein niedrig schmelzender Feststoff wird als Lösungsmittel zur flüssig-flüssig-Extraktion bei erhöhter Temperatur verwendet. Man läßt anschließend erstarren und dekantiert die wäßrige Phase.

Résumé—On utilise un solide à bas point de fusion comme solvant organique pour l'extraction en phase liquide aux témperatures élevées suivie de solidification et de décantation de la phase aqueuse.

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NOTE

NOMENCLATURE IN THERMAL ANALYSIS

NOMENCLATURE in thermal analysis is neither uniform nor consistent and can at times be confusing. Because of this a committee consisting of Dr. R. C. Mackenzie (Chairman), Mr. C. J. Keattch (Secretary), Dr. J. P. Redfern and Dr. A. A. Hodgson was appointed at the First International Conference on Thermal Analysis to explore this field. A report, arrived at after consultation with experts in all major English-speaking countries and in other countries interested in this aspect, was approved in principle at the Second International Conference on Thermal Analysis and the Council of the International Confederation for Thermal Analysis (ICTA) have directed that it be published.

This first report is offered as a definitive document of ICTA, the recommendations in which ought to be adhered to in all publications in the English language. It is appreciated that this is only a beginning and that many aspects still require attention; furthermore, new developments in the science may lead to minor revision. Such matters will be the subject of later reports.

Since linguistic considerations render difficult universal application of terms and it may be that names unacceptable in one language are normal usage in another, sub-committees are at present considering the position regarding the French, German, Japanese and Russian languages. The decisions of these sub-committees will be published later and developments in the field of nomenclature will be reported from time to time in the *ICTA Newsletter.*

I. GENERAL RECOMMENDATIONS

(*a*) *Thermal analysis* and *not* "thermography" should be the acceptable name in English, since the latter has at least two other meanings in this language, the major one being medical (*Sci. Progr. London*, 1967, **55**, 167). The adjective should then be *thermoanalytical* (*cf.* physical chemistry and physicochemical): the term "thermoanalysis" is not supported (on the same logical basis).

(*b*) *Differential* should be the adjectival form of *difference*; *derivative* should be used for the first derivative (mathematical) of any curve.

(*c*) The term "analysis" should be avoided as far as possible since the methods considered do not comprise analysis as generally understood chemically: terms such as *differential thermal analysis* are too widely accepted, however, to be changed.

(*d*) The term *curve* is preferred to "thermogram" for the following reasons:

1. "Thermogram" is used for the results obtained by the medical technique of thermography—see (*a*).
2. If applied to certain curves (*e.g.*, thermogravimetric curves), "thermogram" would not be consistent with the dictionary definition.
3. For clarity there would have to be frequent use of terms such as differential thermogram, thermogravimetric thermogram, *etc*, which are not only cumbersome but also confusing.

(*e*) In multiple techniques, *simultaneous* should be used for the application of two or more techniques to the same sample at the same time: *combined* would then indicate the use of separate samples for each technique.

(*f*) *Thermal decomposition* and similar terms are being further considered by the Committee.

II. TERMINOLOGY

Acceptable names and abbreviations, together with names which were for various reasons rejected, are listed in Table I. The Committee are in accord with the suggestion, made during discussion of the report, that the limited number of abbreviations considered permissible should be adopted internationally, irrespective of language.

The committee do not wish to pronounce on nomenclature in borderline techniques (such as thermometric titrimetry or calorimetry) which are, to its knowledge, being considered by other bodies. Consideration of techniques not yet extensively employed has been deferred.

III. DEFINITIONS AND CONVENTIONS

A. General

Thermal analysis. A general term covering a group of related techniques whereby the dependence of the parameters of any physical property of a substance on temperature is measured.

TABLE I.—RECOMMENDED TERMINOLOGY

Acceptable name	Acceptable abbreviation*	Rejected name(s)
A. *General*		
Thermal analysis		Thermography Thermoanalysis
B. *Methods associated with weight change*		
1. *Static*		
Isobaric weight-change determination		
Isothermal weight-change determination		Isothermal thermogravimetric analysis
2. *Dynamic*		
Thermogravimetry	TG	Thermogravimetric analysis Dynamic thermogravimetric analysis
Derivative thermogravimetry	DTG	Differential thermogravimetry Differential thermogravimetric analysis Derivative thermogravimetric analysis
C. *Methods associated with energy change*		
Heating curves†		Thermal analysis
Heating-rate curves†		Derivative thermal analysis
Inverse heating-rate curves†		
Differential thermal analysis	DTA	Dynamic differential calorimetry
Derivative differential thermal analysis		
Differential scanning calorimetry	DSC	
D. *Methods associated with evolved volatiles*		
Evolved gas detection	EGD	Effluent gas detection
Evolved gas analysis‡	EGA	Effluent gas analysis Thermovaporimetric analysis
E. *Methods associated with dimensional change*		
Dilatometry		
Derivative dilatometry		
Differential dilatometry		
F. *Multiple techniques*		
Simultaneous TG and DTA, *etc.*		DATA (Differential and thermogravimetric analysis) Derivatography Derivatographic analysis

* Abbreviations should be in capital letters without full-stops, and should be kept to the minimum to avoid confusion.

† When determinations are performed during the cooling cycle these become *Cooling curves*, *Cooling-rate curves* and *Inverse cooling-rate curves*, respectively.

‡ The method of analysis should be clearly stated and abbreviations such as MTA (mass-spectrometric thermal analysis) and MDTA (mass spectrometry and differential thermal analysis) avoided.

B. Methods Associated with Weight Change

1. *Static*

Isobaric weight-change determination. A technique of obtaining a record of the equilibrium weight of a substance as a function of temperature (T) at a constant partial pressure of the volatile product or products.

The record is the isobaric weight-change curve; it is normal to plot weight on the ordinate with weight decreasing downwards and T on the abscissa increasing from left to right.

Isothermal weight-change determination. A technique of obtaining a record of the dependence of the weight of a substance on time (t) at constant temperature.

The record is the isothermal weight-change curve; it is normal to plot weight on the ordinate with weight decreasing downwards and t on the abscissa increasing from left to right.

2. *Dynamic*

Thermogravimetry (TG). A technique whereby the weight of a substance, in an environment heated or cooled at a controlled rate, is recorded as a function of time or temperature.

The record is the thermogravimetric or TG curve; the weight should be plotted on the ordinate with weight decreasing downwards and t or T on the abscissa increasing from left to right.

Derivative thermogravimetry (DTG). A technique yielding the first derivative of the thermogravimetric curve with respect to either time or temperature.

The curve is the derivative thermogravimetric or DTG curve; the derivative should be plotted on the ordinate with weight losses downwards and t or T on the abscissa increasing from left to right.

C. *Methods Associated with Energy Change*

Heating curves. These are records of the temperature of a substance against time, in an environment heated at a controlled rate.

T should be plotted on the ordinate increasing upwards and t on the abscissa increasing from left to right.

Heating-rate curves. These are records of the first derivative of the heating curve with respect to time (*i.e.*, $\mathrm{d}T/\mathrm{d}t$) plotted against time or temperature.

The function $\mathrm{d}T/\mathrm{d}t$ should be plotted on the ordinate and t or T on the abscissa increasing from left to right.

Inverse heating-rate curves. These are records of the first derivative of the heating curve with respect to temperature (*i.e.*, $\mathrm{d}t/\mathrm{d}T$) plotted against either time or temperature.

The function $\mathrm{d}t/\mathrm{d}T$ should be plotted on the ordinate and t or T on the abscissa increasing from left to right.

Differential thermal analysis (DTA). A technique of recording the difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

The record is the differential thermal or DTA curve; the temperature difference (ΔT) should be plotted on the ordinate with endothermic reactions downwards and t or T on the abscissa increasing from left to right.

Derivative differential thermal analysis. A technique yielding the first derivative of the differential thermal curve with respect to either time or temperature.

The record is the derivative differential thermal or derivative DTA curve; the derivative should be plotted on the ordinate and t or T on the abscissa increasing from left to right.

Differential scanning calorimetry (DSC). A technique of recording the energy necessary to establish zero temperature difference between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

The record is the DSC curve; it represents the amount of heat applied per unit time as ordinate against either t or T as abscissa.

D. *Methods Associated with Evolved Volatiles*

Evolved gas detection (EGD). This term covers any technique of detecting whether or not a volatile product is formed during thermal analysis.

Evolved gas analysis (EGA). A technique of determining the nature and/or amount of volatile product or products formed during thermal analysis.

E. *Methods Associated with Dimensional Change*

Dilatometry. A technique whereby changes in dimension(s) of a substance are measured as a function of temperature.

The record is the dilatometric curve.

Derivative dilatometry; differential dilatometry. These terms carry the connotations given in I(*b*) above.

F. *Multiple Techniques*

This term covers simultaneous DTA and TG, *etc*, and definitions follow from the above.

IV. ACKNOWLEDGEMENTS

The Committee express their thanks to the Society for Analytical Chemistry and the Thermal Analysis Group of that Society for assistance rendered and also to thermal analysts in many countries for detailed comments at various stages of the programme.

The Macaulay Institute for Soil Research
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Chairman, ICTA Nomenclature Committee

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NOTICE

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24–28 September 1969

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Applications of digital computers in analytical chemistry—II: C. W. Childs, P. S. Hallman and D. D. Perrin, *Talanta*, 1969, **16**, 1119. (Department of Medical Chemistry, John Curtin School of Medical Research, Australian National University, Canberra, Australia.)

Summary—This review deals with applications of digital computers to the evaluation of ionization constants of acids and bases, stability constants of metal complexes, concentrations of equilibrium mixtures, and the solution of rate equations. The use of computers permits systems of greatly increased complexity to be studied, and introduces additional methods of calculation such as numerical integration and Monte Carlo techniques.

Determination of small quantities of xanthate: C. Pohlandt, E. B. T. Cook and T. W. Steele, *Talanta*, 1969, **16**, 1129. (National Institute for Metallurgy, Private Bag 6, Cottesloe, South Africa.)

Summary—A new spectrophotometric method for the determination of very small amounts of xanthate in solutions, particularly cyanide solutions from gold-extraction plants, is described. It is based on the formation and extraction of copper(II) xanthate. The coefficient of variation is 1·0% at the 40-ppm level and 3·4% at the 4-ppm level and the lower limit of determination is approximately 0·5 ppm. Copper(II) xanthate normally decomposes into copper(I) xanthate and dixanthogen, but in the proposed method the decomposition is delayed.

Simultaneous determination of palladium, platinum and rhodium in crude platinum samples by activation analysis and high-resolution gamma spectrometry: J. Turkstra and W. J. de Wet, *Talanta*, 1969, **16**, 1137. (Chemistry Division, Atomic Energy Board, Pelindaba, South Africa.)

Summary—Instrumental neutron-activation analysis using a Ge(Li) detector has been investigated for the simultaneous determination of platinum, palladium and rhodium in crude platinum samples contained in lead cupels. This technique proved feasible and appears promising for extension to the determination of most of the noble metals.

ПРИМЕНЕНИЕ ДИГИТАЛБНЫХ ЭЛЕКТРОННОВЫЧИСЛИТЕЛЕЙ В АНАЛИТИЧЕСКОЙ ХИМИИ—II:

C. W. CHILDS, P. S. HALLMAN and D. D. PERRIN, *Talanta*, 1969, **16**, 1119.

Резюме—В обзоре обсуждены применения дигитальных счетчиков в определении констант ионизации кислот и оснований, констант устойчивости комплексов металлов, концентраций равновесных смесей и разрешение уравнений скорости реакции. Применение счетчиков позволяет изучение гораздо больше комплексных систем и вводит дополнительные методы рассчета, как на пример цифровую интеграцию и Монте Карло методы.

ОПРЕДЕЛЕНИЕ НЕБОЛЬШИХ КОЛИЧЕСТВ КСАНТАТА:

C. POHLANDT, E. B. T. COOK and T. W. STEELE, *Talanta*, 1969, **16**, 1129.

Резюме—Описан новый спектрофотометрический метод определения небольших количеств ксантата в растворах, особенно в цианидных растворах используемых в золотоэкстрагирующих заводах. Метод основан на образовании и экстрагировании ксантата меди(II). Коэффициент вариации равен 1,0% при 40 мг (л и 3,4% при 4 мг/л, а чувствительность ~ 0,5 мг) л. Ксантат меди(II) обычно разлагается в ксантат меди(I) и диксантоген, но в предложенном методе разложение замедлено.

ОДНОВРЕМЕННОЕ ОПРЕДЕЛЕНИЕ ПАЛЛАДИЯ, ПЛАТИНЫ И РОДИЯ В ОБРАЗЦАХ СЫРОЙ ПЛАТИНЫ МЕТОДАМИ РАДИОАКТИВАЦИОННОГО АНАЛИЗА И ВЫСОКОРАЗРЕШАЮЩЕЙ СПЕКТРОМЕТРИИ ГАММА ЛУЧЕЙ:

J. TURKSTRA and W. J. DE WET, *Talanta*, 1969, **16**, 1137.

Резюме—Исследована применимость инструментального метода нейтронно-активационного анализа с использованием Ge(Li) детектора для одновременного определения платины, палладия и родия в образцах сырой платины помещенных в свинцовых куплях. Этим методом получены удовлетворительные результаты и онкажется полезным для определения большинства благородных металлов.

Separation of tervalent rare earths and scandium from aluminium, iron(III), titanium(IV) and other elements by cation-exchange chromatography in hydrochloric acid–ethanol: F. W. E. STRELOW and CYNTHIA BAXTER, *Talanta*, 1969, **16**, 1145. (National Chemical Research Laboratory, P.O. Box 395, Pretoria, S. Africa.)

Summary—Tervalent rare earths and Sc are separated from the silicate-forming elements Al, Fe(III), Mg and Ti(IV), and also from Mn(II), U(VI), Be, Ga, In(III), Tl(III), Bi(III), Ni, Zn, Cu(II), Cd and Pb by cation-exchange chromatography. The other elements are eluted with 3·0*M* HCl containing 50% ethanol from a column of 60 ml of AG50W-X8 resin (200–400 mesh) while the rare earths are retained. Separation factors are larger than in aqueous hydrochloric acid. Th, Zr, Hf, Ba, Sr, Ca, K, and Rb are the only elements which accompany the rare earths group, but these can easily be separated by other methods which are described. Relevant distribution coefficients, elution curves and accurate results of quantitative separations of synthetic mixtures are presented.

Complexes formed in the chloroform extraction of uranium(VI) with oxine: SHŌHACHIRŌ ŌKI, *Talanta*, 1969, **16**, 1153. (Department of Industrial Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu, Japan.)

Summary—Equilibrium distribution ratios have been determined for uranium(VI) with oxine between cholorform and 0·1*M* perchlorate as a function of pH and reagent concentration at 20°. It is concluded that the extractable complex is UO_2Ox_2HOx. The equilibrium constants for the extraction of uranium have been determined as $K_{U,1} = [UO_2Ox_2HOx]_0/[UO_2^{2+}][Ox^-]^3[H^+] = 10^{36.18}$ at low pH and $K_{U,2} = [UO_2Ox_2HOx]_0/[UO_2Ox_2OH^-][Ox^-][H^+]^2 = 10^{25.40}$ at high pH.

Bestimmung von Ionenbeweglichkeiten in nichtwässrigen Elektrolytlösungen—I: G. MARX and D. HENTSCHEL, *Talanta*, 1969, **16**, 1159. (Institut für Anorganische Chemie der Freien Universität Berlin (Abteilung Radiochemie), 1 Berlin 33, B.R.D.)

Summary—The use of radioisotopes for the determination of transport numbers by the moving boundary method has been shown to be applicable in non-aqueous media. The transport number of the sodium ion in 0·01*M* sodium chloride in dry methanol was determined using the γ-emitter ^{24}Na, and the results are in good agreement with those obtained by other means. The accuracy of the technique and its advantages over optical methods are discussed.

ОТДЕЛЕНИЕ ТРЁХВАЛЕНТНЫХ РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ И СКАНДИЯ ОТ АЛЮМИНИЯ, ЖЕЛЕЗА(III), ТИТАНА(IV) И ДРУГИХ ЭЛЕМЕНТОВ МЕТОДОМ КАТИОНООБМЕННОЙ ХРОМАТОГРАФИИ В СМЕСЕ СОЛЯНОЙ КИСЛОТЫ И ЭТИЛОВОГО СПИРТА:

F. W. E. Strelow and Cynthia Baxter, *Talanta*, 1969, **16**, 1145.

Резюме—Трёхвалентные редкоземельные элементы и Sc отделены от силикатыобразующих элементов Al, Fe(III), Mg и Ti(IV), а так же от Mn(II), U(VI), Be, Ga, In(III), Tl(III), Bi(III), Ni, Zn, Cu(II), Cd и Pb методом катионообменной хроматографии. Другие элементы элюированы с 3,0*M* HCl содержащим 50% этанола, из колонки 60 мл смолы AG50W-X8 (200–400 меш), а редкоземельные элементы задерживаются на колонке. Факторы разделения больше чем в водных растворах соляной кислоты. Только Th, Zr, Hf, Ba, Sr, Ca, K и Rb сопровождают редкоземельные элементы, но они легко отделяются другими методами описанными в статье. Приведены козффициенты распределения, крывые элюирования и точные результаты количественного раэделения искусственных смесей.

НОМПЛЕКСЫ ОБРАЗОВАННЫЕ ПРИ ЗКСТРАКДИИ УРАНА (VI) РАСТВОРОМ ОКСИНА Б ХЛОРОФОРМЕ:

Shohachiro Oki, *Talanta*, 1969, **16**, 1153.

Резюме—Определены равновесные отношения распределения урана(VI) с оксином между хлороформом и 0,1 М раствором перхлората, в зависимости от pH и концентрации реагента при 20°. Формула извлекаемого комплекса найдена UO_2Ox_2-HOx. Константы равновесия для экстракции урана $K_{U,1} = [UO_2Ox_2HOx]_0/[UO_2^{2+}][Ox^-]^3[H^+] = 10^{36,18}$ при низком pH, а $K_{U,2} = [UO_2Ox_2HOx]_0/[UO_2Ox_2OH^-][Ox^-][H^+]^2 = 10^{25,40}$ при высоком pH.

ОПРЕДЕЛЕНИЕ ИОННОЙ ПОДВИЖНОСТИ В НЕВОДНЫХ РАСТВОРОВ ЭЛЕКТРОЛИТОВ—I:

G. Marx and D. Hentschel, *Talanta*, 1969, **16**, 1159.

Резюме—Показана применимость в неводных средах радиоизотопов в определении числа переноса методом подвижной границы. Число переноса иона натрия в 0,01*M* хлориде натрия в сухом метиловом спирте определили с использованием ^{24}Na в качестве источника гамма лучей; результаты хорошо соглашаются с полученными другими методами результатами . Обсуждается точность метода и его преимущества в сравнении с оптическими методами.

Novel applications of dipicrylamine as an extractant in the determination of alkali metals: M. Kyrš, J. Rais and P. Selucký, *Talanta*, 1969, **16**, 1169. (Nuclear Research Institute, Řež near Prague, Czechoslovakia.)

Summary—A ten-stage mixer-settler type extraction procedure has been used for the preparation of rubidium-free caesium salts. A nitrobenzene solution of 0·11M CsDPA flows counter to a purified aqueous solution of 0·05M CsCl and $10^{-3}M$ Cs_4(EDTA), which removes Rb, K, Na and most other metals from the organic phase. An extraction colorimetric titration procedure for 0·2–2 mg of caesium is described, and also an indirect method for determination of potassium and sodium in admixture, based upon the difference in the ability of the two ions to replace $^{137}Cs^+$ in a nitrobenzene solution of dipicrylaminate.

Anion-exchange behaviour of several elements in hydrobromic acid–organic solvent media: E. Klakl and J. Korkisch, *Talanta*, 1969, **16**, 1177. (Analytical Institute, University of Vienna, IX Währingerstrasse 38, Austria.)

Summary—The anion-exchange behaviour of 19 elements in hydrobromic acid–organic solvent media has been investigated. The batch distribution coefficients of the metal ions were determined in these systems employing the strongly basic anion-exchange resin Dowex 1 × 8. Organic solvents used were methanol, ethanol, n-propanol, isopropanol, methyl glycol, acetone, tetrahydrofuran and acetic acid. The most suitable conditions for some quantitative separations based on these equilibrium studies are indicated and discussed.

Polarography of arsenic: J. P. Arnold and R. M. Johnson, *Talanta*, 1969, **16**, 1191 (Department of Applied Biology and Food Science, Borough Polytechnic, Borough Road, London S.E.1.)

Summary—The polarographic behavior of arsenic in various media is reviewed with particular emphasis on the mechanisms of the electrode reactions and on the use of polarographic methods for the determination of the element.

НОВЫЕ ПРИМЕНЕНИЯ ДИПИКРИЛАМИНА В КАЧЕСТВЕ ЭКСТРАКТАНТА В ОПРЕДЕЛЕНИИ ЩЕЛОЧНЫХ МЕТАЛЛОВ:

M. Kyrš, J. Rais. and P. Selucký, *Talanta* 1969, **16,** 1169.

Резюме—Метод экстракции на основе десятиступенчатого миксера-отстойника использован в приготовлении свободных от рубидия солей цезия. Раствор 0,11 *M* CsДПА в нитробензоле двигается противоточно очищенному водному раствору 0,05 *M* CsCl и 10^{-3} *M* Cs_4(ЭДТА), который укланяет Rc, K, Na и большинство других металлов из органической фазы. Описан метод экстракции-колориметрической титрации для 0,2–2 мг цезия, так же как и косвенный метод определения калия и натрия в смеси, основан на разници способности этих двух ионов заместить $^{137}Cs^+$ в растворе дипикриламината в нитробензоле.

АНИОНООБМЕННЫЕ ХАРАКТЕРИСТИКИ НЕКОТОРЫХ ЭЛЕМЕНТОВ В СРЕДАХ БРОМИСТОВОДОРОДНОЙ КИСЛОТЫ И ОРГАНИЧЕСКИХ РАСТВОРИТЕЛЕЙ:

E. Klakl and J. Korkisch, *Talanta,* 1969, **16,** 1177.

Резюме—Исследованы анионообменные характеристики 19 элементов в средах состоящихся из бромистоводородной кислоты и органического растворителя. Определены периодические коэффициенты распределения ионов металлов в этих системах с использованием сильноосновной ионообменной смолы Дауекс 1 × 8. Испытаны органические растворители метиловый, этиловый, н-пропиловый и изопропиловый спирты, метилгликол, ацетон, тетрагидрофуран и уксусная кислота. Приведены и обсуждены оптимальные условия для некоторых количественных определений основанных на изучении этих равновесий.

ПОЛЯРОГРАФИЯ МЫШЬЯКА:

J. P. Arnold and R. M. Johnson, *Talanta,* 1969, 16, 1191.

Резюме—Приведен обзор полярографической характеристики мышьяка в разных средах, обращая особенное внимание механизму электродных реакций и применению полярографического метода в определении этого элемента.

Radiochemical separations by the ring-oven technique—IV. The system ^{144}Ce/^{144}Pr: D. Klockow and R. G. Böhmer, *Talanta*, 1969, **16,** 1209. (Chemical Laboratory, University of Freiburg Br., Freiburg Br., German Federal Republic.)

Summary—By using filter papers impregnated with a manganese oxide hydrate having an average oxidation number of +3, it is possible to separate ^{144}Pr from ^{144}Ce rapidly by the ring-oven technique. With 0·06–0·07*M* trichloracetic acid as wash-solution, the daughter nuclide can be concentrated in the ring zone with 80–90% yield and decontamination factors $>10^3$. The half-life of the separated ^{144}Pr was found to be 17·60 ± 0·05 min. The behaviour of other fission nuclides under the same conditions was also investigated.

Zero-current bipotentiometric indication using two differently pretreated platinum electrodes: L. Kékedy and F. Makkay, *Talanta*, 1969, **16,** 1212. (Department of Analytical Chemistry, Babeş-Bolyai University, Cluj, Roumania.)

Summary—A new potentiometric technique of zero-current bipotentiometry using differently pretreated platinum electrodes is described, and its application to various redox titrations discussed. The potential across the electrodes appears to be generated by differences in kinetics of the reactions occurring on the two dissimilar electrode surfaces.

Sequential oxidimetric determination of thallium(I) and (III): S. R. Sagi and K. V. Ramana, *Talanta*, 1969, **16,** 1217. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—The reaction between thallium(III) and oxalic acid in sulphuric acid medium has been investigated. Spectrophotometric results show that thallium(III) can be quantitatively reduced to thallium(I) with oxalic acid in aqueous medium when heated to near boiling point. Conditions for the estimation of the excess of oxalic acid with cerium(IV) sulphate in the presence of thallium(I) and for the estimation of a mixture of thallium(I) and thallium(III) have been investigated. The method is simpler than many other redox methods reported for the determination of thallium(III) and is free from many interferences encountered in these titrations. The reagents are cheap and quite stable.

РАДИОХИМИЧЕСКИЕ РАЗДЕЛЕНИЯ С ИСПОЛЬЗОВАНИЕМ МЕТОДА КОЛЬЦЕВОЙ ПЕЧИ—IV. Система ^{114}Ce/^{114}Pr:

D. Klockow and R. G. Böhmer, *Talanta*, 1969, **16**, 1209.

Резюме—Применение фильтровальной бумаги пропитанной с гидроокисью марганца имеющей среднее окислительное число +3 позволяет быстрое отделение ^{114}Pr от ^{114}Ce с использованием кольцевой печи. Пользуясь 0,06–0,07*M* раствором трихлоруксусной кислоты в качестве промывного раствора удается концентрировать дочерний нуклид в кольцевой зоне с выходом 80–90% и факторами деконтаминации $>10^3$. Полупериод отделенного ^{114}Pr найден 17,60 ± 0,05 мин. Так же изучены характеристики других нуклидов фиссии в тех же самых условиях.

НУЛЕВОГО ТОКА БИПОТЕНЦИОМЕТРИЧЕСКОЕ ИНДИЦИРОВАНИЕ С ИСПОЛЬЗОВАНИЕМ ДВУХ РАЗЛИЧНО ОБРАБОТАННЫХ ПЛАТИНОВЫХ ЭЛЕКТРОДОВ:

L. Kékedy and F. Makkay, *Talanta*, 1969, **16**, 1212.

Резюме—Описан новый потенциометрический метод бипотенциометрии нулевого тока с использованием различно обработанных платиновых электродов и его применение в разных окислительно-восстановительных титрованиях. Кажется что потенциал на электродах образуется на основе различной кинетики реакций протекающих на поверхностях двух несходных электродов.

ПОСЛЕДОВАТЕЛЬНОЕ ОКСИДИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ТАЛЛИЯ(I) И (III):

S. R. Sagi and K. V. Ramana, *Talanta*, 1969, **16**, 1217.

Резюме—Исследована реакция таллия(III) с щавелевой кислотой в сернокислой среде. Полученные спектрофотометрическим методом результаты показывают возможность количественного восстановления таллия(III) в таллий(I) щавелевой кислотой в водной среде при нагревании близ точки кипения. Исследованы условия для определения(IV) избытка щавелевой кислоты в присутствии таллия(I) и для определения смеси таллия(I) и таллия(III). Метод простее многих других окислительно-восстановительных методов определения таллия(III) и свободен от многих мешающих факторов встречающихся в этих титрованиях. Реагенты являются дешевыми и почти устойчивыми.

A simple low-power, reduced-pressure microwave plasma source for emission spectroscopy: D. N. HINGLE, G. F. KIRKBRIGHT and R. M. BAILEY, *Talanta*, 1969, **16**, 1223. (Chemistry Department, Imperial College, London, S.W.7.)

Summary—The construction of a simple low-power microwave plasma source for emission spectroscopy is described.

Solid–liquid separation after liquid–liquid extraction: TAITIRO FUJINAGA, TORU KUWAMOTO and EIICHIRO NAKAYAMA, *Talanta*, 1969, **16**, 1225. (Department of Chemistry, Faculty of Science, University of Kyoto, Kyoto, Japan.)

Summary—A low-melting solid is used as organic solvent for liquid–liquid extraction at elevated temperatures followed by solidification and decantation of the aqueous phase.

НЕСЛОЖНЫЙ НИЗКО ЭНЕРГИИ МИКРОВОЛНОВЫЙ ПЛАЗМА-ИСТОЧНИК С ПРИВЕДёННЫМ ДАВЛЕНИЕМ ДЛЯ ЭМИССИОННОЙ СПЕКТРОСКОПИИ:

D. N. HINGLE, G. F. KIRKBRIGHT and R. M. BAILEY, *Talanta,* 1969, **16**, 1223.

Резюме—Описана конструкция несложного микроволнового плазма-источника низкой энергии и с приведённым давлением для эмиссионной спектроскопии.

ТВЕРДО-ЖИДКОСТНОЕ РАЗДЕЛЕНИЕ ПОСЛЕ ЖИДКОФАЗНОЙ ЭКСТРАКЦИИ:

TAITIRO FUJINAGA, TORU KUWAMOTO and EIICHIRO NAKAYAMA, *Talanta,* 1969, **16**, 1125.

Резюме—Низкоплавкое твердое тело использовано в качестве органического растворителя для жидкофазной экстракции при повышенной температуре с последующим отвердеванием и декантацией водной фазы.

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