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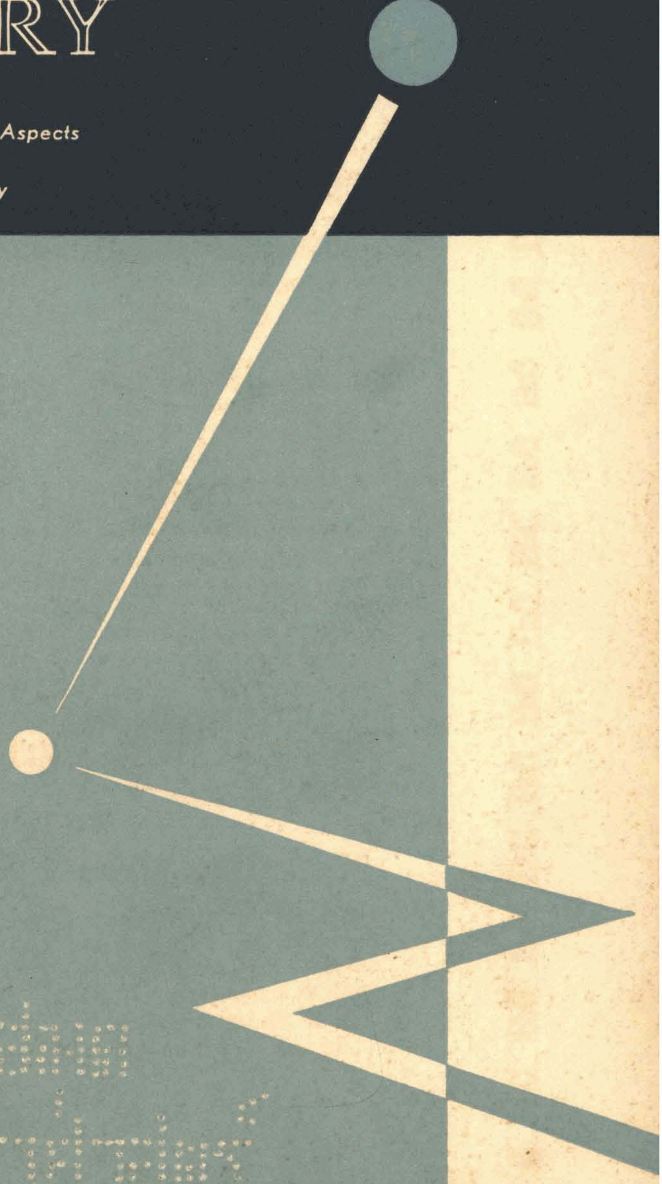

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SUMMARIES OF PAPERS PUBLISHED IN JOURNAL OF ELECTROANALYTICAL CHEMISTRY

Vol. 7, No. 3, March 1964

REPORT: A RESUME OF THE SEVENTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY

M. T. Kelley, C. D. Susano, J. S. Eldridge, C. Feldman, D. J. Fisher, W. S. Lyon, D. L. Manning, R. W. Stelzner and P. F. Thomason,

J. Electroanal. Chem., 7 (1964) 165–170.

THE DIFFUSION-EQUATION IN PULSE POLAROGRAPHY

A diffusion equation valid for pulse polarography has been derived. Let t_1 be the time during which a mercury drop has grown prior to the application of the voltage and let t be measured from that moment on, then, if $\vartheta = t/t_1$, the instantaneous current is given by

$$i = 0.732nF(c^* - c_0)\sqrt{D}t^{1/6}m^{2/3}\frac{(1+\vartheta)^{4/3}}{\vartheta^{1/6}\{(1+\vartheta)^{7/3}-1\}^{1/2}} \times \left[1 + 0.886\frac{\{(1+\vartheta)^{7/3}-1\}^{1/2}}{\vartheta^{1/6}(1+\vartheta)}\xi\right]$$

for $\vartheta < 1$, and by

$$i = 0.732nF(c^* - c_0)\sqrt{D}t^{1/6}m^{2/3}\frac{(1+\vartheta)^{1/6}}{\vartheta^{1/6}}\left[1 + 0.787\frac{(1+\vartheta)^{1/6}}{\vartheta^{1/6}}\xi\right]$$

for $\vartheta > 3$, where

$$\xi = 5.04D^{1/2}t^{1/6}m^{-1/3} = \eta^{1/3}\vartheta^{1/6}$$

The average current for $\vartheta < 1$ is

$$i = 0.627nF(c^* - c_0)\sqrt{D}t_1{}^{1/6}m^{2/3}\frac{\{(1+\vartheta)^{7/3}-1\}^{1/2}}{(\vartheta'' - \vartheta')} \times \left[1 + 0.776\frac{(1+\vartheta)^{4/3}}{\{(1+\vartheta)^{7/3}-1\}^{1/2}}\eta^{1/3}\right]\Bigg|_{\vartheta'}^{\vartheta''}$$

Numerical factors apply to 25°.

The spherical-correction term is negligibly small only for extremely small values of ϑ ($\vartheta = 0.0001$); for $\vartheta > 0.35$ it is even larger than in normal polarography.

Pulse-polarographic currents have been compared with those of normal polarography.

A. A. A. M. Brinkman and J. M. Los,

J. Electronal Chem. 7 (1964) 171–183.

DETERMINATION OF SULFUR DIOXIDE IN SOLUTION BY ANODIC VOLTAMMETRY AND BY U.V. SPECTROPHOTOMETRY

A voltammetric method has been developed for the determination of total sulfite in sulfuric acid solutions using activated platinum electrodes. The diffusion coefficient for sulfur dioxide in 0.1 F H_2SO_4 is $2.1 \cdot 10^{-5}$ cm^2/sec on the basis of the voltammetric data. The proper conditions for the spectrophotometric determination of total sulfite have been established. The molar absorptivity in 0.1 F H_2SO_4 is 388 l/moles cm at the absorption maximum, 276 mμ.

E. T. Seo and D. T. Sawyer,

J. Electroanal. Chem., 7 (1964) 184–189.

THE DETERMINATION OF PLUTONIUM BY A.C. POLAROGRAPHY

A method is described for the determination of plutonium in the range $4 \cdot 10^{-6}$ to $4 \cdot 10^{-4}$ M by a.c. polarography. It is based on a peak at -0.42 V *vs.* a mercury pool anode from a citrate supporting electrolyte (pH 4.5). This peak is produced by plutonium in either the trivalent or the tetravalent state, due to the reversibility of the Pu^{4+}/Pu^{3+} couple. Spectrophotometry has shown that the tetravalent plutonium–citrate complex is more stable than the trivalent complex, which oxidizes to the tetravalent state. The peak for tetravalent plutonium is preferred for analytical work, but unfortunately interference can be caused by some elements, especially iron. An ion-exchange procedure has been developed for the separation of plutonium from interfering elements. This method has been applied to the determination of the plutonium contents of uranium–plutonium alloys containing 0.25–1.0% of plutonium.

G. W. C. Milner and A. J. Wood,

J. Electroanal. Chem., 7 (1964) 190–205.

A NEW AND SIMPLE APPROACH TO SQUARE-WAVE POLAROGRAPHY

A new method has been developed for instrumenting square-wave polarography. It is simpler, more reliable, and much less expensive than equipment used in the past. This paper describes the design, construction and performance of the instrument.

J. H. Taylor,

J. Electroanal. Chem., 7 (1964) 206–210.

THE POLAROGRAPHIC ESTIMATION OF THORIUM USING SOLOCHROME VIOLET R.S. IN ALKALINE MEDIA

An estimation of thorium in dilute solutions (0–0.6 mM) is described. A solution of 0.546 mM solochrome violet R.S. (the sodium salt of 5-sulfo-2-hydroxy-α-benzene-azo-2-naphthol) is used in 0.1 M sodium potassium tartrate solution at pH 12.0 as supporting electrolyte, and methyl cellulose (0.002%) as maximum suppressor. The height of the dye reduction wave is inversely proportional to thorium concentration, while that of the dye–thorium complex reduction wave is proportional to thorium concentration. Either wave height may be compared with a previously prepared calibration graph.

D. S. Turnham,

J. Electroanal. Chem., 7 (1964) 211–217.

VOLTAMMETRIC EVALUATION OF THE STABILITY OF TRICHLORIDE, TRIBROMIDE, AND TRIIODIDE IONS IN NITROMETHANE, ACETONE, AND ACETONITRILE

The formation constants of trichloride, tribromide, and triiodide ions in acetonitrile and tribromide and triiodide ions in nitromethane and in acetone have been evaluated from electrochemical data. In addition, lower limits for the formation constant of the trichloride ion in acetone and in nitromethane have been calculated. The order of stability of the trihalides in these three aprotic solvents is $Cl_3^- > Br_3^- > I_3^-$, the reverse of that found in water.

I. V. Nelson and R. T. Iwamoto,

J. Electroanal. Chem., 7 (1964) 218–221.

OSCILLOGRAPHIC POLAROGRAPHY OF INORGANIC POLYPHOSPHATES

A sensitive oscillopolarographic method has been worked out for the detection and quantitative analysis of inorganic condensed phosphates.

A relationship has been established between the depths of indentations and the molecular weight of polyphosphates.

The principal factor responsible for the production of an indentation is the polymeric nature of polyphosphates.

The electrode process is of capacity nature.

J. Boháček and C. Singh,

J. Electroanal. Chem., 7 (1964) 222–232.

INVESTIGATION OF THE ELECTROCHEMICAL GENERATION AND THE VISIBLE SPECTRA OF FREE RADICAL ANIONS OF THE MONO-NITRONAPHTHALENES AND NITROMESITYLENE, IN DIMETHYLFORMAMIDE

As a result of certain polarographic investigations, the free radical anions of α- and β-nitronaphthalenes and nitromesitylene were generated by electrolysis in a 0.2 *N* solution of $NaNO_3$ in dimethylformamide. The free radical anions of the mono-nitronaphthalenes were green in solution and those of nitromesitylene pinkish-red. The visible spectra of the free radical anions were determined, using their polarographic oxidation current as a measure of their concentration.

The interpretation of the spectra of the free radical anions and nitrobenzene free radical anion, and their correlation with the u.v. spectra of the nitro-compounds has been discussed.

It has been suggested that in the free radical anions of the aromatic nitro-compounds, the unpaired electron occupies a *low-energy* orbital of the nitro-group. The visible absorption bands of the free radical anions correspond to transitions of the unpaired electron from this orbital to higher molecular orbitals.

W. Kemula and R. Sioda,

J. Electronal. Chem., 7 (1964) 233–241.

THE USE OF PROGRAMMED CURRENT CHRONOPOTENTIOMETRY IN THE STUDIES OF ADSORPTION

(Short Communication)

R. W. Murray,

J. Electroanal. Chem., 7 (1964) 242–245.

A SIMPLE ELECTRONIC-SCAN, CONTROLLED-POTENTIAL POLAROGRAPH

(Short Communication)

R. A. Durst, J. W. Ross and D. N. Hume,

J. Electroanal. Chem., 7 (1964) 245–248.

TRANSFERENCE NUMBERS IN CONCENTRATED SODIUM PERCHLORATE SOLUTIONS

(Short Communication)

R. A. Durst and D. N. Hume,

J. Electroanal. Chem., 7 (1964) 248–251.

REPORT

A RESUME OF THE SEVENTH CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR TECHNOLOGY

ANALYTICAL INSTRUMENTATION: MOLTEN SALT SYSTEMS, RADIOACTIVITY STANDARDS, NUCLEAR ANALYSIS, SPECTROSCOPY, GAS CHROMATOGRAPHY, AUTOMATION, ELECTROANALYTICAL TECHNIQUES

The tenor of the Seventh Conference on Analytical Chemistry in Nuclear Technology, which was held in Gatlinburg, Tennessee, on October 8–10th, was not unlike a number of other conferences which are being held throughout the world on the explosive developments in instrumental methods of analysis. The topics covered at this meeting were slanted primarily toward the needs of the nuclear analytical chemist: the analysis of molten salt systems at high temperatures; the utilization and standardization of instrumental devices in nuclear analysis; spectroscopy in its broadest aspects; gas chromatography; electroanalytical chemistry; and the automation of all such methods, procedures and devices where it is practicable or desirable to do so.

This conference has generally been reported as being one of the more successful in the series. Approximately 300 interested scientists, including 30 analytical chemists or instrumentation experts from 11 different foreign countries, participated in the conference either by presenting one or more of the 50 papers that were given or by engaging in the two panel discussions.

The first panel discussion was, in fact, a continuation of a meeting which was held on the day preceding the conference by a Sub-Committee of the National Research Council on the knotty problem of the availability, development and use of radioactivity standards. The inter-relationship and inter-dependence of absolute activity measurements, half-lives, and beta- and gamma-ray branchings were never more clearly delineated than they were in this panel discussion. The recurring thought throughout the presentations of the panel members, and re-emphasized by questions and comments from the audience, was the basic need of the importance of knowing and using best values for these nuclear parameters. A second point frequently mentioned was the significance of differentiating between when absolute measurements, and hence accurate standards, are necessary and when relative measurements are sufficient. The panel of experts included: S. B. GARFINKEL (National Bureau of Standards, NBS); G. I. GLEASON (Abbott Laboratories); H. HOUTERMANS (International Atomic Energy Agency, IAEA); BERND KAHN (U. S. Public Health Service, USPHS); D. S. KIM (Nuclear-Chicago Corp.); J. G. V. TAYLOR (Atomic Energy of Canada Limited, AECL); and the Moderator, W. S. LYON (Oak Ridge National Laboratory, ORNL). They discussed the present state of standardization techniques, areas for future research, and the immediate and long-term needs for standards. It was reported that the National Research Council Sub-Committee on the Use of Radioactivity Standards has under way several projects which will alleviate some of the present difficulties in the use of standards. These projects include the compilation and publication of best half-lives, decay schemes, gamma branchings, and conversion coefficients for many of the more commonly used radionuclides, and also the publication of a user's guide of radioactivity standards. Research work at Chalk River, Oak Ridge National Laboratory, and other institutions, directed toward the accumulation of better values for these nuclear data was also reported. The number and types of radioactivity standards available are expected to continue to increase, judging from reports of proposed expansions in the programs of standards distribution at the National Bureau of Standards, Nuclear-Chicago Corp., and the International Atomic Energy Agency.

The second panel discussion dealt with recent developments in analytical instrumentation, emphasizing the attitude and philosophy of the analytical chemist in regard to the acquisition of the knowledge of the principles on which instrumental devices are constructed and utilized. In selecting the panelists, an effort was made to include experts proficient in different aspects of instrumentation. Each of the panel members spoke for a short time on a subject of his own choice relevant to the general topic of the session. After the first three presentations, and again at the end of the session, the meeting was thrown open for discussions by the panel and for participation of the audience. G. MILAZZO (Rome) led off the discussion with a description of his work with a hollow cathode light source for the spectrographic determination of non-metals. He also described a vacuum ultraviolet spectrograph that was designed to measure the emission characteristics of these elements in the far ultraviolet. He revealed that 10^{-7}–10^{-8} g of iodine could be detected in this manner. H. V. MALMSTADT (Illinois) told the audience about his efforts to develop an understanding of electronics in chemists and other scientists and thus remove some of the mystery about the *black boxes*. He has developed a laboratory for experimental work in electronic circuitry which makes use of simple units, power supplies, operational amplifiers, and other components which can be interconnected with suitable networks fitted with clips, so that several types of circuits can be studied in a short time. C. W. WEBER described some of the unique gas analysis instruments that have been developed at the Oak Ridge Gaseous Diffusion Plant (ORGDP) and which are based on the use of very sensitive differential pressure transmitters, such as a continuous gas titration analyzer and a condensation pressure analyzer.

H. I. SHALGOSKY (England) presented some of his ideas on analytical instrumentation. He expressed the thought that chemists should be able to communicate and co-operate closely and intelligently with instrumentation engineers in designing and utilizing instrumental devices. H. M. DAVIS (England) formerly worked with SHALGOSKY and agreed fully with him on the relationship between the chemist and design engineer. As an example of the greater adequacy of instrumentation developed as a consequence of this philosophy, he cited the integrating flame photometer, a device of very high sensitivity which was designed at the Woolwich Outstation of the United Kingdom Atomic Energy Authority (UKAEA).

H. M. KELLEY (DuPont) described some of the instrumentation in use in the laboratory of the Savannah River Plant of the U. S. Atomic Energy Commission. He cited the scanning coulometer as an instrument suitable for the highly precise analysis of small amounts of reducible substances such as uranium and plutonium. He described the application of the Technicon Autoanalyzer to laboratory problems but also stressed the importance of not over-emphasizing the completely instrumental approach to analytical problems. G. L. BOOMAN (Phillips Petroleum Co., Idaho Falls) advocated the applications of the principles of cybernetics to the design of instruments and to automatic control systems. In designing instruments involving the use of operational amplifiers, he emphasized the advantages that may be gained by experimentally measuring the transfer function or functions of the system rather than by using a more empirical approach.

In the first general session of the conference, H. A. LAITINEN (Illinois), one of the first to apply electroanalytical measurements to molten salts at high temperatures, presented a review on methods for purifying molten mixtures, the construction of reference and indicator electrodes, and materials of construction. Voltammetry, chronopotentiometry, coulometry, coulometric titrations and impedance measurements were also discussed. LAITINEN used the complicated reduction of V_2O_5 in LiCl–KCl to illustrate the advantages of two or more types of measurements on a particular solution. L. C. HALL (Vanderbilt) reported on a third order disproportionation of $EuCl_3$, $YbCl_3$ and $SmCl_3$ in a molten mixture of LiCl and KCl. Computer programs are being tested to evaluate the forward and backward reaction rates. GLEB MAMANTOV (Tennessee and ORNL) reviewed the voltammetric and chronopotentiometric studies of molten mixtures of LiF, NaF and KF and of LiF and BeF_2 which are being carried out at Oak Ridge. Current–voltage curves and potential–time curves were discussed for iron, nickel, uranium and zirconium for systems in which pyrolytic graphite sheathed in boron nitride was used as an indicator electrode.

In the area of optical measurements, D. M. GRUEN (Argonne) discussed electronic absorption spectroscopy both as an analytical tool and as a means of elucidating oxidation states. GRUEN also pointed out that transition-metal ion spectra (octahedral–tetrahedral transitions) provide an important insight to melt structures. W. T. CARNALL (Argonne) reported on spectrophotometric studies of lanthanides and actinides in a molten mixture of $LiNO_3$ and KNO_3. It was reported that absorption bands in the 1.4–2.6-micron region correlate with predicted bands in this area and that transitions of highly radioactive promethium and curium were observed in melts stable to radiation. J. R. MORREY (Hanford) described furnaces which were designed for use with the Cary Model-14 spectrophotometer. Spectra of U(III) and U(IV) in fused chloride were presented as examples of solvent effect on the spectra of the solute. Specialized techniques for spectrophotometric studies of molten fluorides were discussed by J. P. YOUNG (ORNL). Of special interest in this talk was the description of a new high-temperature cell assembly and a unique "windowless" sample holder.

At the sessions on instrumentation and techniques for nuclear analysis, PETER CROWTHER (South Africa) and J. S. ELDRIDGE (ORNL) reported on a number of inconsistencies that appear in published decay schemes of radioactive nuclides and told how inter-comparison measurements by beta–gamma coincidence counting, $4\pi\gamma$ ionization counting, and absolute NaI gamma-ray spectrometry have yielded more reliable gamma branchings for a number of radioactive nuclides. S. B. GARFINKEL (NBS) outlined the techniques used in the standardization of electron-capture nuclides; of particular interest is the sum-coincidence method, used for ^{125}I, in which the singles and coincidence sum peaks from the *K* x-rays of ^{125}I are measured by gamma-ray spectrometry. A. CHETHAM-STRODE and J. R. TARRANT (ORNL) described the use of solid-state detectors and presented recent evidence of great improvements in the resolution of the Frisch grid ionization chamber through use of mixed-gas fillings. Resolution of 16 keV at 2π geometry has been observed with alpha emitters in the uranium series. This compares favorably with resolutions obtained with solid-state detectors.

Another session of the conference was devoted to a discussion on instrumentation for the remotely controlled analysis of radioactive materials. One of the problems that has consistently presented difficulty in the analytical chemistry associated with chemical processing of uranium by the Purex process was given a new solution by KENJI MOTOJIMA (Japan), who told the conference about a modified alkalimetric method for the determination of free acid and uranium based on the use of ammonium sulfate as a masking agent, and of H_2O_2 for evaluating the hydrolytic equivalent of the uranyl ion. Further refinements in the automation of the remotely operated specific gravity apparatus (falling-drop method) at the Idaho Chemical Processing Plant were described by F. W. DYKES. Specific gravity in the range of 1.00–1.40 can be determined routinely on highly radioactive solutions with a standard deviation of 0.0017 units. Something akin to the *chemist-in-a-box* approach to automatic chemical analysis was described by J. C. GILLESPIE (Union Carbide Corp., Paducah, Kentucky). He described a simple system where as many as 200 separate events per sample can be programmed in equipment that is operated by laboratory technicians.

Recent developments in in-line chemical instrumentation at the UKAEA Windscale and Calder Works was the topic of J. K. FOREMAN (England). An automatic coulometric acidity meter, a ferrous sulfamate concentration monitor, and a nitrite detector based upon the color reaction with starch–iodide solution were described. The instrumentation, in addition to providing continuous chemical analysis at a reduced cost, serves an an approach-to-criticality alarm system. A versatile, low-cost, remote-handling system for making chemical analyses designed for use at Windscale was presented by A. J. HOWARTH (England) (paper read by J. K. FOREMAN). The system is based on the use of a gantry crane device to handle activities up to 100 curies in fully shielded operations. Analytical methods and remote-handling facilities for the Molten Salt Reactor Experiment and for the Transuranium Program at the Oak Ridge National Laboratory were described by L. T. CORBIN (ORNL). Specialized handling equipment and remotely operated instrumental methods which are to be used for the analyses of the materials involved in these two programs were discussed briefly. L. L. MERRITT, Jr. (Indiana) described an automatic, electrically controlled analytical balance suitable for remote weighing which is also suitable for continuous recording, giving 4-digit accuracy for both 0.1- and 0.01-mg sensitivity ranges.

In the session on electroanalytical instrumentation, IRVING SHAIN (Wisconsin) reported on advances that have been made in the theory of stationary electrode voltammetry, particularly the cyclic methods. He expects to publish the results of this work soon. A number of diagnostic criteria were described which characterize the mechanisms of the electrode reactions, including coupled processes. Applications of operational amplifiers in electroanalytical chemistry at the Oak Ridge National Laboratory were summarized by M. T. KELLEY (ORNL). He reported that operational amplifier systems have been used extensively for a wide variety of purposes, including potentiostatic and galvanostatic electrolysis, current integration, time derivative computations, impedance matching, voltage inversion, d.c. or tuned a.c. voltage gain, current amplification, and end-point detection. G. MILAZZO (Rome) presented a paper on the design and performance of an automatic electrometric titrator in which a delay circuit was described which prevents final stoppage at premature end-points in slow reactions. He stated that this titrator can be used either manually or automatically with very good performance in potentiometry and amperometry, and with the addition of certain accessories can also be used satisfactorily in conductometry and coulometry.

H. I. SHALGOSKY (England) spoke on the technique of and results obtained by high-precision, comparative polarography with the Davis Differential Cathode Ray polarograph. When the cells contain solutions of nearly the same concentration, one being a reference standard, the species in the other cell can be determined with very high precision. H. M. DAVIS (England) described the design features of a new instrument, the prototype of which was developed by DAVIS and others at Harwell. The mechanism for synchronizing the drops is of advanced design. High sensitivity and resolution were reported. The instrument can be used in the subtractive mode with either base electrolyte and reagent blank or with a standard solution in the reference cell or for derivative display. This polarograph can be used for single-cell methods.

H. L. PARDUE (Purdue) related the details of an automatic method for measuring the slope of kinetic curves including a discussion of the principles of a servo, direct-reading instrument. He also gave some examples of the utility of this method in measuring concentrations of certain organic compounds in the p.p.m. range. T. M. GAYLE and T. A. GENS (ORNL) described the instrumentation for the continuous detection of hexavalent chromium for use in the control of a DAREX process. They found that methods based on oxidation potential were more satisfactory than those methods based on ultraviolet absorption in the continuous monitoring of a DAREX dissolver effluent stream.

R. MAVRODINEANU (Philips Laboratories), co-author of the first comprehensive textbook on flame photometry, led off the discussion on spectroscopy by describing some of his recent investigations of excitation phenomena in pre-mixed flames. By using specially constructed burners which produced widely separated inner and outer cones, he was able to secure greatly enhanced emission of some species and total suppression of others. When the nitrogen in the air fed to pre-mixed air–acetylene flames was replaced by argon, the spectra showed little change, indicating that the role of nitrogen in this flame, if any, was not a chemical one. He suggested the use of the term *over-excitation* rather than *chemiluminescence* to cover the phenomena responsible for the presence of difficultly excited lines in flames. R. C. HUGHES, of the same laboratory, described a four-channel, direct-reading Fery prism spectrometer being developed especially for use with flame sources. He reported that the device has a single readout unit, with digital display, which can be switched to the tubes in sequence. As a method of volatilizing solutes for atomic absorption analysis, flames have the disadvantages of turbulence, inherent absorption bands and unwieldiness. J. P. MISLAN (Canada) showed that the passing of an aerosol of a cadmium solution through a quartz tube furnace will produce detectable absorption below the level of 0.03 μg/ml. The speaker revealed that he hoped to adapt this approach to on-stream analysis.

R. S. VOGEL (Mallinckrodt Chemical Works) described a meticulously carried out investigation in which he obtained emission spectra of sample areas 5–10 μ in diameter by refinement of the point-to-plane technique. A paper by A. G. COLLINS and C. A. PEARSON (Bureau of Mines) related the details of an acetyl acetone extractionemission spectrochemical technique for determining beryllium in oil-field waters. R. N. WHITTEM (Australia) talked on the construction of a spectrographic device for monitoring beryllium in paper smear samples. A paper by S. HANAMURA (Japan) illustrated the advantages of signal integration in overcoming the noise problems encountered in determining magnesium and sodium by flame photometric methods.

At the final session, DAVID BANDEL (Bendix Corp.) discussed the high degree of resolution of a Hypeac interference spectrometer and related how the improvements which have been made in utilizing a sealed-source, hollow-cup cathode discharge tube for the excitation of samples has made this instrument readily adaptable to the analysis of radioactive materials without requiring a prior chemical separation. This instrument has been used to measure lithium, plutonium and uranium isotopic abundances on samples ranging in size from several milligrams to 2 or 3 grams. The $^{235}U/^{238}U$ ratio in natural uranium can be measured to within ± 1%. P. J. BOURKE (England) presented a paper on the gas chromatographic determination of impurities in helium down to a fractional part per million by utilizing a sensitive ionization detector to measure concentrations as low as 0.02 p.p.m. of CO_2 and 0.05 p.p.m. for CO, with decreasing orders of sensitivity for oxygen, argon, nitrogen and hydrogen.

B. D. LA MONT (Westinghouse Electric Corp.) discussed methods for the analysis of uranium carbide, for total carbon, free or uncombined carbon, oxygen, nitrogen, and hydrogen. Total carbon is determined gravimetrically after combustion in oxygen. Free or uncombined carbon is also determined gravimetrically after selective dissolution of combined carbon and uranium with nitric acid. For the determination of oxygen and nitrogen, uranium carbide is reacted with BrF_3 at room temperature, thus releasing combined oxygen and nitrogen as elemental gases, which are then determined by gas chromatography.

Contrary to the precedent established through the first six conferences, the proceedings of this conference will not be published, as such, but some of the papers will undoubtedly be published in the open literature.

The conference was sponsored by the Analytical Chemistry Division of the Oak Ridge National Laboratory, which is operated by the Nuclear Division of Union Carbide Corporation for the U. S. Atomic Energy Commission.

ADDENDUM

The Eighth Conference in this series will be held at Gatlinburg, Tennessee, on October 6–8th, 1964. Any inquiries concerning this meeting should be addressed to: C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37831, U.S.A.

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THE DIFFUSION-EQUATION IN PULSE POLAROGRAPHY

A. A. A. M. BRINKMAN AND J. M. LOS

Laboratory of Physical Chemistry, Free University, Amsterdam (The Netherlands)

(Received December 5th, 1963)

Pulse polarography differs from normal polarography (d.c.) in that the potential is applied to the expanding mercury drop after the latter has been allowed to grow for some time (t_1). During the time t_1, the potential is considered to be at an arbitrary zero value, such that no faradaic current can flow*. Enhanced sensitivity might be expected in general and for analytical purposes this constitutes a significant improvement[1]. Quantitative studies of diffusion currents with normal polarography are impeded by such effects as depletion of the solution around the capillary orifice due to incomplete removal of the diffusion-layer of the preceding drop, partial collapse of the diffusion-layer (which generally occurs at drop times greater than 2 sec) and inconstancy of the rate of flow of mercury, particularly at early stages of drop life[2]. It may be expected that these effects will be less troublesome in pulse polarography, especially if t/t_1 remains small (t being the time during which the potential is applied).

These expectations would seem to indicate that pulse polarography will be used to an increasing extent in future research and a consideration of the relevant diffusion equation should therefore be of interest. This has been attempted in the present study.

An approximate method, essentially VON STACKELBERG's method of diffusion-layers for linear diffusion[3], taking the electrode curvature into account according to the method of LINGANE AND LOVERIDGE[4], has been attempted as a first approach. For the exact solution of the problem we have used KOUTECKÝ's method of dimensionless parameters[5].

APPROXIMATE SOLUTION

(a) Expanding plane electrode

For a homogeneous linear diffusion problem the *integral* thickness of the diffusion layer Δ at time t is given by

$$\Delta = \frac{1}{(c^* - c_0)} \int_0^\infty (c^* - c)\,\mathrm{d}z \qquad (1)$$

where $c = c(z,t)$ is the concentration of depolariser, $c^* = c(\infty,t)$ its *bulk* concentration, $c_0 = c(0,t)$ the corresponding concentration at the electrode surface and z the

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* For the purpose of this paper, this is the only kind of pulse polarography that will be considered.

distance away from the electrode surface.

The *differential* thickness δ is defined as

$$\delta = (c^* - c_0) \Big/ \left(\frac{\partial c}{\partial z}\right)_{z=0} \tag{2}$$

For a non-expanding, plane electrode the following relation holds

$$\Delta = \frac{2\delta}{\pi} \tag{3}$$

We will assume, following VON STACKELBERG[3], that eqn. (3) also applies to an expanding plane electrode.

Let

$$q_t = \text{electrode surface} = 4\pi a^2 (t + t_1)^{2/3} \tag{4}$$

$$a = \left(\frac{3m}{4\pi d}\right)^{1/3} = 0.26(\text{cm g}^{-1/3}) m^{1/3} \ (25°) \tag{5}$$

m = rate of flow of mercury (g sec^{-1});

d = density of mercury (g cm^{-3});

D = diffusion coefficient ($\text{cm}^2\ \text{sec}^{-1}$).

The current will be expressed in amperes, the concentrations in moles cm^{-3}.

The flux at the electrode surface is given by

$$D\left(\frac{\partial c}{\partial z}\right)_{z=0} = D\varrho \frac{(c^* - c_0)}{(\pi D t)^{1/2}} \tag{6}$$

where $(c^* - c_0)/(\pi D t)^{1/2}$ is the concentration gradient at the surface of a plane electrode and ϱ is an, as yet, unknown function of time. The following equality is evident

$$q_t \Delta (c^* - c_0) = \int_0^t q_\tau D \left(\frac{\partial c}{\partial z}\right)_{z=0} \mathrm{d}\tau \tag{7}$$

Substitution of eqns. (2), (3), (4) and (6) into eqn. (7) gives

$$\frac{2}{\varrho}(t_1 + t)^{2/3} t^{1/2} = \int_0^t \varrho (t_1 + \tau)^{2/3} \frac{\mathrm{d}\tau}{\tau^{1/2}} \tag{8}$$

Differentiation with respect to t gives

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} = \frac{2\varrho}{3(t_1 + t)} + \frac{\varrho}{2t} - \frac{\varrho^3}{2t} \tag{9}$$

which can be made linear by substituting $y = \varrho^{-2}$

$$\frac{\mathrm{d}y}{\mathrm{d}t} + \frac{4y}{3(t_1 + t)} + \frac{y}{t} = \frac{1}{t} \tag{10}$$

Equation (10) has an integrating factor $t(t_1 + t)^{4/3}$ so that

$$\mathrm{d}\{t(t_1 + t)^{4/3} y\} = (t_1 + t)^{4/3} \mathrm{d}t$$

Integration gives

$$y = \varrho^{-2} = \frac{3}{7}\left\{\frac{t_1}{t} + 1 - \frac{t_1/t}{(1 + t/t_1)^{4/3}}\right\} \tag{11}$$

where we have assumed that y remains finite for $t = 0$ After introduction of a reduced time $\vartheta = t/t_1$, eqn. (11) gives

$$y = \varrho^{-2} = \frac{3}{7}\left[1 + \frac{1}{\vartheta}\{1 - (1 + \vartheta)^{-4/3}\}\right] \tag{12}$$

The instantaneous current i is given by

$$i = nFq_tD\left(\frac{\partial c}{\partial z}\right)_{z=0} \tag{13}$$

Substitution of eqns. (4), (6) and (12) yields

$$i = 4nFa^2\sqrt{\frac{7\pi D}{3}}\,(c^* - c_0)t_1^{1/6}\,\frac{(1 + \vartheta)^{4/3}}{\{(1 + \vartheta)^{7/3} - 1\}^{1/2}} \tag{14}$$

where $4Fa^2\sqrt{7\pi/3} = 706 \cdot 10^2(\text{A cm}^2\text{sec}\,\text{g}^{-2/3}\text{equiv}^{-1})m^{2/3}$. The average current is then

$$i = 8nFa^2\sqrt{\frac{3\pi D}{7}}(c^* - c_0)\frac{t_1^{1/6}}{(\vartheta'' - \vartheta')}\{(1 + \vartheta)^{7/3} - 1\}^{1/2}\Big|_{\vartheta'}^{\vartheta''} \tag{15}$$

where $8Fa^2\sqrt{3\pi/7} = 607 \cdot 10^2$ $(\text{A cm}^2\text{sec}\,\text{g}^{-2/3}\text{equiv}^{-1})m^{2/3}$.

(b) Correction for spherical diffusion

In making the transition from a stationary spherical, to an expanding spherical electrode, LINGANE AND LOVERIDGE assumed that[4]

$$\left(\frac{\partial c}{\partial r}\right)_{r=R} = (c^* - c_0)\left\{\frac{\varrho}{(\pi Dt)^{1/2}} + \frac{1}{R}\right\} \tag{16}$$

where $\varrho = \sqrt{7/3}$ in normal polarography. Instead, we shall apply eqn. (12) for ϱ and by substituting at the same time $R = at_1^{1/3}(1 + \vartheta)^{1/3}$ for the radius of the electrode, we obtain for the instantaneous current

$$i = nFq_tD\left(\frac{\partial c}{\partial r}\right)_{r=R} = 4\pi nFa^2(t_1 + t)^{2/3}D(c^* - c_0)\left[\sqrt{\frac{7\vartheta}{3\pi Dt}}\,\frac{(1 + \vartheta)^{2/3}}{\{(1 + \vartheta)^{7/3} - 1\}^{1/2}} + \frac{1}{at_1^{1/3}(1 + \vartheta)^{1/3}}\right] \tag{17}$$

Using KOUTECKÝ's parameter for spherical correction[5]

$$\xi = \sqrt{\frac{12D}{7a^2}}\,t^{1/6} = \eta^{1/3}\vartheta^{1/6} \tag{18}$$

eqn. (17) becomes

$$i = 4nFa^2\sqrt{\frac{7\pi D}{3}}\,(c^* - c_0)t_1^{1/6}\,\frac{(1 + \vartheta)^{4/3}}{\{(1 + \vartheta)^{7/3} - 1\}^{1/2}}\left[1 + \frac{\sqrt{\pi}}{2}\,\frac{\{(1 + \vartheta)^{7/3} - 1\}^{1/2}}{\vartheta^{1/6}(1 + \vartheta)}\xi\right] \tag{19}$$

while for the average current we have

$$i = 8nFa^2\sqrt{\frac{3\pi D}{7}}(c^* - c_0)\,\frac{t_1^{1/6}}{(\vartheta'' - \vartheta')}\{(1 + \vartheta)^{7/3} - 1\}^{1/2}\left[1 + \frac{7}{16}\sqrt{\pi}\,\frac{(1 + \vartheta)^{4/3}}{\{(1 + \vartheta)^{7/3} - 1\}^{1/2}}\,\eta^{1/3}\right]\Bigg|_{\vartheta'}^{\vartheta''} \tag{20}$$

EXACT SOLUTION

The spherical diffusion problem can be described by[6]

$$\frac{\partial c}{\partial t} = D\left[\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right] - \frac{a^3}{3r^2}\frac{\partial c}{\partial r} \tag*{(21}$$

with boundary conditions

$$\left.\begin{array}{lll} t > 0; & r = a(t_1 + t)^{1/3} & c = c_0 \\ t = 0; & r > 0 & c = c^* \\ t > 0; & r \to \infty & c = c^* \end{array}\right\} \tag{22}$$

We introduce again the reduced time $\vartheta = t/t_1$ and transform by the following substitutions

$$s = \sqrt{\frac{7}{12Dt_1\vartheta}}\,\{r - at_1^{1/3}(1+\vartheta)^{1/3}\} \tag{23}$$

$$\eta = \left(\frac{12D}{7a^2}\right)^{3/2} t_1^{1/2} \tag{24}$$

After rearrangement, the following differential equation in the dimensionless parameters s and ϑ is obtained

$$\frac{\partial^2 c}{\partial s^2} + \frac{6}{7}s\frac{\partial c}{\partial s} - \frac{12}{7}\vartheta\frac{\partial c}{\partial \vartheta} = -\frac{\partial c}{\partial s}\Phi\,(\vartheta, s) \tag{25}$$

$$\Phi(\vartheta, s) = \frac{2\eta\sqrt{\vartheta}}{\{\eta s\sqrt{\vartheta} + \eta^{2/3}(1+\vartheta)^{1/3}\}} + \frac{4\sqrt{\vartheta}}{7\eta^{1/3}(1+\vartheta)^{2/3}} - \frac{4\eta\sqrt{\vartheta}}{7\{\eta s\sqrt{\vartheta} + \eta^{2/3}(1+\vartheta)^{1/3}\}^2} \tag{26}$$

while the conditions (22) transform to

$$\left.\begin{array}{ll} s \to 0; & c = c_0 \\ s \to \infty; & c = c^* \end{array}\right\} \tag{27}$$

Upon expanding the first and third terms on the right-hand side of eqn. (26) into powers of $\eta^{1/3}s\sqrt{\vartheta}/(1+\vartheta)^{1/3}$, which is allowed for all values of ϑ if we assume that $\eta^{1/3}s$ is a small quantity[5], we obtain

$$\Phi(\vartheta, s) = \frac{4\sqrt{\vartheta}}{7\eta^{1/3}(1+\vartheta)^{2/3}} + \sum_{i=0} 2(-1)^i s^{i-1}\eta^{(i-2)/3}\frac{\vartheta^{i/2}}{(1+\vartheta)^{(i+1)/3}}\left(s\eta\vartheta^{1/2} + \frac{2i}{7}\right) \tag{28}$$

It is convenient to distinguish two cases.

1. $\vartheta < 1$

Expand $(1+\vartheta)^{-(i+1)/3}$ into powers of ϑ and also transform s by substitution of

$$\sigma = \sqrt{\tfrac{3}{7}}\, s \tag{29}$$

The transformation (29) produces a differential equation of the same form as that obtained by KOUTECKÝ. Further we assume c to be of the form

$$c = \sum_{j=0} \varphi_j(\sigma)\vartheta^{j/2} \tag{30}$$

Application of these expansions to eqn. (25) yields a differential equation in σ only

$$\sum_{j=0} \varphi_j''(\sigma)\vartheta^{j/2} + 2\sigma \sum_{j=0} \varphi_j'(\sigma)\vartheta^{j/2} - 2 \sum_{j=0} j\varphi_j(\sigma)\vartheta^{j/2}$$

$$= -\sqrt{\frac{3}{7}} \sum_{r=0} \varphi_r'(\sigma)\vartheta^{r/2}\left[\frac{4}{3\eta^{1/3}}\vartheta^{1/2}\left\{1 + \sum_{k=1} (-1)^k \frac{{}^2/_3 \cdot {}^5/_3 \cdot {}^8/_3 \ldots (k - {}^1/_3)}{k!}\vartheta^k\right\}\right.$$

$$\left. + \sum_{i=0} 2(-1)^i\left(\sqrt{\frac{7}{3}}\sigma\right)^{i-1} \eta^{(i-2)/3} \left\{\frac{2i}{3} + \left(\frac{7}{3}\right)^{3/2} \sigma\eta\vartheta^{1/2}\right\}\vartheta^{i/2}\left\{1 + \sum_{l=1} (-1)^l \frac{\left(\frac{i+1}{3}\right)\left(\frac{i+4}{3}\right)\ldots\left(l + \frac{i-2}{3}\right)}{l!}\vartheta^l\right\}\right] \quad (31)$$

with the boundary conditions (27) written as

$$\left.\begin{array}{llll} \sigma \to 0: & \varphi_0 = c_0; & \varphi_j = 0 & \text{for } j \neq 0 \\ \sigma \to \infty: & \varphi_0 = c^*; & \varphi_j = 0 & \text{for } j \neq 0 \end{array}\right\} \quad (32)$$

The solution of eqns. (31) and (32) is most easily accomplished by writing the right-hand side of eqn. (31) as follows

$$\sum_i k_i\sigma^i e^{-\sigma^2} + \sum_i l_i\Psi_i \quad (33)$$

where the functions Ψ_i are the solutions of the homogeneous differential equations; they are given in Appendix A. The solution of eqn. (31) is of the form

$$\varphi_j = \sum_i \gamma_i\sigma^i e^{-\sigma^2} + \sum_i \alpha_i\Psi_i + h_j\Psi_j \quad (34)$$

where only those γ_i and α_i occur for which the corresponding k_i and l_i in eqn. (33) are different from zero.

The solutions are

$$\varphi_0 = c_0 + \frac{2}{\sqrt{\pi}}(c^* - c_0) \int_0^\sigma e^{-x^2}dx \quad (35)$$

$$\varphi_1 = \sqrt{\frac{7}{3}}\,\eta^{1/3} \frac{(c^* - c_0)}{\sqrt{\pi}} (e^{-\sigma^2} - \Psi_1) \quad (36)$$

$$\varphi_2 = \frac{(c^* - c_0)}{\sqrt{\pi}}\left[\left(\frac{2}{3} - \frac{7}{3}\eta^{2/3}\right)\sigma e^{-\sigma^2} + \frac{7}{6}\,\eta^{2/3}p_1(\Psi_0 - \Psi_2)\right] \quad (37)$$

where p_1 is defined in Appendix A.

We note that terms which refer to the expanding plane electrode, *i.e.*, those that do not contain η, occur for even values of j only, while terms pertaining to the spherical correction of the first order, *i.e.*, those containing $\eta^{1/3}$, occur for odd values of j only. Since these are the only terms of interest for the polarographic current, all other terms have been omitted in the equations for φ_j with $j > 2$. These φ_j equations may be found in Appendix BI.

After calculating the expressions for $(\partial\varphi_j/\partial\sigma)_{\sigma=0}$, we obtain for the instantaneous current i

$$i = 2nFa^2\sqrt{\pi D}(c^* - c_0)t_1^{1/6}\frac{(1 + \vartheta)^{2/3}}{\vartheta^{1/2}}\left\{\left(2 + \frac{2}{3}\vartheta - \frac{11}{27}\vartheta^2 + \frac{20}{81}\vartheta^3 - \frac{49}{324}\vartheta^4 + \ldots\right) + \right.$$

$$\left. + p_1\sqrt{\frac{7}{3}}\,\xi\vartheta^{-1/6}\left(\vartheta^{1/2} - \frac{1}{3}\vartheta^{3/2} + \frac{17}{144}\vartheta^{5/2} + \frac{1}{81}\vartheta^{7/2} + \ldots\right)\right\} \quad (38)$$

where ξ is defined by eqn. (18).

2. $\vartheta > 1$

Starting again from eqn. (28), we now divide numerator and denominator of the first term by $\vartheta^{2/3}$ and those of the second term by $\vartheta^{(i+1)/3}$ after which we expand into negative powers of ϑ. There is no need to use transformation (29), for a differential equation of the same form as KOUTECKÝ's is obtained at once. We now expand c as follows

$$c = \sum_{j=0} \sum_{k=0} \varphi_{j,k}(s)\eta^{k/3}\vartheta^{(k/6)-j} = \sum_{j=0} \sum_{k=0} \varphi_{j,k}(s)\xi^k\vartheta^{-j} \tag{39}$$

The problem is now described by

$$\begin{aligned}
&\sum_{j,k=0} \varphi_{j,k}''(s)\eta^{k/3}\vartheta^{(k/6)-j} + 2s \sum_{j,k=0} \varphi_{j,k}'(s)\eta^{k/3}\vartheta^{(k/6)-j} - \frac{2}{7} \sum_{j,k=0} (k-6j)\varphi_{j,k}(s)\eta^{(k/3)}\vartheta^{(k/6)-j} \\
&\qquad = - \sum_{p,q=0} \varphi_{p,q}'(s)\,\eta^{q/3}\vartheta^{(q/6)-p}\left\{\frac{8}{7}s \sum_{r=1} (-1)^r\vartheta^{-r}\right. \\
&+ \sum_{i=0} 2(-1)^i s^i \eta^{(i+1)/3}\vartheta^{(i+1)/6}\left[\left\{1 + \sum_{l=1}(-1)^l \frac{\left(\frac{i+1}{3}\right)\left(\frac{i+4}{3}\right)\ldots\left(l+\frac{i-2}{3}\right)}{l!}\vartheta^{-l}\right\} + \right. \\
&\qquad \left.\left.\left. -\frac{2}{7}(i+3)s^2\left\{1 + \sum_{n=1}(-1)^n \frac{\left(\frac{i+4}{3}\right)\left(\frac{i+7}{3}\right)\ldots\left(n+\frac{i+1}{3}\right)}{n!}\vartheta^{-n}\right\}\right]\right]\right\}
\end{aligned} \tag{40}$$

while the boundary conditions (27) are given as

$$\left.\begin{aligned} s \to 0&: \quad \varphi_{0,0} = c_0\,; \quad \varphi_{j,k} = 0 \\ s \to \infty&: \quad \varphi_{0,0} = c^*; \quad \varphi_{j,k} = 0 \end{aligned}\right\} \text{ with } j \text{ and } k \text{ not simultaneously zero} \tag{41}$$

For the limit of $t_1 = 0$, hence $\vartheta \to \infty$, only the terms with $j = 0$ are retained in eqns. (39) and (40)

$$\sum_{k=0} \varphi_{0,k}''\xi^k + 2s \sum_{k=0} \varphi_{0,k}'\xi^k - \frac{2}{7} \sum_{k=0} k\varphi_{0,k}\xi^k = - \sum_{q=0} \varphi_{0,q}'\xi^q \sum_{i=0} 2(-1)^i s^i \xi^{i+1}\left\{1 - \frac{2}{7}(i+3)s^2\right\} \tag{42}$$

This is the same differential equation as the one obtained by KOUTECKÝ for normal polarography. The solutions of eqn. (42) are[5]

$$\varphi_{0,0} = c_0 + \frac{2}{\sqrt{\pi}}(c^* - c_0)\int_0^s \mathrm{e}^{-x^2}\,\mathrm{d}x \tag{43}$$

$$\varphi_{0,1} = \frac{14\,(c^* - c_0)}{11\sqrt{\pi}}\left\{\left(1 - \frac{3}{7}s^2\right)\mathrm{e}^{-s^2} - \Psi_{1/7}\right\} \tag{44}$$

For $j \neq 0$, by a procedure similar to the one outlined above for the case of $\vartheta < 1$ we obtain the expressions listed in Appendix BII, for the terms $\varphi_{j,0}$ (expanding plane electrode) and $\varphi_{j,1}$ (first-order spherical correction).

The current is given by

$$\begin{aligned}
i = 4nFa^2\sqrt{\frac{7\pi D}{3}}\,(c^* - c_0)t_1^{1/6}\,\frac{(1+\vartheta)^{2/3}}{\vartheta^{1/2}} \\
\left\{\left(1 - \frac{1}{2\vartheta} + \frac{3}{8\vartheta^2} - \frac{5}{16\vartheta^3} + \frac{35}{128\vartheta^4} - \frac{63}{256\vartheta^5} + \ldots\right) + \frac{7}{11}p_{1/7}\xi\left(1 - \frac{1}{3\vartheta} + \frac{2}{9\vartheta^2} + \ldots\right)\right\}
\end{aligned} \tag{45}$$

For $\vartheta > 3$ eqn. (45) can be written in closed form

$$i = 4nFa^2\sqrt{\frac{7\pi D}{3}}(c^* - c_0)t_1^{1/6}(1+\vartheta)^{1/6}\left\{1 + \frac{7}{11}p_{1/7}\xi\frac{(1+\vartheta)^{1/6}}{\vartheta^{1/6}}\right\} \tag{46}$$

where

$$\frac{7}{11}p_{1/7} = 0.787$$

COMPARISON OF APPROXIMATE AND EXACT SOLUTIONS

Comparison of the resulting solutions for instantaneous current is most conveniently accomplished by maintaining the distinction $\vartheta < 1$ and $\vartheta > 1$. In each case the terms in the equations corresponding to the expanding plane electrode and those related to the (relative) spherical correction will be dealt with separately. The general result for both methods is of the form

$$i = 4nFa^2\sqrt{\frac{7\pi D}{3}}(c^* - c_0)t_1^{1/6}A(\vartheta)\{1 + B(\vartheta)\xi\} \tag{47}$$

where $B(\vartheta)\xi$ is the relative spherical correction term.

(1a) Expanding plane electrode for $\vartheta < 1$

Values of $A(\vartheta)$ computed with the approximate method (eqn. (19)) and the exact method (eqn. (38)) are given in Table 1. In order to indicate the rate of convergence of the first series in eqn. (38), values with both four and five terms have been listed. Table 1 shows clearly that the agreement is very good; even for $\vartheta = 0.90$ the deviation with five terms is only 1.5% and would probably be less if a sixth term in eqn. (38) had been considered.

TABLE 1

$\vartheta < 1$, COMPARISON OF EQNS. (19) AND (38)

ϑ	*$A(\vartheta)$ from eqn. (19)*	*$A(\vartheta)$ from eqn. (38) with:*		*$B(\vartheta)$ from eqn. (19)*	*$B(\vartheta)$ from eqn. (38)*
		4 terms	*5 terms*		
0.0005	29.288	29.293	29.293	0.1074	0.1074
0.001	20.724	20.723	20.723	0.1353	0.1353
0.005	9.3032	9.3045	9.3045	0.2308	0.2307
0.01	6.6120	6.6119	6.6119	0.2897	0.2897
0.05	3.0734	3.0734	3.0734	0.4829	0.4827
0.10	2.2753	2.2753	2.2753	0.5902	0.5896
0.25	1.6291	1.6295	1.6291	0.7383	0.7351
0.50	1.3680	1.3723	1.3667	0.8324	0.8237
0.75	1.2857	1.3036	1.2773	0.8715	0.8626
0.90	1.2631	1.2967	1.2443	0.8844	0.8814
0.99	1.2545	1.3014	1.2258	0.8900	0.8930

(1b) (Relative) spherical correction for $\vartheta < 1$

Approximate and exact values of $B(\vartheta)$ computed with eqns. (19) and (38) respectively, are given in the last two columns of Table 1. The agreement is again very good, the greatest deviation (for $\vartheta = 0.50$) being 1%.

(2a) Expanding plane electrode for $\vartheta > 1$

Values of $A(\vartheta)$ computed from eqn. (19) (approximate) and eqn. (46) (derived from eqn. (45), which is exact) are given in Table 2. $A(\vartheta)$ in eqn. (46) can be in error by a little over 1% at $\vartheta = 2$ and by 0.1% at $\vartheta = 3$.
It is evident that the approximate equation can be used only for $\vartheta > 4$, its values in the range $1 < \vartheta < 4$ being too high.

(2b) (Relative) spherical correction for $\vartheta > 1$

Values of $B(\vartheta)$ computed with eqns. (19) and (46) respectively, are given in the last two columns of Table 2. It can be seen that $B(\vartheta)$ values from eqn. (19) are too high throughout. In particular, this is borne out by the limiting case of $\vartheta = \infty$, where eqn. (46) becomes identical with KOUTECKÝ's equation.

TABLE 2

$\vartheta > 1$, COMPARISON OF EQNS. (19) AND (46)

ϑ	*$A(\vartheta)$ from eqn. (19)*	*$A(\vartheta)$ from eqn. (46)*	*$B(\vartheta)$ from eqn. (19)*	*$B(\vartheta)$ from eqn. (46)*
2	1.25007	1.20094	0.9109	0.8418
3	1.28547	1.25992	0.9112	0.8254
4	1.32322	1.30766	0.9090	0.8180
7	1.41977	1.41421	0.9026	0.8045
26	1.73245	1.73205	0.8916	0.7918
63	2.00006	2.00000	0.8885	0.7889
∞	∞	∞	0.8862	0.7868

DISCUSSION

To facilitate discussion, the data given in the tables have been plotted in part in Figs. 1 and 2, from which the following conclusions can be drawn:

(1) The closed-form expression, eqn. (46) cannot be exact, for eqn. (46) cannot possibly provide continuity at $\vartheta = 1$ for $A(\vartheta)$ (Fig. 1).

(2) Agreement between eqn. (38) and eqn. (46) at $\vartheta = 1$ cannot be effected through extrapolation, as the latter procedure is complicated by the fact that both $A(\vartheta)$ and $B(\vartheta)$ should have extreme values in the range $0.90 < \vartheta < 3$.

(3) The approximate method of LINGANE AND LOVERIDGE[4] for curvature correction is valid for $\vartheta < 1$.

A consequence of conclusions (1) and (2) above, *i.e.*, of the inaccuracy of our equations for instantaneous current in the region $1 < \vartheta < 3$, is that average currents can be derived for $\vartheta < 1$ only. Hence eqn. (20) must not be used for $\vartheta > 1$. Since, in pulse polarography ϑ values greater than one are not of great practical interest, this is not objectionable.

It is worth noting that the pulse-polarographic method will abolish spherical effects only at extremely small values of ϑ. According to Table 1, in a practicable case of $t_1 = 2$ sec and $t = 1/25$ sec, $\vartheta = 0.02^1$, the relative spherical correction is some 45%, and for $\vartheta = 0.005$ it is still 30% of the corresponding value for instantaneous current in normal polarography ($\vartheta = \infty$).

Furthermore, it is of interest to compare the pulse-polarographic current with that of normal polarography. By leaving out the spherical correction terms, this can be

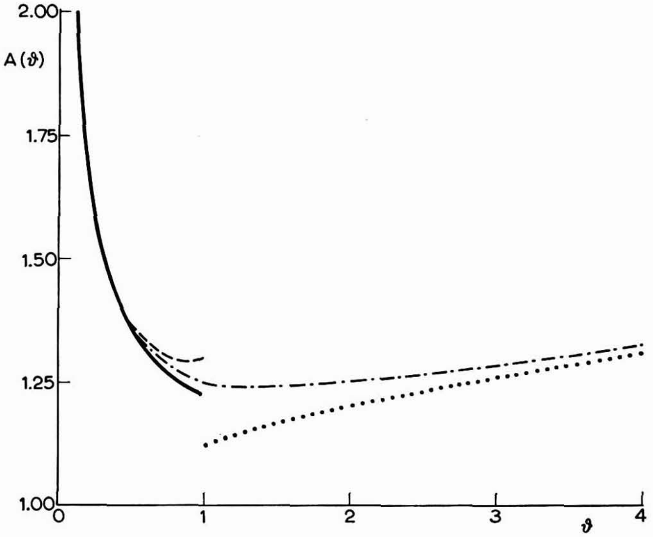

Fig. 1. $A(\vartheta)$ *vs.* ϑ: —·—·—, eqn. (19); – – – – – –, eqn. (38) with 4 terms; ———, eqn. (38) with 5 terms; · · · · · ·, eqn. (46).

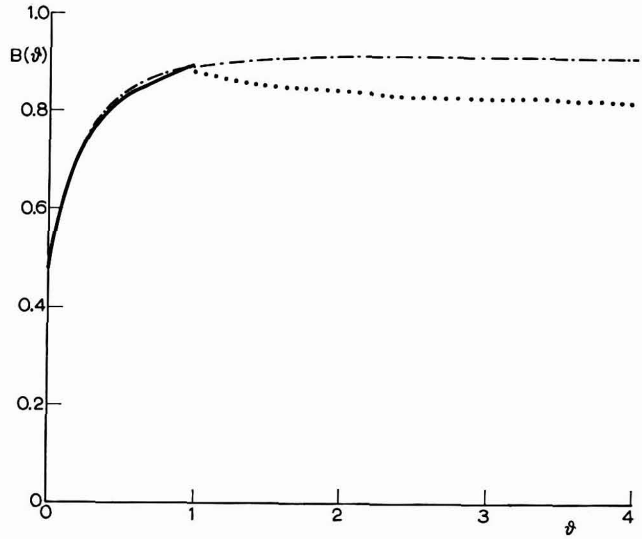

Fig. 2. $B(\vartheta)$ *vs.* ϑ: —·—·—, eqn. (19); ———, eqn. (38); · · · · · ·, eqn. (46).

done in a simple way, since, for instantaneous currents according to eqn. (19) we have

$$\frac{i_{\text{pulse}}}{i_{\text{normal}}} = \frac{(1+\vartheta)^{4/3}}{\vartheta^{1/6}\{(1+\vartheta)^{7/3}-1\}^{1/2}} \qquad \text{for } \vartheta < 1 \tag{48}$$

and according to eqn. (46)

$$\frac{i_{\text{pulse}}}{i_{\text{normal}}} = \frac{(1+\vartheta)^{1/6}}{\vartheta^{1/6}} \qquad \text{for } \vartheta > 3 \tag{49}$$

For average currents this ratio is known only for $\vartheta < 1$, where according to eqn. (20) we obtain

$$\frac{\bar{i}_{\mathrm{pulse}}}{\bar{i}_{\mathrm{normal}}} = \frac{\{(1+\vartheta)^{7/3}-1\}^{1/2}\Big|_{\vartheta'}^{\vartheta''}}{(\vartheta'')^{7/6}-(\vartheta')^{7/6}} \tag{50}$$

These ratios are valid if we compare equal periods of voltage application (t) under otherwise identical circumstances. Equations (48) and (50) have been plotted in Fig. 3.

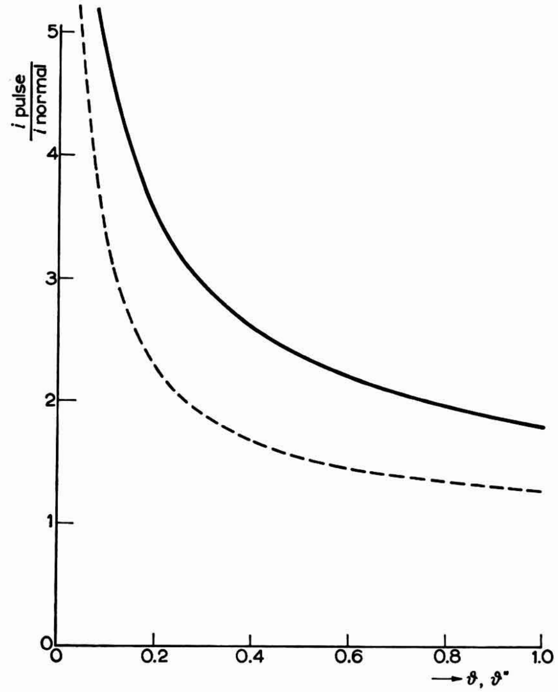

Fig. 3. - - - - -, $\frac{i_{\mathrm{pulse}}}{i_{\mathrm{normal}}}$ *vs.* ϑ, eqn. (48); ———, $\frac{\bar{i}_{\mathrm{pulse}}}{\bar{i}_{\mathrm{normal}}}$ *vs.* ϑ'' for $\vartheta' = 0.02$, eqn. (50).

The current ratio of eqn. (49) approaches the value of unity very rapidly (at $\vartheta = 4$, it is 1.038).

APPENDIX

A. Ψ_α and p_α (*cf.*[5])

The differential equation

$$\frac{\mathrm{d}^2\varphi(x)}{\mathrm{d}x^2} + 2x\,\frac{\mathrm{d}\varphi(x)}{\mathrm{d}x} - 2\alpha\varphi(x) = 0 \tag{A1}$$

has two linearly independent solutions

$$K_\alpha = \sum_{i=0} a_{\alpha,i}x^i; \quad L_\alpha = \sum_{i=0} c_{\alpha,i}x^{i+1} \quad (i \text{ only even}) \tag{A2}$$

where

$$\left.\begin{aligned} \frac{a_{\alpha,i+2}}{a_{\alpha,i}} = \frac{2(\alpha - i)}{(i+1)(i+2)}\,; \quad \frac{c_{\alpha,i+2}}{c_{\alpha,i}} = \frac{2(\alpha - i - 1)}{(i+2)(i+3)} \\ a_{\alpha,0} = c_{\alpha,0} = 1 \end{aligned}\right\} \tag{A3}$$

If we define

$$p_\alpha = \lim_{x\to\infty} \frac{K_\alpha(x)}{L_\alpha(x)} \tag{A4}$$

then

$$p_\alpha \cdot p_{\alpha+1} = 2(\alpha + 1) \tag{A5}$$

We next define

$$\Psi_\alpha = K_\alpha - p_\alpha L_\alpha \tag{A6}$$

The functions Ψ_α have the following properties

$$\frac{\mathrm{d}\Psi_\alpha}{\mathrm{d}x} = -\,p_\alpha \Psi_{\alpha-1} \tag{A7}$$

$$x\Psi_\alpha = \frac{1}{2} p_\alpha(\Psi_{\alpha-1} - \Psi_{\alpha+1}) \tag{A8}$$

The combination of (A5) and (A8) is frequently used

$$x p_\alpha \Psi_{\alpha-1} = \alpha(\Psi_{\alpha-2} - \Psi_\alpha) \tag{A9}$$

B. The functions φ

(I) $\vartheta < 1$

The solutions φ_j of eqn. (31) are for $j > 2$:

$$\varphi_3 = (c^* - c_0)\sqrt{\frac{7}{3\pi}}\,\eta^{1/3}\left(-\frac{4}{3}\sigma^2 \mathrm{e}^{-\sigma^2} - \frac{2}{3}\Psi_1 + \frac{2}{3}\Psi_3\right)$$

$$\varphi_4 = \frac{(c^* - c_0)}{\sqrt{\pi}}\left(-\frac{11}{27}\sigma - \frac{2}{9}\sigma^3\right)\mathrm{e}^{-\sigma^2}$$

$$\varphi_5 = (c^* - c_0)\sqrt{\frac{7}{3\pi}}\,\eta^{1/3}\left\{\left(\frac{2}{3}\sigma^4 + \frac{26}{27}\sigma^2 + \frac{1}{18}\right)\mathrm{e}^{-\sigma^2} - \frac{5}{9}\Psi_1 + \frac{4}{3}\Psi_3 - \frac{5}{6}\Psi_5\right\}$$

$$\varphi_6 = \frac{(c^* - c_0)}{\sqrt{\pi}}\left(\frac{4}{81}\sigma^5 + \frac{20}{81}\sigma^3 + \frac{20}{81}\sigma\right)\mathrm{e}^{-\sigma^2}$$

$$\varphi_7 = (c^* - c_0)\sqrt{\frac{7}{3\pi}}\,\eta^{1/3}\left\{\left(-\frac{16}{81}\sigma^6 - \frac{66}{81}\sigma^4 - \frac{43}{81}\sigma^2 + \frac{17}{162}\right)\mathrm{e}^{-\sigma^2} - \frac{52}{81}\Psi_1 + \frac{37}{18}\Psi_3 - \frac{25}{9}\Psi_5 + \frac{34}{27}\Psi_7\right\}$$

$$\varphi_8 = \frac{(c^* - c_0)}{\sqrt{\pi}}\left(-\frac{2}{243}\sigma^7 - \frac{19}{243}\sigma^5 - \frac{295}{1458}\sigma^3 - \frac{49}{324}\sigma\right)\mathrm{e}^{-\sigma^2}$$

where only the terms without η or with $\eta^{1/3}$ have been considered.

(II) $\vartheta > 1$

The solutions $\varphi_{j,0}$ and $\varphi_{j,1}$ of eqn. (40) are for $j > 0$:

$$\varphi_{1,0} = -\frac{(c^* - c_0)}{\sqrt{\pi}}\, s\mathrm{e}^{-s^2}$$

$$\varphi_{2,0} = \frac{(c^* - c_0)}{\sqrt{\pi}}\left(-\frac{1}{2}s^3 + \frac{3}{4}s\right)\mathrm{e}^{-s^2}$$

$$\varphi_{3,0} = \frac{(c^* - c_0)}{\sqrt{\pi}}\left(-\frac{1}{6}s^5 + \frac{5}{6}s^3 - \frac{5}{8}s\right)\mathrm{e}^{-s^2}$$

$$\varphi_{4,0} = \frac{(c^* - c_0)}{\sqrt{\pi}}\left(-\frac{1}{24}s^7 + \frac{7}{16}s^5 - \frac{35}{32}s^3 + \frac{35}{64}s\right)\mathrm{e}^{-s^2}$$

$$\varphi_{5,0} = \frac{(c^* - c_0)}{\sqrt{\pi}}\left(-\frac{1}{120}s^9 + \frac{3}{20}s^7 - \frac{63}{80}s^5 + \frac{21}{16}s^3 - \frac{63}{128}s\right)\mathrm{e}^{-s^2}$$

$$\varphi_{1,1} = \frac{(c^* - c_0)}{\sqrt{\pi}}\left\{\left(-\frac{6}{11}s^4 + \frac{19}{11}s^2 + \frac{7}{33}\right)\mathrm{e}^{-s^2} - \frac{1}{11}\Psi_{-13/7} - \frac{4}{33}\Psi_{1/7}\right\}$$

$$\varphi_{2,1} = \frac{(c^* - c_0)}{\sqrt{\pi}}\left\{\left(-\frac{3}{11}s^6 + \frac{18}{11}s^4 - \frac{65}{44}s^2 - \frac{35}{396}\right)\mathrm{e}^{-s^2} + \frac{13}{308}\Psi_{-27/7} - \frac{2}{231}\Psi_{-13/7} + \frac{38}{693}\Psi_{1/7}\right\}$$

C. Simple solution for expanding plane electrode

The exact solution in the case of the expanding plane electrode can easily be obtained in the following way:

The relevant differential equation is (*cf.*[7])

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} + \frac{2z}{3(t_1 + t)}\frac{\partial c}{\partial z} \tag{C1}$$

$$\left.\begin{array}{l} t = 0;\ z > 0\ :\ c = c^* \\ t > 0;\ z \to \infty :\ c = c^* \\ t > 0;\ z = 0\ :\ c = c_0 \end{array}\right\} \tag{C2}$$

Transformation to the following dimensionless parameters is performed

$$\left.\begin{array}{l} \vartheta = \dfrac{t}{t_1} \\ s = \sqrt{\dfrac{7}{12 t_1 \vartheta D}}\, z \end{array}\right\} \tag{C3}$$

After rearrangement we obtain

$$\frac{\partial^2 c}{\partial s^2} + \frac{8}{7}s\frac{\vartheta}{(1 + \vartheta)}\frac{\partial c}{\partial s} + \frac{6}{7}s\frac{\partial c}{\partial s} - \frac{12}{7}\vartheta\frac{\partial c}{\partial \vartheta} = 0 \tag{C4}$$

For $\vartheta < 1$. Expanding $(1 + \vartheta)^{-1}$, substituting $\sigma = \sqrt{3/7}\ s$ and writing $c = \sum\limits_{i=0} \varphi_i(\sigma)\vartheta^i$ gives

$$\sum_{i=0} \varphi_i''(\sigma)\vartheta^i + 2\sigma \sum_{i=0} \varphi_i'(\sigma)\vartheta^i - 4 \sum_{i=0} i\varphi_i(\sigma)\vartheta^i = \frac{8}{3}\sigma \sum_{j=0} \sum_{r=0} (-1)^{r+1}\varphi_j'(\sigma)\vartheta^{r+j+1} \tag{C5}$$

For $\vartheta > 1$. Dividing numerator and denominator in the second term by ϑ, expanding $[1 + (1/\vartheta)]^{-1}$ and writing $c = \sum_{i=0} \varphi_i(s)\, \vartheta^{-i}$, gives

$$\sum_{i=0} \varphi_i''(s)\vartheta^{-i} + 2s \sum_{i=0} \varphi_i'(s)\vartheta^{-i} + \frac{12}{7} \sum_{i=0} i\varphi_i(s)\vartheta^{-i} = \frac{8}{7}s \sum_{j=0} \sum_{r=0} (-1)^r\varphi_j'(s)\vartheta^{-(r+j+1)} \tag{C6}$$

(C5) and (C6) can be solved in the usual manner.

SUMMARY

A diffusion equation valid for pulse polarography has been derived. Let t_1 be the time during which a mercury drop has grown prior to the application of the voltage and let t be measured from that moment on, then, if $\vartheta = t/t_1$, the instantaneous current is given by

$$i = 0.732nF(c^* - c_0)\sqrt{D}t^{1/6}m^{2/3} \frac{(1 + \vartheta)^{4/3}}{\vartheta^{1/6}\{(1 + \vartheta)^{7/3} - 1\}^{1/2}} \left[1 + 0.886 \frac{\{(1 + \vartheta)^{7/3} - 1\}^{1/2}}{\vartheta^{1/6}(1 + \vartheta)}\xi\right]$$

for $\vartheta < 1$, and by

$$i = 0.732nF(c^* - c_0)\sqrt{D}t^{1/6}m^{2/3} \frac{(1 + \vartheta)^{1/6}}{\vartheta^{1/6}} \left[1 + 0.787 \frac{(1 + \vartheta)^{1/6}}{\vartheta^{1/6}}\xi\right]$$

for $\vartheta > 3$, where

$$\xi = 5.04D^{1/2}t^{1/6}m^{-1/3} = \eta^{1/3}\vartheta^{1/6}$$

The average current for $\vartheta < 1$ is

$$i = 0.627nF(c^* - c_0)\sqrt{D}t_1{}^{1/6}m^{2/3} \frac{\{(1 + \vartheta)^{7/3} - 1\}^{1/2}}{(\vartheta'' - \vartheta')} \left[1 + 0.776 \frac{(1 + \vartheta)^{4/3}}{\{(1 + \vartheta)^{7/3} - 1\}^{1/2}}\eta^{1/3}\right]\Bigg|_{\vartheta'}^{\vartheta''}$$

Numerical factors apply to 25°.

The spherical-correction term is negligibly small only for extremely small values of ϑ ($\vartheta = 0.0001$); for $\vartheta > 0.35$ it is even larger than in normal polarography.

Pulse-polarographic currents have been compared with those of normal polarography.

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DETERMINATION OF SULFUR DIOXIDE IN SOLUTION BY ANODIC VOLTAMMETRY AND BY U.V. SPECTROPHOTOMETRY

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Although there have been several studies of the anodic electrochemical behavior of dissolved sulfur dioxide[1-5], these have been primarily directed to the study of electrode mechanisms. The use of a stationary disc electrode covered with a gas-permeable membrane has indicated the usefulness of voltammetry for the determination of sulfur dioxide[6], but only in a qualitative fashion. The present study has resulted from a general investigation of the electrochemical behavior of dissolved sulfur dioxide at solid electrodes. The necessary conditions, in terms of solution composition and electrode preconditioning, have been established for the voltammetric determination of sulfur dioxide in solution by an anodic reaction at stationary platinum electrodes. The best analytical data are obtained by using millimolar sulfite samples in a 0.1 F sulfuric acid solution and by using a simple preconditioning procedure for the platinum electrode. During the course of the investigation a simple and reliable method has been developed for determining the amount of total sulfite in solution using ultraviolet spectrophotometry. The details of this method are discussed.

EXPERIMENTAL

Apparatus

The voltammetric waves were recorded with a Sargent Model-XV Polarograph using a scan rate of 300 mV per min (+1.5 V to −1.5 V voltage setting). In order to obtain a chart with the anodic wave in a convenient Cartesian co-ordinate quadrant, the cell leads were connected in the usual manner, the cell set for *reverse polarity*, and the scan driven *0–100%*. All potentials are reported *vs.* the saturated calomel electrode (S.C.E.).

The electrolytic cell was of the Pecsok–Juvet type[7], but was modified by replacing the original solution compartment with a Leeds and Northrup Model 7961 Coulometric Titration Cell assembly. Solution stirring was accomplished magnetically using a Will-Bronwill compressed-air driven Mag-Jet. Both the cell and stirrer were immersed in a thermostatted bath regulated at 25.00 ± 0.01°. The supporting electrolyte solution, 0.1 F sulfuric acid, was deaerated before introducing the sulfite sample. Other cell systems are equally satisfactory as long as a closed system which prevents loss of sulfur dioxide is possible.

The electrode consisted of a length of 22-gauge (B. and S.) platinum wire sealed into soft-glass tubing and ground to a flat surface. The resulting exposed surface resembled a platinum disc with a 0.0253-in. diameter. Electrical contact was made through copper wire silver-soldered to the platinum.

Reagents

All reagents were reagent grade. The distilled water was redistilled from alkaline permanganate in an all-Pyrex still. The sodium sulfite as well as the sulfite solutions were iodometrically standardized[8] using primary standard grade arsenious oxide (Mallinckrodt) as the reference standard.

Spectrophotometry

Spectral data were obtained with a Cary Model-14 Recording Spectrophotometer using matched 1-cm cells at 25°. The reference cell contained 0.1 *F* sulfuric acid.

RESULTS AND DISCUSSION

Analytical Procedure

The key to successful electrooxidation of sulfur dioxide in acid media is the electrode preconditioning process. The necessary *active* electrode surface is obtained by introducing into the electrolytic cell a sample of sulfite in 0.1 *F* sulfuric acid and sealing the cell compartment. The solution is stirred to ensure homogeneity and then allowed to become quiescent. Next, the applied potential is scanned from −0.15 V to +1.5 V (*vs.* S.C.E.). The stirring and scan processes are repeated two or three times. At this stage current–voltage traces should be reproducible and should have reached a maximum in limiting peak current; also the slope for $\Delta i/\Delta e$ should have reached a

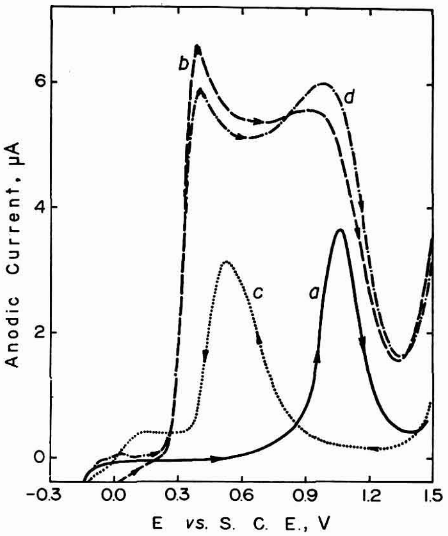

Fig. 1. Current–voltage scans for millimolar sulfite in 0.1 *F* H_2SO_4 at a platinum electrode. Curve (a), anodic scan with an inactive electrode; curve (b), anodic scan with an active electrode; curve (c), reverse scan from +1.5 V for an anodized electrode; curve (d), anodic scan begun at −0.3 V illustrating effect of excessive cathodization. Scan rate, 300 mV per min.

maximum and the overvoltage a minimum. The electrode now is activated and ready to be used for analytical purposes. It can be calibrated with known concentrations of sulfite solutions. No other preconditioning or cleaning procedure is necessary to obtain reproducible results.

The initial scan to a high anodic voltage during the preconditioning step causes an oxide film to be formed on the electrode surface. This is then stripped when the repeat scan is started at a negative voltage corresponding to that at which hydrogen evolution begins. The resulting *stripped* electrode has the desired surface characteristics.

A supporting electrolyte solution of 0.1 *F* sulfuric acid has been found to be an ideal medium. Although good reproducibility is obtained in other media at pH values as high as 5, maintenance of electrode activity becomes more difficult. Figure 1 illustrates the effect of initial electrode preconditioning. Curve (a) represents the initial scan of an inactive electrode from −0.15 V to +1.5 V in a sulfite-containing solution. A repeat scan over the same voltage range is shown by curve (b) and the strip-off following an anodic scan is shown by curve (c). The effect of excessive cathodization at potentials more negative than −0.15 V is shown by curve (d). Thus, the initial voltage is chosen to correspond to the start of hydrogen evolution (−0.15 V).

When the electrode is properly conditioned successive scans of a 10^{-3} *F* solution are completely reproducible; in fact three successive scans produce a curve essentially identical to curve (b), Fig. 1. The only variations occur as slight deviations in the wave shape past the peak potential.

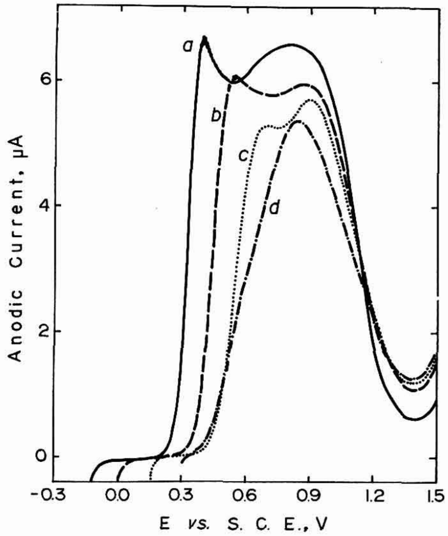

Fig. 2. Current–voltage scans for millimolar sulfite in 0.1 *F* H_2SO_4 at a platinum electrode illustrating effect of different starting voltages. Curves (a), (b), (c), and (d) represent starting voltages of −0.15 V, 0.00 V, +0.15 V, and +0.30 V, respectively. Scan rate, 300 mV per min.

Figure 2 shows a composite of traces representing several degrees of electrode activity: (a) active with scan initiated at −0.15 V; (b), (c), and (d) scans started at 0, +0.15, and +0.30 V, respectively. Curves (b), (c), and (d) illustrate the effect of incomplete stripping.

The linear dependence of peak current upon concentration in the millimolar region is shown in Fig. 3. By using these data and a value of 0.76 for αn_a (as measured from chronopotentiometric data) in the equation of DELAHAY[9], the diffusion coefficient, D, for sulfur dioxide in 0.1 F H_2SO_4 is calculated to be 2.1×10^{-5} cm²/sec.

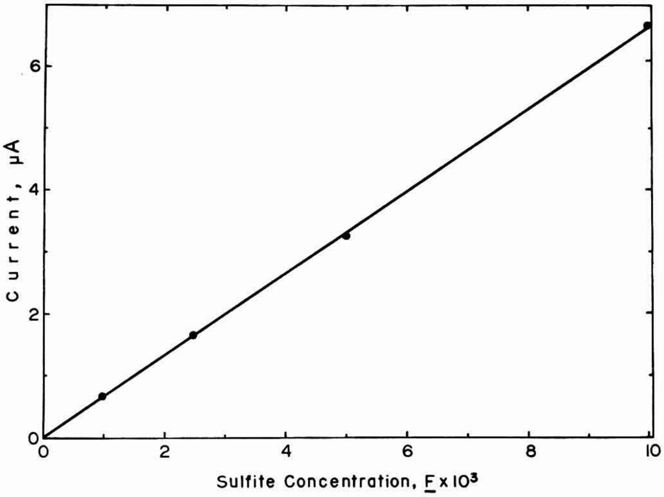

Fig. 3. Peak current *vs.* total sulfite concentration in 0.1 F H_2SO_4 using an activated platinum electrode. Scan rate, 300 mV per min.

Spectrophotometry

Although sulfite in acid solutions produces two distinct absorption bands in the ultraviolet region, their use for the determination of sulfite has been essentially ignored[10,11]. GOLDING[12] has investigated the bisulfite–pyrosulfite equilibrium in aqueous solution, especially in the pH range from 3.5–5.5. The low wave-length band occurs at 205 mμ for concentrations below $3 \cdot 10^{-3}$ M, but shifts to 215 mμ at

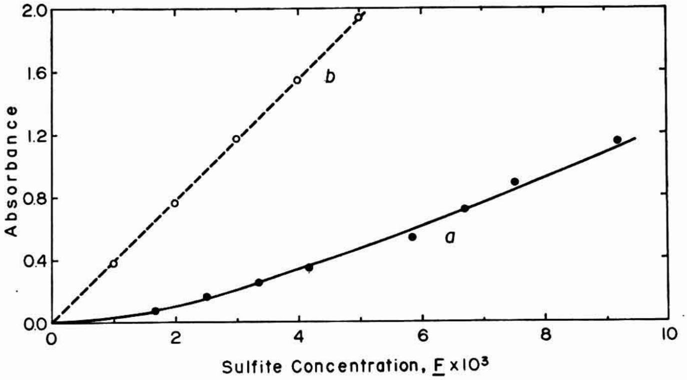

Fig. 4. Absorbance *vs.* total sulfite concentration. Curve (a), DE MAINE'S data at 278 mμ for sulfur dioxide solutions using water; curve (b), data at 276 mμ for sodium sulfite dissolved in 0.1 F sulfuric acid. Both sets of data taken at 25° using 1-cm path-length cells.

higher concentrations. These peaks are assigned to the $HOSO_2^-$ and HSO_3^- isomers of bisulfite, respectively. The peak at 255 mμ is assigned to pyrosulfite ion, $S_2O_5^{2-}$. The method thus provides a means for determining the bisulfite–pyrosulfite ratio. DE MAINE[13] has studied the water–sulfur dioxide system and has reported a band near 278 mμ. His data for total sulfur dioxide concentrations ranging from $1.7 \cdot 10^{-3}$–$9.2 \cdot 10^{-3}$ M are plotted as curve (a) in Fig. 4.

The long wave-length peak can be conveniently used for analytical purposes in the millimolar region if the spectral measurements are made at a constant pH below 2. The spectrum which is obtained for $2 \cdot 10^{-3}$ F sodium sulfite in 0.1 F sulfuric acid is reproduced in Fig. 5. The relationship between total sulfite concentration and absorbance, which obeys Beer's law, is shown by curve (b) in Fig. 4. These data give a molar absorptivity for sulfur dioxide in 0.1 F H_2SO_4 of $3.88 \cdot 10^2$ l/moles cm at 276 mμ.

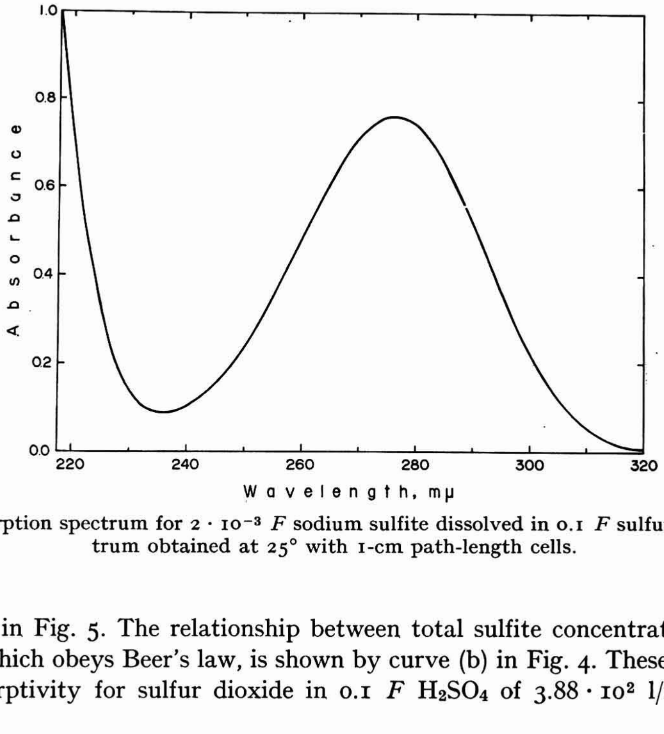

Fig. 5. Absorption spectrum for $2 \cdot 10^{-3}$ F sodium sulfite dissolved in 0.1 F sulfuric acid. Spectrum obtained at 25° with 1-cm path-length cells.

Accuracy

Both the voltammetric and the spectrophotometric methods are subject to the usual errors that accompany the analysis of sulfite in solution; namely the volatility of sulfur dioxide in acidic media, air oxidation, and possible changes in the oxidation–reduction properties upon aging of the solution. Loss through volatilization is minimized by using a sealed cell, and air oxidation in strong acid media is minimal if simple precautions such as deaeration of the sulfuric acid solution are taken.

For routine voltammetric analysis with a properly functioning electrode the estimated error is about ±2%. The reproducibility of the peak current for repetitive scans gives an error of less than ±1%. The spectrophotometric method gives errors of less than ±1% without taking special precautions.

ACKNOWLEDGEMENT

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SUMMARY

A voltammetric method has been developed for the determination of total sulfite in sulfuric acid solutions using activated platinum electrodes. The diffusion coefficient for sulfur dioxide in 0.1 F H_2SO_4 is $2.1 \cdot 10^{-5}$ cm²/sec on the basis of the voltammetric data. The proper conditions for the spectrophotometric determination of total sulfite have been established. The molar absorptivity in 0.1 F H_2SO_4 is 388 l/moles cm at the absorption maximum, 276 mμ.

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THE DETERMINATION OF PLUTONIUM BY A.C. POLAROGRAPHY

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Although square-wave polarography has been established for many years as a technique for the determination of trace amounts of many metals, little attempt has been made to apply it to the determination of small amounts of plutonium. Plutonium occurs in aqueous solutions as one or more of the following ionic species — Pu^{3+}, Pu^{4+}, PuO_2^{+} and PuO_2^{2+}. The Pu^{4+}/Pu^{3+} and PuO_2^{2+}/PuO_2^{+} couples both behave reversibly with formal potentials, in non-complexing solutions, of +0.9818 V and +0.9133 V *vs.* N.H.E. respectively[1]. There are two possible methods of employing these couples in polarographic analysis. One method involves the use of a solid electrode, instead of a dropping mercury electrode. The other depends upon the use of complexing agents to complex the oxidized form preferentially, thereby moving the potential of the couple into a region more suitable for the use of a dropping mercury electrode.

KOYAMA[2] attempted the former approach by using a stationary platinum electrode in conjunction with a square-wave polarograph. He obtained peaks for the reduction of Pu^{4+} ions below 10^{-5} moles per litre in 1 M HCl and in 2 M HNO_3; the peaks occurred at +0.71 V and +0.66 V *vs.* S.C.E. respectively. Interference from a ferric iron peak at +0.45 V *vs.* S.C.E. was more pronounced in nitric acid than in hydrochloric acid solutions. The peaks were not very well-defined due to noise from a preamplifier in the polarograph. In addition, continual scanning, particularly in nitric acid solutions, produced an oxide layer on the surface of the electrode. This resulted in a high residual current which virtually masked the peak for plutonium. This peak has found little application in plutonium analysis.

COOK, FOREMAN AND KEMP[3] have applied the second approach to the PuO_2^{2+}/PuO_2^{+} couple. They obtained waves with a d.c. polarograph for the reduction of hexavalent plutonium in several complexing media, but the best results were produced in an oxalate supporting electrolyte. Under these conditions a single wave was obtained due to a one-electron reduction of plutonyl ions to the plutonium(V) state. However, the height of this wave was not related to the plutonium concentration, and this nonlinear dependence was found to be consistent with the induced disproportionation of plutonium(V) in oxalate solutions.

In this investigation the use of complexing agents for moving the Pu^{4+}/Pu^{3+} couple into the range of the dropping mercury electrode has been studied. By employing a citrate supporting electrolyte, methods have been developed for the determination of plutonium by square-wave polarography.

EXPERIMENTAL

1. The determination of tetravalent plutonium

Choice of supporting electrolyte. Although the Pu^{4+}/Pu^{3+} couple has a formal potential of $+0.9818$ V *vs.* N.H.E. in a non-complexing medium, the preferential complexing of Pu^{4+} ions by certain complexing agents should shift this potential into the potential range suitable for the dropping mercury electrode. Experimental verification of this was forthcoming from the coulometric studies of SCOTT AND PEEKEMA[4] who reported on the complexing of plutonium with oxalate, acetate, citrate and tartrate ions. An oxalate supporting electrolyte was considered to be unreliable for polarographic work, since both trivalent and tetravalent plutonium form insoluble oxalates. Previous experience had indicated that a citrate or tartrate electrolyte would be more suitable for study than an acetate supporting electrolyte. Whilst this work was in progress, NEBEL AND SCHWABE[5] reported on the use of an acetate supporting electrolyte for the determination of plutonium by conventional d.c. polarography. In the studies reported in this paper, experimental work has been concentrated on the evaluation of a citrate supporting electrolyte for the polarographic determination of plutonium.

Initial experiments were carried out with a citrate solution, consisting of 1 *M* citric acid $+0.1$ *M* aluminium sulphate, adjusted to pH 4.5 with potassium hydroxide. A peak for tetravalent plutonium was obtained with a square-wave polarograph at -0.42 V *vs.* a mercury pool anode, but the use of purified reagents was found to be essential to prevent the occurrence of unwanted peaks in the polarogram. Initially the aluminium sulphate was purified by recrystallization, but subsequently Analar-grade material was found to be suitable without further purification. A satisfactory supporting electrolyte was prepared by dissolving 52.5 g of citric acid (B.D.H. Foodstuffs Analysis Grade) and 16.5 g of aluminium sulphate in about 150 ml of water, and then adjusting to pH 4.5, as shown by a pH-meter, by the careful addition of 60% w/v potassium hydroxide solution. After cooling, the solution was diluted to 250 ml with water.

Development of suitable solution conditions. Before recording the polarogram, plutonium must be converted quantitatively to the tetravalent state, before the addition of the citrate supporting electrolyte. This valency adjustment presented some problems because it must be carried out in a limited volume of solution. Under such conditions controlled-potential electrolysis at a platinum cathode is a possible technique for this adjustment. However, this is not an attractive method because of the special equipment needed for the automatic control of the cathode potential. Chemical methods were considered to be more suitable provided that they did not introduce impurities into the solution to cause interfering polarographic peaks. A possible chemical method consists in the addition of hydroxylamine hydrochloride, followed by immersion in a water bath at 60° for 30 min to effect complete reduction of the plutonium to the trivalent state. The plutonium is then oxidized to the tetravalent state by adding nitric acid + sodium nitrite and immersing the solution in a boiling water bath for 5 min. After the addition of the citrate supporting electrolyte to a solution conditioned in this way, the peak for plutonium proved to be poorly-defined due to the presence of an interfering peak at -0.3 V *vs.* the mercury pool anode. This interfering peak was found to be due to an impurity in the hydroxylamine hydrochloride which resisted complete removal by chemical means, and therefore other methods for the chemical reduction of plutonium were investigated. Satisfactory reduction was obtained by dissolving Specpure magnesium metal in a sulphuric acid solution of the sample in the presence of platinum. This method proved to be a quick means of reduction without introducing impurities.

Procedure for the determination of tetravalent plutonium. Take a suitable aliquot of plutonium solution in hydrochloric acid, add 1 ml 1.8 M H_2SO_4 and evaporate carefully to dryness. Dissolve the residue in 1 ml 1.8 M H_2SO_4 and evaporate just to fumes of sulphuric acid. Cool, dilute to 1 ml with water and transfer to a stoppered tube of 10-ml capacity by using a spitzer. Weigh out 3 small pieces of Specpure magnesium metal to give a total weight of about 30 mg. Put a small piece of platinum foil into the tube and add 1 piece of magnesium at a time, allowing each piece to dissolve before the addition of the next*. On completion of the reduction process, cool the solution to room temperature and add 1 ml HNO_3 (sp.gr. 1.42) plus 0.2 ml 5 M $NaNO_2$. Immerse the tube in a boiling water bath for 5 min. Cool again to room temperature, add a further 0.1 ml 5 M $NaNO_2$ and again immerse in a boiling water bath for 5 min. Cool, add 4 ml of citrate supporting electrolyte and adjust the solution to pH 4.5 by the addition of 9.6 M KOH ($\sim$2 ml required). Dilute with water to 10 ml in a volumetric flask. Then transfer a small aliquot to a polarograph cell, deaerate with nitrogen and record the polarogram starting from -0.1 V *vs.* the mercury pool anode.

A typical peak obtained with a square-wave polarograph for tetravalent plutonium is shown in Fig. 1A. This peak is for a 8.4×10^{-5} M plutonium concentration and its width at half the peak height is consistent with a reversible one-electron process occurring at the dropping mercury electrode. Linear calibration graphs of peak height *vs.* concentration were obtained for the range $4 \cdot 10^{-5}$ to $4 \cdot 10^{-4}$ M with a square-wave amplitude of 8 mV and a gain of 3, and also for the range $4 \cdot 10^{-6}$ to $4 \cdot 10^{-5}$ M with an amplitude of 32 mV and a gain of 4. The proportionality of peak height *vs.* concentration for the first range can be seen from the results in Table 1.

Unfortunately, this polarograph did not produce clearly-defined peaks for plutonium concentrations below 10^{-6} M due to the occurrence of a high background current. Satisfactory polarograms were also obtained with a Univector-type a.c. polarograph with peak heights proportional to concentration. A typical polarogram is shown in Fig. 1B. However, the square-wave polarograph is the more sensitive of the two instruments for the determination of plutonium, being about twelve times as sensitive as the Univector polarograph.

Influence of solution conditions on peak height. The peak for tetravalent plutonium in citrate solutions was observed to decrease in height on reducing the pH and to disappear completely below pH 1.7. Experiments were therefore carried out to study in detail the influence of pH on peak height. A series of solutions was prepared, each containing 200 μg of plutonium adjusted to the tetravalent state by reduction with magnesium followed by oxidation with HNO_3–nitrite. 4 ml of citrate supporting electrolyte was added to each solution followed by an accurately measured volume of 9.6 M KOH. The required pH range was covered by using volumes of KOH from

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* It is important that no appreciable loss of sulphuric acid should take place and that the weight of magnesium should not exceed 30 mg, to ensure that sufficient free acid is available to prevent the hydrolysis of tetravalent plutonium.

1.4–2.4 ml. After diluting each solution to 10 ml with water, a small aliquot was taken for polarography and the remainder used for measuring the pH with a micro glass electrode–S.C.E. electrode system. The plutonium peak for each solution was recorded with a square-wave polarograph and peak heights were measured in the usual

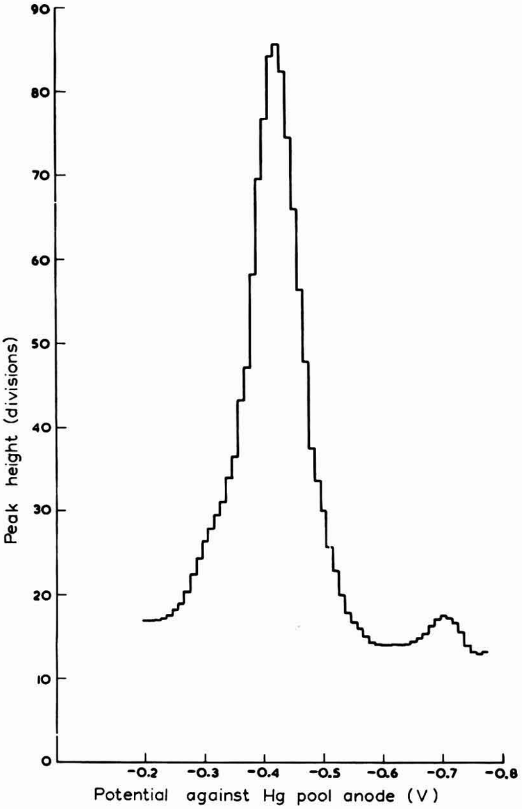

Fig. 1A. Square-wave polarogram for an 8.4 · 10^{-5} M solution of plutonium(IV). Amplitude, 16 mV; gain, 4.

TABLE 1

THE LINEARITY OF PEAK HEIGHT WITH CONCENTRATION FOR Pu(IV)

Concn. of Pu(IV) (moles/l)	*Peak height (divisions)*	*Peak height / concn.*
4.2×10^{-5}	9.3	2.22×10^{5}
6.7×10^{-5}	15.6	2.33×10^{5}
8.4×10^{-5}	18.3	2.18×10^{5}
1.34×10^{-4}	31.0	2.31×10^{5}
2.01×10^{-4}	45.4	2.26×10^{5}
2.68×10^{-4}	60.3	2.29×10^{5}
3.35×10^{-4}	72.5	2.16×10^{5}

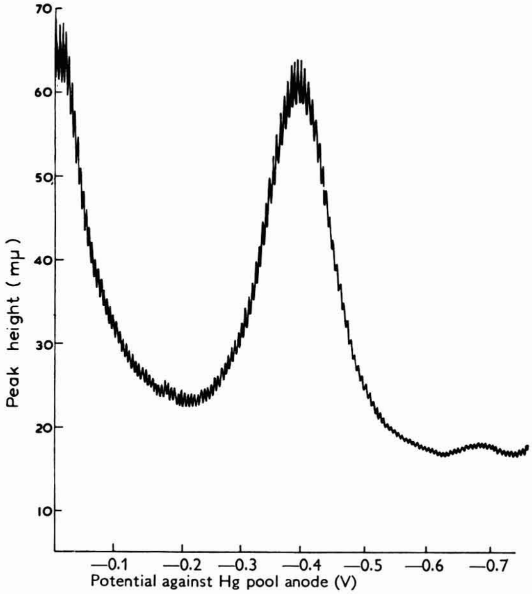

Fig. 1B. A.C. Univector polarogram for a 2.5 · 10^{-4} *M* solution of plutonium(IV). Sensitivity, 6.10.

way. On plotting peak height *vs.* pH, a variation was obtained as shown in Fig. 2. A constant maximum height was found to occur over the pH range 4.0–4.8, and for quantitative analysis it was necessary to adjust the pH of each solution within this range.

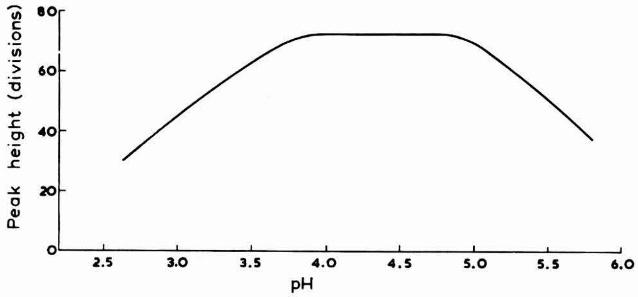

Fig. 2. The effect of pH on the polarographic peak height for solutions of plutonium(IV).

Experiments were carried out to determine if variations in the volume of citrate supporting electrolyte had any influence on peaks in the pH range for maximum peak height. On varying the volume of the citrate solution from 3 to 5.5 ml in a final volume of 10 ml, it was found that the polarographic peaks were well-defined and no variation in peak height occurred. However, for all the polarographic work described in this paper the volume of the citrate supporting electrolyte was maintained at 4 ml.

Effects of other elements. A study of the polarographic behaviour of other elements under the final solution conditions is of importance in assessing the applicability of the method in analysis. The full procedure for plutonium was applied to solutions containing $2 \cdot 10^{-3}$ or 10^{-4} M concentrations of various elements with the further addition of 0.25 ml of 20% w/v sulphamic acid solution after the 2 ml of 9.6 M KOH. The sulphamic acid was necessary to remove the effects of any excess nitrite which produces a peak at about −0.9 V *vs.* the mercury pool. Although this peak does not interfere with the plutonium peak, it was an advantage to remove it in studying the behaviour of other elements, since an applied voltage from 0 to −1.6 V could then be used without difficulty. Results for the various elements are given in Table 2.

TABLE 2

DATA ON PEAKS FOR VARIOUS ELEMENTS IN THE METHOD FOR Pu(IV)

Element	*Molarity*	$E_{\frac{1}{2}}$ *(V vs. Hg pool)*	*Peak height*	*Sensitivity*
Pu	10^{-4}	−0.42	22.0	8.3
Cd	10^{-4}	−0.86	55.6	4.3
Cu	10^{-4}	−0.34	62.0	8.3
Pb	10^{-4}	−0.70	55.0	4.3
Fe	$2 \cdot 10^{-3}$	−0.30, −0.53	53.0, 16.7	4.2
Mo	$2 \cdot 10^{-3}$	−1.0	62.3	4.3
U	$2 \cdot 10^{-3}$	−0.75	56.3	4.2
Sb	$2 \cdot 10^{-3}$	−0.88, −1.19	48.7, 30.0	8.3
Bi	$2 \cdot 10^{-3}$	−0.59, −0.87	38.0, 40.3	4.3
In	$2 \cdot 10^{-3}$	−0.90	47.2	8.4
Mn	$2 \cdot 10^{-3}$	−0.56	12.5	32.4
Np	10^{-4}	No peak	—	32.4
Sn	$2 \cdot 10^{-3}$	Final solution cloudy due to precipitation of tin		
W	$2 \cdot 10^{-3}$	Tungstic acid precipitated on fuming with H_2SO_4		

Uranium is often present in plutonium solutions, and fortunately the uranium peak at −0.75 V is sufficiently well-separated to give no interference except for very high ratios of uranium to plutonium. The behaviour of copper and lead is also important because of the difficulty of avoiding contamination from these elements. Small amounts of copper do not interfere, but for high ratios of copper to plutonium some masking of the plutonium peak takes place. However, the greatest interference comes from the double peak produced by ferric iron at −0.30 V and −0.53 V respectively, as shown in Fig. 3. The relative heights of these peaks were found to depend on the temperature attained by the solution on the addition of 9.6 M KOH during the adjustment of the pH. On cooling the solution during neutralisation, the polarogram gave a sharp first peak followed by a small drawn-out second peak. The height of the first peak slowly decreased on standing at room temperature with an increase in the height of the second peak, and after 24 h the second peak was roughly 2/3rd the height of the first peak. This process could be speeded up by immersing the solution in a boiling water bath for about 10 min shortly after preparation. The usual method employed in conventional polarography for preventing interference from ferric iron by reducing it chemically to the ferrous state, could not be used because of the simultaneous reduction of plutonium to the trivalent state. Interference from this element could only be eliminated by chemical separation of iron from plutonium.

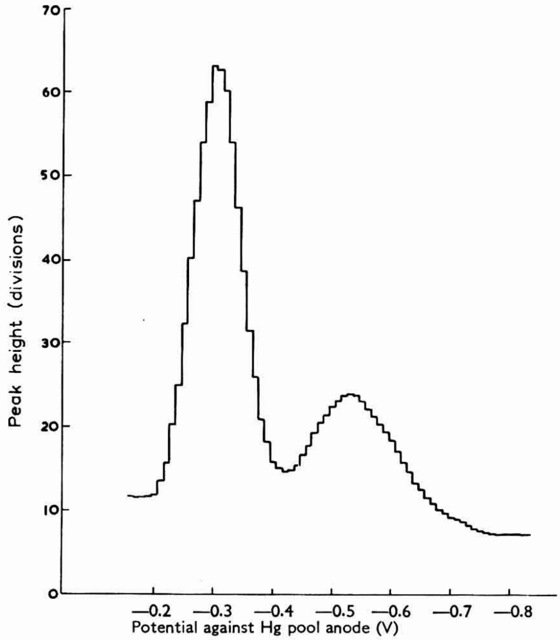

Fig. 3. Square-wave polarogram for a 2 · 10^{-3} M solution of iron(III). Amplitude, 2 mV; gain, 3.

2. *The determination of trivalent plutonium*

In view of the reversibility of the Pu^{4+}/Pu^{3+} couple, it should be possible to obtain a peak for trivalent plutonium in a citrate supporting electrolyte with an a.c. polarograph of the square-wave type. The existence of this peak was confirmed experimentally by reducing plutonium (200 μg) in 1 ml of 1.8 M H_2SO_4 to the trivalent state with 30 mg of Specpure magnesium, followed by the addition of 4 ml of citrate supporting electrolyte and 9.6 M KOH to give a solution of suitable pH in a final volume of 10 ml. As with tetravalent plutonium, the height of the peak was found to be dependent on pH, and this effect was studied in detail with the results shown in Fig. 4. A pH range 4.4–4.6 was identified for the best reproducibility, but for many

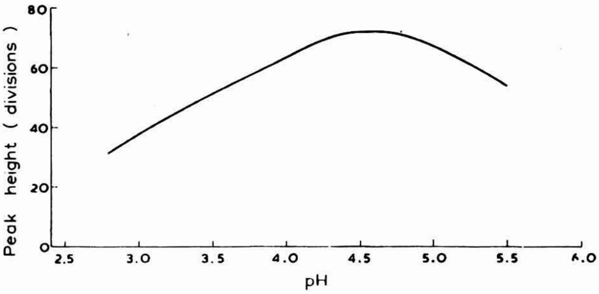

Fig. 4. The effect of pH on the polarographic peak height for solutions of plutonium(III).

analytical purposes a pH range 4.3–4.7 should be satisfactory. Even so, this latter range is only half that available in the determination of tetravalent plutonium. On fixing the pH at 4.5, a linear calibration graph was obtained for trivalent plutonium over the concentration range 4×10^{-5} to $3.35 \times 10^{-4}\,M$ with a slope equal to that for the tetravalent plutonium graph. Although plutonium can be conditioned more readily to the trivalent than to the tetravalent state by chemical means, the limited range of pH for this method constitutes a disadvantage.

Effects of other elements. The behaviour of some elements was found to be different under these solution conditions, compared with their behaviour under the conditions for tetravalent plutonium. For example, iron gives a single peak which is fairly well-separated from the plutonium peak, and thus there is no difficulty with small amounts of iron. For higher concentrations of iron, however, the resolution is less satisfactory and the direct determination of plutonium becomes impossible. Some elements are precipitated in the reduction process and remain out of solution in the final solution for polarography. The precipitation of bismuth and tin would appear to be complete since no peaks are obtained for these elements, whereas molybdenum and indium are partially precipitated. Further details of the behaviour of several elements are given in Table 3.

TABLE 3

DATA ON PEAKS FOR OTHER ELEMENTS IN THE METHOD FOR Pu(III)

Element	*Molarity*	$E_{\frac{1}{2}}$ *(V vs. Hg pool)*	*Peak height*	*Sensitivity*
Cd	10^{-4}	-0.87	65.1	4.3
Cu	10^{-4}	-0.32	68.3	8.3
Pb	10^{-4}	-0.70	48.3	4.3
Fe	10^{-4}	-0.28	53.8	16.3
Mo	$2 \cdot 10^{-3}$	-0.56, -0.89	14.2, 18.2	8.3
U	$2 \cdot 10^{-3}$	-0.72	57.8	4.3
Sb	$2 \cdot 10^{-3}$	-0.94, -1.30	45.0, 41.0	8.3
Bi	$2 \cdot 10^{-3}$	Precipitation during reduction		
In	$2 \cdot 10^{-3}$	-0.92, -1.02	50.2, 29.8	16.3
Mn	$2 \cdot 10^{-3}$	No peak		
Np	10^{-4}	No peak		
Sn	$2 \cdot 10^{-3}$	Precipitation during reduction		
W	$2 \cdot 10^{-3}$	Precipitation of tungstic acid		

The stability of trivalent plutonium in citrate solutions. Although trivalent plutonium gives a quantitative polarographic peak, the trivalent valency is not the most stable for plutonium, and the citrate complex may be unstable under the solution conditions employed. This aspect has been investigated spectrophotometrically by making use of characteristic sharp absorption peaks given by the different plutonium valency states. A suitable solution of trivalent plutonium was prepared by dissolving a piece of plutonium metal (22.7 mg) in 1 ml of 10% v/v H_2SO_4, followed by evaporation just to fumes. After dilution with 1 ml of water, the reduction with magnesium and the preparation of the solution were carried out by exactly the same method as for the polarographic determination, with the exception that 5.5 ml of the citrate supporting electrolyte was employed. The spectrum, plotted immediately after preparation with a Uvispec Spectrophotometer, was exactly as expected, with absorption peaks at 565, 603 and 665 mμ as shown in Fig. 5. However, this spectrum changed with time and the height of the 603 mμ peak was observed to decrease considerably. Only a small peak occurred after 7 h, whilst after 70 h this peak was not observed indicating complete conversion of trivalent plutonium to another form. The wavelengths of the peaks in the new spectrum showed that the trivalent plutonium had been oxidized to the tetravalent state.

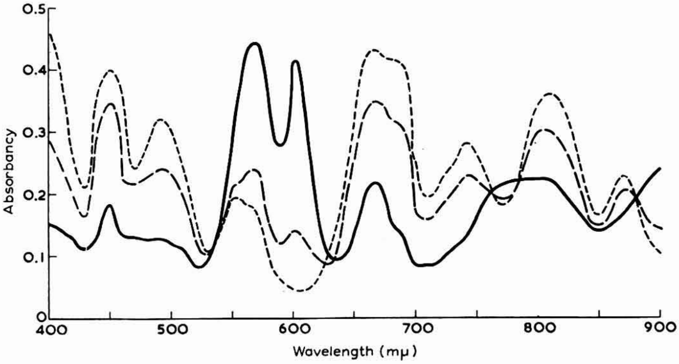

Fig. 5. The stability of plutonium(III) citrate complex with time: ——, immediately after preparation; — —, after 7 h; - - -, after 70 h.

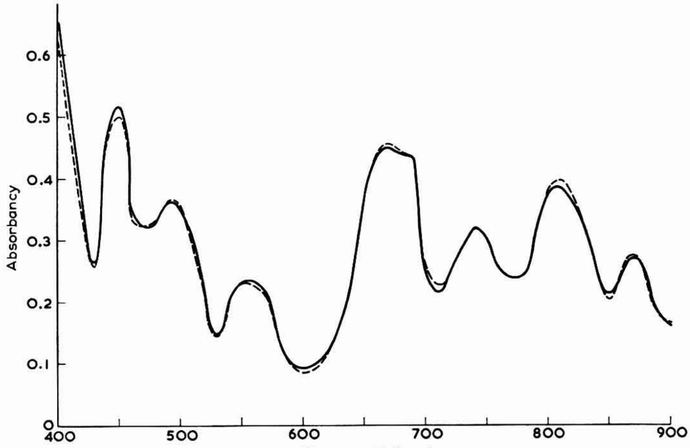

Fig. 6. The stability of plutonium(IV) citrate complex with time: ——, immediately after preparation; - - -, after 100 h.

The tetravalent state is the most stable valency state for plutonium, but it may disproportionate into the trivalent and hexavalent states. To investigate the magnitude of this effect under the existing conditions, a suitable solution was prepared by dissolving a piece of metal (101.8 mg) in 10 ml of 10% v/v H_2SO_4, and oxidizing the plutonium to the tetravalent state by controlled-potential electrolysis with a platinum electrode maintained at +0.64 V *vs.* S.C.E. The oxidation was followed by observing the decay of the electrolysis current and stopping the electrolysis when it reached a value of a few microamperes. A 1-ml aliquot of this solution was transferred to a small beaker containing 6 ml of the citrate supporting electrolyte. After adjustment of the pH to 4.5, the solution was diluted to 10 ml with water and the absorption spectrum was recorded without delay (see Fig. 6). No changes were observed in this absorption spectrum with time and no significant decrease in the height of the tetravalent plutonium peak at 680 mμ was detected over a period of 100 h. Hexavalent plutonium gives a single sharp peak at 840 mμ in citrate solutions of pH 4.5 (see Fig. 7), but there was no evidence for the existence of this peak in the tetravalent plutonium spectrum after 100 h and it could be calculated that any plutonium in the hexavalent state would be less than 3% of the total plutonium present.

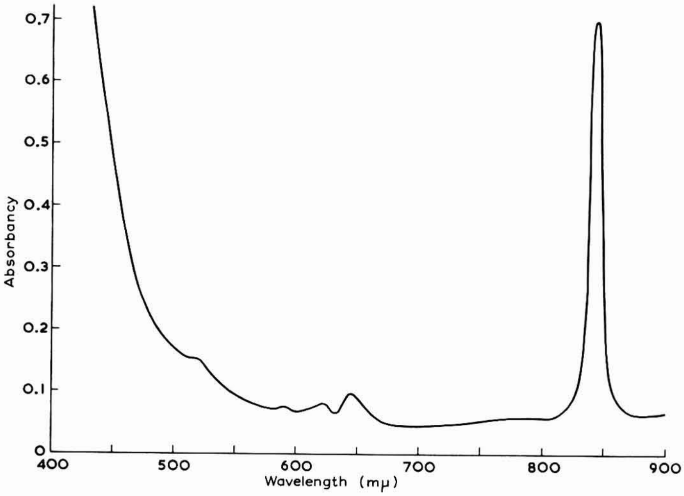

Fig. 7. Absorption spectrum of plutonium(VI) citrate complex.

The absence of disproportionation is due to the strong complexing of tetravalent plutonium in citrate solutions, since this behaviour is in general agreement with findings reported by KATZ AND SEABORG[6] for sulphate solutions. They report that the disproportionation of tetravalent plutonium is greatly decreased in sulphate solutions due to the formation of strong sulphate complexes. However, since citrate ions produce a greater effect than sulphate on the shift of the formal potential of the Pu^{4+}/Pu^{3+} couple, the absence of disproportionation in citrate solutions is consistent with the very stable complex formed by citrate with tetravalent plutonium.

The variation in height of the polarographic peak with time for a solution containing 40 μg/ml of plutonium in the trivalent state initially, was studied. It remained constant to within ±1.5% (1σ) over a period of 30 h. This constancy can only be due to the identical slopes of the peak height–concentration graphs for trivalent and tetravalent plutonium, since after 30 h the plutonium is mainly in the tetravalent state. For analytical applications the trivalent peak is less satisfactory than the tetravalent plutonium peak because of the greater effect on peak height of any error in adjusting the pH and because of the instability of the trivalent plutonium–citrate complex with time.

Applications of the plutonium peak in analysis

When using the plutonium peak for the analysis of samples, some preliminary separation of the plutonium is essential in many cases because of the serious interference from iron and the close proximity of the peaks of some other elements (see Table 2). A fairly specific anion-exchange procedure is available for the separation of tetravalent plutonium as $Pu(NO_3)_6^{2-}$ ions from 8 M nitric acid solutions, and this has been employed successfully for many years in this laboratory for the separation of macro amounts of plutonium using the anion-exchange resin, Deacidite FF. FUDGE, WOOD AND BANHAM[7] modified this procedure for the separation of small amounts (1–10 mg) of plutonium from uranium and fission products, prior to the determination of plutonium by potentiometric titration. This approach appeared to be suitable for further modification for the determination of plutonium by polarography. Reduction in the size of the anion-exchange column was desirable in view of the need to separate microgram amounts (20–1000 μg) of plutonium, without seriously contaminating the final solution with organic matter from the resin. There is evidence that breakdown products from ion-exchange resins cause poorly-defined peaks to be obtained for inorganic ions by square-wave polarography[8].

It is necessary to condition plutonium to the tetravalent state before proceeding with the ion-exchange separation. This involves the reduction of plutonium of all valencies to the trivalent state, before the addition of nitric acid containing nitrite to oxidize plutonium to the tetravalent state. The reductant used depends upon the mineral acids chosen for the dissolution of the sample. Hydroxylamine hydrochloride is used for samples dissolved in hydrochloric acid, and also for those dissolved in nitric acid provided that the solutions are first evaporated to low bulk followed by dilution with molar hydrochloric acid. Magnesium metal is suitable for the reduction of plutonium in sulphuric acid solutions. Details of the hydroxylamine hydrochloride method are as follows: transfer the sample in 2 ml of M HCl to a 10-ml stoppered tube, and add 10–20 mg of hydroxylamine hydrochloride. Allow the solution to stand overnight to ensure complete reduction of plutonium. If this is inconvenient, speed up the reduction process by warming the solution gently and maintaining just below boiling for 30 min. Add 2 ml HNO_3 (sp.gr. 1.42), and stand overnight or warm gently for 30 min to ensure quantitative oxidation of plutonium to the tetravalent state*. Transfer to a suitable column of Deacidite FF with the aid of 8 M HNO_3.

The reduction of plutonium in sulphuric acid by magnesium is carried out as follows: evaporate the sample solution to fumes of sulphuric acid and continue heating to remove excess of this acid. After dissolution of the salts in 1 ml of 1.8 M H_2SO_4, carry out the reduction of plutonium with 30 mg of Specpure magnesium and then oxidise to the tetravalent state with nitric acid containing sodium nitrite, as described previously. Transfer the tetravalent plutonium solution to a suitable column of

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* HNO_3 (sp.gr. 1.42) usually contains sufficient nitrite for the oxidation of plutonium to the tetravalent state. The addition of more nitrite in the form of sodium nitrite solution, may result in a vigorous reaction taking place with the hydroxylamine hydrochloride in solution.

Deacidite FF with the aid of 8 *M* HNO_3 and carry out the separation.

Experiments were carried out to establish the optimum size of ion-exchange column necessary to retain the amount of plutonium needed for determination by polarography. Small columns of Deacidite FF (150–200 mesh) of height 3 cm and volume 0.5 ml were found to be suitable for the retention of several hundred microgram amounts of plutonium from 8 *M* HNO_3 solutions, and under the best conditions they could retain a maximum of about 4 mg of plutonium. For this size of column, 25 ml of 8 *M* HNO_3 was satisfactory for the removal from plutonium of those elements with low K_D values for Deacidite FF.

The usual procedure for recovering plutonium from resin columns uses hydroxylamine hydrochloride, which reduces plutonium to the trivalent state and thereby destroys the anionic complex. This reagent was found to be unsuitable in this instance because of the presence of impurities which produced interfering polarographic peaks,

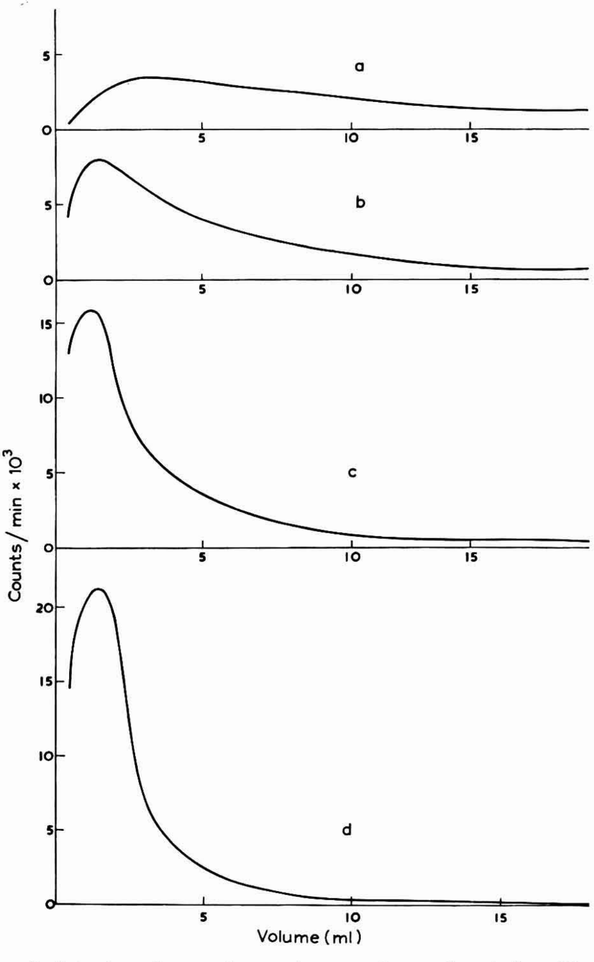

Fig. 8. The elution of plutonium from anion-exchange columns by nitric acid solutions. a, 1.5 *M* HNO_3; b, 1.0 *M* HNO_3; c, 0.5 *M* HNO_3; d, 0.3 *M* HNO_3.

and alternative reagents such as dilute mineral acid solutions were investigated. In these experiments, 100 μg amounts of plutonium were transferred to columns and then washed with 25-ml aliquots of 8 M HNO_3. Solutions of HNO_3, HCl, H_2SO_4 and $HClO_4$ of various strengths were examined for the recovery of plutonium. The efficiency for each set of conditions was determined by collecting the column eluant in 1-ml fractions using a flow rate of 6 drops per min, and determining the plutonium content of each fraction by alpha counting. By plotting counts per min for each fraction, against the volume of solution passing through the column, an indication of the efficiency of each particular solution for plutonium recovery could be obtained.

Graphs obtained for nitric acid in the range 1.5–0.3 M are shown in Fig. 8. From these it is clear that 1.0 and 1.5 M HNO_3 solutions are unsuitable, and although there is some improvement with 0.5 and 0.3 M solutions, appreciable volumes would be needed to obtain a full recovery of plutonium. The use of perchloric acid did not produce any marked improvements, as shown by Fig. 9. Considerable tailing of

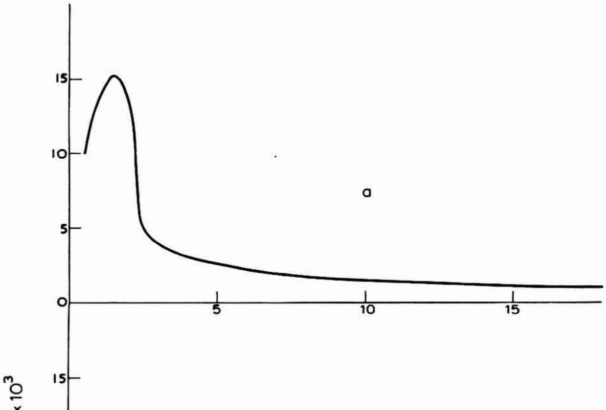

Fig. 9. The elution of plutonium from anion-exchange columns by perchloric acid solutions. a, 1.5 M $HClO_4$; b, 1.0 M $HClO_4$; c, 0.5 M $HClO_4$.

plutonium occurred with 1.5 *M* $HClO_4$ solutions, and although this effect decreased with a reduction in the molarity of the perchloric acid, the behaviour of this acid was so poor compared with hydroxylamine hydrochloride that it could not be recommend-

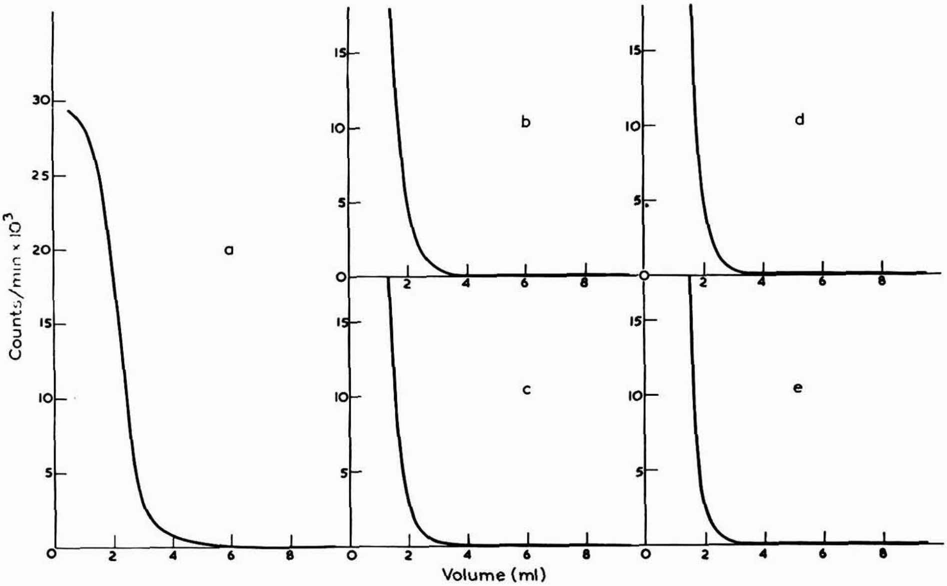

Fig. 10. The elution of plutonium from anion-exchange columns by hydrochloric acid solutions. a, 0.5 *M* HCl; b, 1.0 *M* HCl; c, 1.5 *M* HCl; d, 2.0 *M* HCl; e, 2.5 *M* HCl.

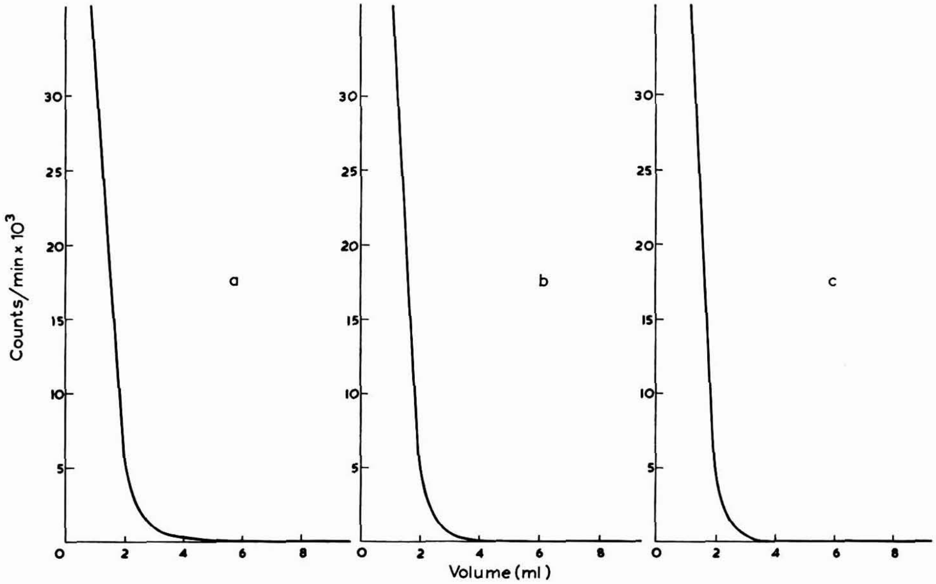

Fig. 11. The elution of plutonium from anion-exchange columns by sulphuric acid solutions. a, 0.5 *M* H_2SO_4; b, 1.5 *M* H_2SO_4; c, 2.5 *M* H_2SO_4.

ed. A marked improvement was achieved, however, by employing dilute solutions of hydrochloric acid (see Fig. 10). Very little tailing occurred, and examination of 1-ml fractions revealed that less than 0.01% of the total activity was present in the tenth fraction using 1.0, 1.5, 2.0 and 2.5 *M* HCl solutions. The efficiency was only slightly less for 0.5 *M* HCl solutions, but for general application, solutions in the range 1–2 *M* HCl were chosen for the complete recovery of plutonium using a total volume of 10 ml. The elution of plutonium with H_2SO_4 (0.5–2.5 *M*) was efficient and very similar to that with hydrochloric acid, as shown by the graphs in Fig. 11.

The definition of the polarograms for plutonium recovered from ion-exchange columns was found to be poor due to the presence of organic matter picked up from the ion-exchange resin. Attempts to remove this organic matter by passing the solutions through columns of either alumina or activated charcoal were unsuccessful. The only satisfactory method involved the destruction of the organic matter by wet oxidation with a nitric–sulphuric acid mixture, and for this reason the use of sulphuric acid for the recovery of plutonium from ion-exchange columns was preferred. The full procedure has been applied to the analysis of synthetic uranium alloys containing 0.25–1.0% of plutonium, and the satisfactory results obtained are given in Table 4. For each sample, examination of the 25-ml 8 *M* HNO_3 wash solution for plutonium content, by α particle counting showed that less than 0.03% of the total plutonium was lost in this part of the procedure.

TABLE 4

RESULTS FOR THE ANALYSIS OF SYNTHETIC URANIUM–PLUTONIUM ALLOYS

Composition of sample		*Pu content* (%)	*Pu by analysis* (%)	*Deviation* (%)
Uranium (mg)	*Plutonium (µg)*			
—	160	100	99.6	−0.4
—	160	100	100.6	+0.6
15.8	160	1.002	0.985	−1.7
16.1	160	0.984	0.99	+0.6
64.2	160	0.248	0.245	−1.2
64.5	160	0.247	0.245	−0.8

ACKNOWLEDGEMENTS

The assistance of Mr. G. PHILLIPS in the spectrophotometry studies and in the preparation of tetravalent plutonium by controlled-potential coulometry, and also the helpful advice of Dr. H. W. NURNBERG are gratefully acknowledged.

SUMMARY

A method is described for the determination of plutonium in the range $4 \cdot 10^{-6}$ to $4 \cdot 10^{-4}$ *M* by a.c. polarography. It is based on a peak at −0.42 V *vs.* a mercury pool anode from a citrate supporting electrolyte (pH 4.5). This peak is produced by plutonium in either the trivalent or the tetravalent state, due to the reversibility of the Pu^{4+}/Pu^{3+} couple. Spectrophotometry has shown that the tetravalent plutonium–citrate complex is more stable than the trivalent complex, which oxidizes to the tetravalent state.

The peak for tetravalent plutonium is preferred for analytical work, but unfortunately interference can be caused by some elements, especially iron. An ion-exchange procedure has been developed for the separation of plutonium from interfering elements. This method has been applied to the determination of the plutonium contents of uranium–plutonium alloys containing 0.25–1.0% of plutonium.

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A NEW AND SIMPLE APPROACH TO SQUARE-WAVE POLAROGRAPHY

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(Received December 9th, 1963)

Polarography has shown itself to be a useful tool for performing electrochemical analyses, but the direct-current method has shortcomings when applied to the analysis of low concentrations (*i.e.*, $2 \cdot 10^{-5}\,M$ Pb^{2+}). This is due to the charging current of the capacitive double-layer of the mercury drop. In 1952, BARKER AND JENKINS[1] offered a solution to the problem with the introduction of square-wave polarography. The instrumentation which has been used in implementing square-wave polarography has been inconvenient, however, in that it has contained electronic circuitry which is both complex and expensive. R. E. HAMM[2] provided a partial solution to these problems by simplifying and economizing the circuitry.

The desirability of an even simpler and more economical method of instrumenting square-wave polarography led to the development of the instrument to be described.

INSTRUMENT BACKGROUND AND DESIGN

In the method of square-wave polarography, a small square-wave voltage is superimposed on the d.c. voltage of the polarograph and a square-wave cell current flows, the amplitude of which is proportional to the slope of the conventional polarogram at the applied d.c. potential. Peak to peak height of the square-wave cell current is measured to determine the slope, which is proportional to concentration; thus, a derivative-type polarogram is obtained and there is no need to determine the height of the diffusion plateau. Figure 1 illustrates this concept by showing the output *vs.* input at three points on the voltage span. Although the square-wave technique eliminates the effect of capacitive current which interferes in conventional polarography, the capacitance of the electrode causes an unwanted transient current to flow in response to the impressed square-wave voltage. The method used in the past to deal with this problem involves multivibrators and gating circuits. The circuitry is expensive and complex.

A square-wave polarographic instrumentation technique which would eliminate some or all of these problems was desirable. The instrument which was developed is shown schematically in Fig. 2. The new circuitry consists of a full-wave rectifier bridge and a passive integration circuit. The full-wave rectifier bridge used consisted of four type 1N34A semiconductor diodes. The integration circuit was merely a series R–C circuit consisting of a 330,000 Ω resistor and a 1 μF capacitor. Choice of these components is completely arbitrary beyond insuring that the time constant of the integration circuit is long compared to the period of the square wave used. A factor of 20 is sufficient to provide accurate results. The functions of these components are shown in Fig. 3. The input-wave form is the amplified form of the signal obtained

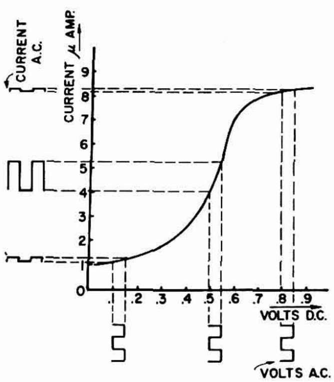


Fig. 1. Illustration of relationship between the impressed square-wave voltage and the square-wave cell current at three separate points along a polarographic wave.

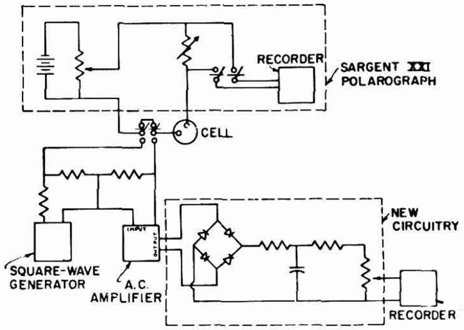
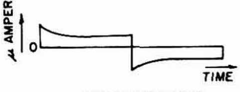
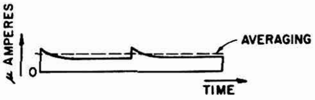


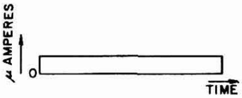
Fig. 2. Schematic diagram of complete square-wave polarograph.



INPUT WAVEFORM



FULL WAVE RECTIFIED WAVEFORM



OUTPUT WAVEFORM

Fig. 3. Illustration of wave form as it is acted upon by the circuit.

from the cell current. The full-wave rectified wave form is the output from the full-wave rectifier bridge. The dotted line indicates the effect of the passive integration circuit which is to obtain the average value of the rectified signal. The output wave form is the signal as it appears across the capacitor in the integration circuit. In actual use, a high resistance voltage divider is attached across the capacitor to reduce the voltage to the millivolt level acceptable to a potentiometer recorder.

One factor that should be noted is the square-wave frequency. For the work reported here, it was found that 80 c/sec was the optimum operating frequency. This is in contrast with 230 c/sec which is commonly used for the conventional square-wave method. It is definitely desirable to reduce the frequency with the new circuitry, since the lower the frequency, the farther apart the transients, and the farther apart the transients, the closer the average value is to the *true* faradic current value. The limiting factor here is the attenuation present in an a.c. amplifier at the very low frequencies.

EXPERIMENTAL RESULTS

Cell and electrode system

A standard H-type electrolysis cell was used. The electrode system consisted of a dropping mercury electrode and a saturated calomel reference electrode. The height of mercury level in the reservoir was 38.3 cm which gave a drop time of 3.85 ± 0.15 sec and a delivery rate of 1.78 ± 0.02 mg of mercury per sec at zero applied potential. The tolerances are observed day to day variations. The same electrode system was used for all experiments.

Solutions

Stock solutions were made from hydrated acetate salts (reagent grade) of the respective metal ions. The inorganic solutions were aqueous with 1 *M* potassium chloride as the supporting electrolyte and oxygen was removed by purging with nitrogen.

Results

Figures 4 and 5 show the results obtained with square-wave polarography, of known solutions of Cd^{2+} and Pb^{2+} ions, respectively. These curves are the results of

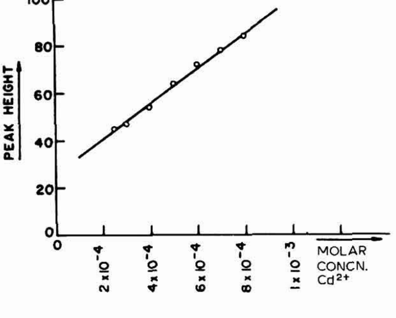


Fig. 4. Calibration curve: Peak height *vs.* molar concentration of Cd^{2+} ion.

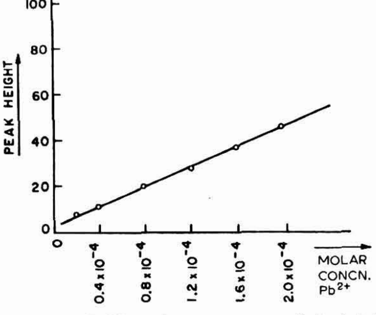


Fig. 5. Calibration curve: peak height *vs.* molar concentration of Pb^{2+} ion.

two specific experiments and in no way indicate limitations for the instrument. The important result verified was that the peak height obtained with this instrument was linear with concentration. Figure 6 is a sample square-wave polarogram demonstrating the type of curves obtained from the instrument. A fast pen-response recorder was used and therefore the envelope of the curves can be taken as representative without being affected by the periodic dropping of the electrode. The sample square-wave polarogram shows the distinct separation between Cd^{2+} and Pb^{2+} in a mixture. This sample, again, expresses no limitation on the instrument but rather indicates the type of information it delivers. In one experiment the instrument showed a distinct separation for a mixture of two species whose half-wave potentials differed by only 80 mV. Separations at even closer half-wave potentials are indicated but have not yet been proved experimentally.

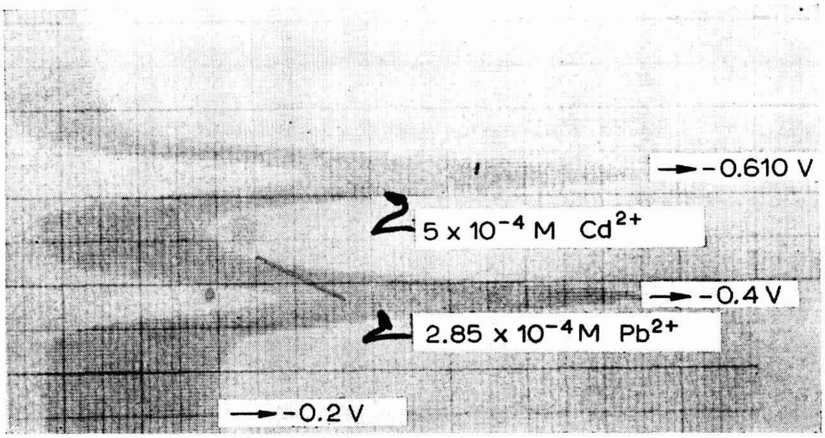


Fig. 6. Sample square-wave polarogram; two-component run.

Several experiments were run on organic compounds and the results were found to be comparable to those discussed above for metal ions. One additional parameter became involved, however; it was found, that for organic compounds, proper selection of the base electrolyte was a major factor in determining the peak heights. For the organic compounds tested, the best base electrolyte was found to be 1 M CH_3COOK.

CONCLUSIONS

An instrument has been developed which eliminates some of the inconveniences associated with the method of square-wave polarography. The unit is very inexpensive when compared with the cost of constructing a conventional gating-type circuit or when compared with the prices of the commercially available square-wave polarographs. Another feature of the instrument is that it is extremely simple to construct. Advantages of the circuit are that it requires no high voltage power supplies and that there are no tubes or transistors in the signal processing circuit that can deteriorate or change with age. In this sense the instrument is highly reliable since constant characteristics over a long period of time are assured. One additional advantage of the device is its compactness.

The instrument is inexpensive and simple, allowing schools and smaller laboratories to expand their conventional polarographic facilities for square wave-polarography without a major expenditure of time or money.

This circuit is not quite as sensitive as devices employing gating circuitry. It does, however, approach the more sensitive instruments in both low concentration analysis and resolution of mixtures and is thus a useful tool.

ACKNOWLEDGEMENT

The author would like to acknowledge the valuable work done by R. D. BANKERT, presently at the University of Illinois, in carrying out the chemical experimentation and helping the author to see square-wave polarography through the eyes of a chemist.

SUMMARY

A new method has been developed for instrumenting square-wave polarography. It is simpler, more reliable, and much less expensive than equipment used in the past. This paper describes the design, construction and performance of the instrument.

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THE POLAROGRAPHIC ESTIMATION OF THORIUM USING SOLOCHROME VIOLET R.S. IN ALKALINE MEDIA

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Since the standard electrode reduction potential of thorium ion to the metal[1] is −1.90 V, the polarographic reduction wave would be masked by the larger reduction wave of hydrogen preceding it. In alkaline solution the reduction potential of the reaction[2]

$$\mathrm{Th(OH)_4} + 4\,e \rightarrow \mathrm{Th} + 4\,\mathrm{OH^-}$$

is −2.48 V which makes the direct polarographic estimation of thorium by its reduction wave virtually impossible.

However, KRAULEDAT[3] states that thorium determination is possible, using potassium chloride as supporting electrolyte or potassium nitrate as a complexing electrolyte, the diffusion current obtained being proportional to the thorium concentration only at low thorium concentrations.

GRAHAM AND LARRABEE[4] describe the precipitation of thorium with organic reagents and the subsequent liberation and polarography of the organic reagent. FLASCHKA, KHALAFALLA AND SADEK[5] suggest the displacement of the equivalent of lead from its E.D.T.A. complex and its polarographic estimation. PATZAK AND ZAKI[6] have investigated the reduction of thorium (0–3 mM) in solochrome violet R.S. in an acid nitrate solution of pH 2.5–2.6 using an acetate buffer solution. They show that the thorium reduction wave-height is pH dependent and conclude that there is a straight line relationship between thorium concentration and diffusion current even though four out of the five points shown for the determination at pH 3.0 could equally well fit a curve; for the determination at pH 3.7 only three points are given.

EXPERIMENTAL DETAILS

Materials, solutions, and apparatus

All chemicals were supplied by British Drug Houses Limited, and were of 'AnalaR' quality; nitrogen, supplied by the British Oxygen Company Limited, was the commercial grade and was bubbled through alkaline pyrogallol before it was used for deoxygenating the test solution. The solutions were prepared by weighing the solid materials, dissolving and making up to the appropriate volume for the concentrations required. The solutions were 25 mM thorium nitrate, 0.25 M sodium potassium tartrate, 1% methyl cellulose and 1.366 mM solochrome violet R.S.

A Cambridge Pen-Recording Polarograph at a sensitivity of 1/20 and damping 5, together with a water bath controlled to 25° ± 0.1° and incorporating four cells, was used. The pH-meter used was a Model-30 manufactured by Electronic Instruments Limited and calibrated at pH 4 and pH 9 according to the makers instructions.

Experimental procedure

5 ml of sodium potassium tartrate solution was placed in a small beaker with 10 ml of solochrome violet R.S. solution followed by the requisite volume of thorium nitrate solution and 0.05 ml of methyl cellulose. At this stage the pH was adjusted to that required (12.0) by adding sodium hydroxide. The solution was then carefully transferred to a 25-ml flask and made up to the mark. An aliquot was transferred to the polarographic cell within the water bath, deoxygenated for at least 15 min and polarographed from -0.2 to -1.4 V *vs.* the mercury pool.

This procedure was repeated using different quantities of thorium nitrate solution.

EXPERIMENTAL RESULTS

The reduction wave of solochrome violet R.S. is well defined at about -0.6 V *vs.* the mercury pool, the exact position of the $E_{\frac{1}{2}}$ being pH-dependent. On the addition of thorium ions the height of the dye reduction wave is decreased, the decrease being dependent on the concentration of thorium, while a second wave, the height of which is proportional to the thorium concentration, appears at a point about 0.5 V more negative than the dye reduction wave (Fig. 1). The height of these waves is pH-dependent and in acid solution was also found to be dependent on the time elapsing between preparation of the solution and the polarographic measurements. In alkaline solution the wave heights are not time-dependent.

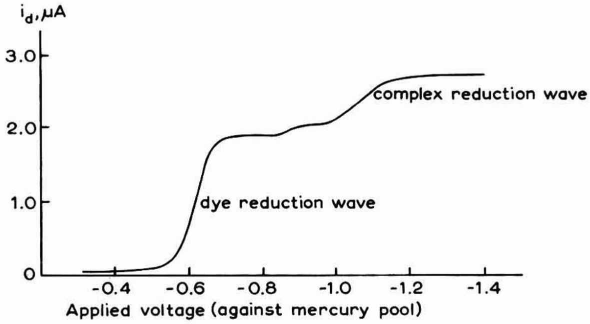


Fig. 1. Polarogram of 0.2 m*M* Th^{4+} in 0.1 *M* sodium potassium tartrate with 0.5464 m*M* solochrome violet and 0.002% methyl cellulose at pH 12.0.

Figures 2 and 3 show the effect of thorium ion concentration on the diffusion current for the dye and dye–thorium complex waves respectively. At pH 12.0 the average diffusion current constant

$$I = \frac{i_d}{C_{\mathrm{Th}^{4+}}\, m^{2/3} t^{1/6}}$$

for the second wave is 2.098 ± 0.17 over the thorium range 0–0.6 m*M*.

The dye wave can be shown to be irreversible since the anodic–cathodic wave ratio is 0.325 : 1, and as a curve is obtained for the graph of diffusion current *vs.* the square root of head of mercury, the reaction is not diffusion-controlled. On the other hand,

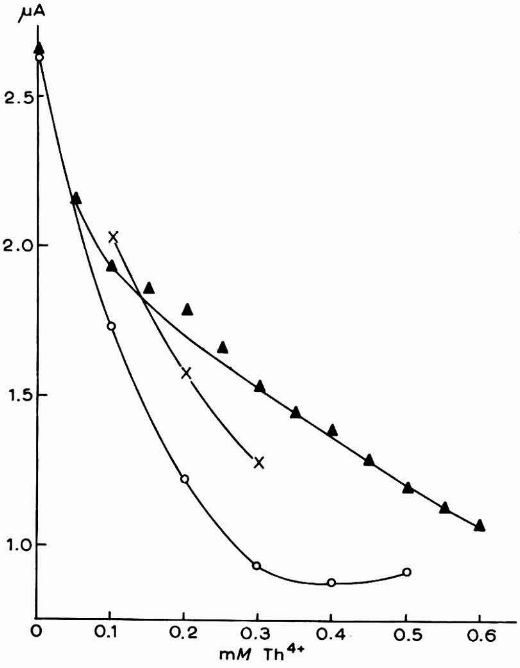


Fig. 2. Diffusion current for dye wave *vs.* thorium concn. at various pH values: ▲, pH 12.0, $E_{\frac{1}{2}} = -0.622$ V, $m^{2/3}t^{1/6} = 3.744$; ×, pH 11.5, $E_{\frac{1}{2}} = -0.623$ V, $m^{2/3}t^{1/6} = 3.744$; ○, pH 11.0, $E_{\frac{1}{2}} = -0.597$ V, $m^{2/3}t^{1/6} = 3.719$. $E_{\frac{1}{2}}$ with respect to the mercury pool.

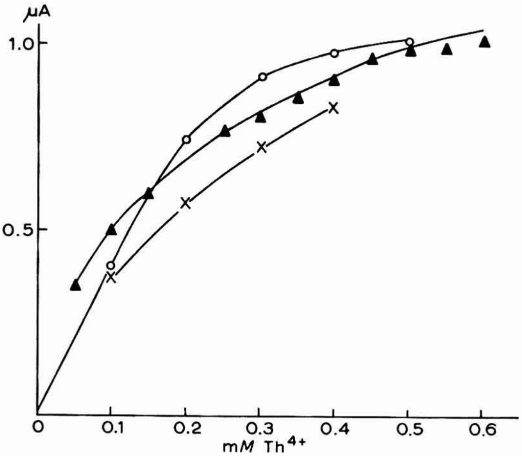


Fig. 3. Diffusion current for the dye–thorium complex wave *vs.* thorium concn. at various pH values: ▲, pH 12.0, $E_{\frac{1}{2}} = -1.067$ V, $m^{2/3}t^{1/6} = 3.879$; ×, pH 11.5, $E_{\frac{1}{2}} = -1.100$ V, $m^{2/3}t^{1/6} = 3.879$; ○, pH 11.0, $E_{\frac{1}{2}} = -1.120$ V, $m^{2/3}t^{1/6} = 3.879$. $E_{\frac{1}{2}}$ with respect to the mercury pool.

the dye–thorium complex wave is shown to be reversible and diffusion-controlled since the anodic–cathodic wave ratio is 1.14 : 1 and diffusion current plotted against the square root of head of mercury gives a straight line, Determinations of the number of electrons transferred per molecule reduced, were made for both dye and complex at pH 12.0, and diffusion coefficients were calculated from the values obtained. The two methods used were:

(a) calculation of n from the slope of log $i/(i_d - i)$ drawn against applied voltage after cell resistance correction; this method is only reliable for the reversible, diffusion-controlled dye–thorium complex wave.

(b) the coulometric method described by REYNOLDS AND SHALGOSKY[7] using also an alternative calculation by the method of GILBERT AND RIDEAL[8]; this was done for both waves.

The values of n found by these two methods are given in Table 1.

TABLE 1

Method	*Dye wave*
log $i/(i_d - i)$ *vs.* voltage	1.01
REYNOLDS AND SHALGOSKY	1.14
GILBERT AND RIDEAL	1.03

The result of electrolysing a solution containing 0.2 mM Th^{4+} in 0.546 mM solochrome violet R.S. at a pH of 12.0 gives a constant diffusion current over a period of 80 min, and no calculations with regard to n may be made from the coulometric method.

It would thus appear, that the dye–thorium complex concentration is constant and that this could only happen if the complex were reduced at the dropping electrode in such a way that the thorium was returned to solution and complexed with uncombined dye. From the diffusion current curves obtained, it seems that there is an equilibrium between thorium, the dye and the complex.

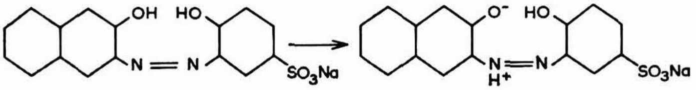
$$Th^{4+} + x(\text{dye})^- \rightleftharpoons [Th(\text{dye})x]^{(4-x)+} \qquad (1)$$

However, the equation

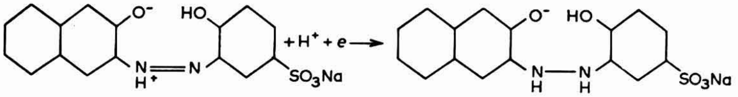
$$\frac{\Delta E_{\frac{1}{2}}}{\Delta \log C} = -\frac{p}{n}0.0591 \qquad (2)$$

gives $p/n = 1.14$. These results can be explained as follows.

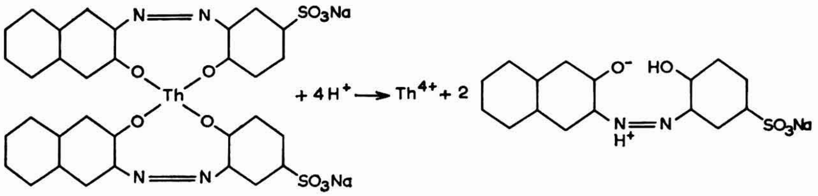
In alkaline solution with a relatively high concentration of sodium and potassium ions the dye molecule has a stabilized labile hydrogen atom, so that only one electron is required for reduction, *viz.*,



then



Since thorium is four-valent the complex is probably



i.e., $p = 2$

When the complex is reduced, thorium(IV) is released to combine with more uncomplexed dye, while the two dye molecules require 1 electron each for reduction, *i.e.*, $n = 2$.

If $b \times 10^{-3}\ M$ is the complex concentration, $(a - b) \times 10^{-3}\ M$ is the concentration of the uncomplexed thorium ion where a is the initial concentration of the thorium ion and $(0.546 - bx) \times 10^{-3}\ M$ is the concentration of the uncomplexed dye. Then from eqn. (1)

$$K_c = \frac{[\mathrm{Th(dye)}x]}{[\mathrm{dye}]^x\,[\mathrm{Th}^{4+}]} \tag{3}$$

which reduces to

$$K_c = \log b - \log(a - b) - x \log (0.546 - bx) + 3\,x \tag{4}$$

Table 2 gives the value of log K_c calculated according to eqn. (4) and from the height ~~of the first wave, assuming that there are two molecules of dye complexing with one~~ thorium ion.

TABLE 2

Th^{4+} (mM) (a)	Uncombined dye (mM) (0.546 − 2b)	$x = 2$			
		Combined dye (mM) (2b)	Complex (mM) (b)	Uncombined Th^{4+} (mM) (a − b)	log K_c
0.05	0.444	0.102	0.051		
0.10	0.402	0.144	0.072	0.028	7.28
0.15	0.382	0.164	0.082	0.068	6.91
0.20	0.360	0.186	0.093	0.107	6.83
0.25	0.341	0.205	0.103	0.147	6.78
0.30	0.316	0.230	0.115	0.185	6.79
0.35	0.299	0.247	0.124	0.227	6.78
0.40	0.283	0.263	0.132	0.268	6.79
0.45	0.264	0.282	0.141	0.304	6.81
0.50	0.248	0.298	0.149	0.351	6.84
0.55	0.236	0.311	0.155	0.395	6.85
~~0.60~~	~~0.219~~	~~0.327~~	~~0.163~~	0.437	6.89

INTERFERING IONS

A large number of ions interfere with the use of solochrome violet R.S. in polarographic work, a comprehensive survey having been given by PERKINS AND REYNOLDS[9]. Beryllium, boron, calcium, magnesium, zinc, manganese and uranium in large concentration have no effect on the dye reduction step, but antimony, lead, cobalt, titanium, vanadium, zirconium, iron, and nickel effect the reduction step. Copper and tin precipitate the dye; fluorides, citrates and oxalates reduce the wave height in proportion to their concentrations.

The coefficient of diffusion of the dye calculated from the value of n found using the wave observed in the absence of thorium (*i.e.*, 0.546 mM solochrome violet R.S.) and the Ilkovič equation,

$$i_d = 607\, n\, C D^{1/2} m^{2/3} t^{1/6}$$

is

$$4.60 \times 10^{-6}\ \text{cm}^2/\text{sec}$$

This is in reasonable agreement with the value, 4.80×10^{-6} cm²/sec at pH 4.6, found by PERKINS AND REYNOLDS[10].

CONCLUSIONS

Small quantities of thorium in solution may be estimated by using solochrome violet R.S. in potassium sodium tartrate supporting electrolyte at pH 12.0 with methyl cellulose as maximum suppressor. The thorium concentration is found by comparing either the dye reduction wave height or the complex reduction wave height against a previously calibrated graph. Limitations of this method are:

(a) The dye concentration should be in excess of the thorium concentration so that the readings do not come on the more horizontal part of curve (Figs. 2 and 3). Since the dye solubility is limited (about 1.4 mM) this limits the thorium concentration in the polarographic solutions to about 0.6 mM.

(b) Ions which precipitate the dye, such as sulphate, chloride, copper and tin and those which complex with the dye must be absent[9]. However, most interfering metals may be removed before polarographing, by controlled-potential electrolysis.

SUMMARY

An estimation of thorium in dilute solutions (0–0.6 mM) is described. A solution of 0.546 mM solochrome violet R.S. (the sodium salt of 5-sulfo-2-hydroxy-α-benzene-azo-2-naphthol) is used in 0.1 M sodium potassium tartrate solution at pH 12.0 as supporting electrolyte, and methyl cellulose (0.002%) as maximum suppressor. The height of the dye reduction wave is inversely proportional to thorium concentration, while that of the dye–thorium complex reduction wave is proportional to thorium concentration. Either wave height may be compared with a previously prepared calibration graph.

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VOLTAMMETRIC EVALUATION OF THE STABILITY OF TRICHLORIDE, TRIBROMIDE, AND TRIIODIDE IONS IN NITROMETHANE, ACETONE, AND ACETONITRILE

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Recent results of electrochemical studies in this laboratory and in the literature[1-5] on the nature and behavior of halide ions in non-aqueous solvents reveal an interesting aspect of the chemistry of the trihalides (trichloride, tribromide, and triiodide) which has not previously been reported. In aprotic solvents, the order of stability of the trihalides is $Cl_3^- > Br_3^- > I_3^-$, the reverse of that in water.

EXPERIMENTAL

The voltammetric equipment and technique[6,7], the purification of nitromethane[6] and of acetone[8], and the preparation of tetraethylammonium perchlorate[9] have been described previously. Tetrabutylammonium iodide (Eastman), tetraethylammonium bromide (Eastman), and tetraethylammonium chloride monohydrate (K and K Laboratories) were used without further purification.

RESULTS

A summary of the voltammetric data obtained from our investigation of the oxidation of chloride, bromide, and iodide ions at the rotating platinum electrode in nitromethane and acetone, and of those reported previously for acetonitrile is presented in Table 1.

DISCUSSION

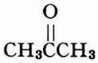
The electro-oxidation of iodide and bromide ions to iodine and bromine, respectively, at the rotating platinum electrode, in nitromethane[5] and in acetone takes place, as in acetonitrile[1,2], in two steps with i_{d_1}/i_{d_2} of *ca.* 2. The first step involves the oxidation of the halide ion to the trihalide ion and is a two-electron step; the second involves oxidation of the trihalide ion to the halogen and is a one-electron step.

$E^{\circ\prime}$ values for the X_3^-, X^- and X_2, X_3^- couples were obtained using the following relationships:

$$E_{\frac{1}{2}(X_3^-,X^-)} = E^{\circ\prime}_{(X_3^-,X^-)} - \frac{0.059}{2} \log \frac{3}{4} C^2_{X^-} \qquad (1)$$

TABLE 1

ELECTROCHEMICAL DATA ON THE OXIDATION OF HALIDES AND THE FORMATION CONSTANTS FOR THE TRIHALIDES IN NITROMETHANE, ACETONE, AND ACETONITRILE

Solvent[a]	*Couple*	$E_{\frac{1}{2}}$ *vs. S.C.E.(V)*	*0.059/n*	$i_d(\mu A)$	$[X^-]\cdot 10^4$	$E^{\circ\prime}$ *vs. S.C.E.(V)*	$K_f(X_3^-)$
CH_3NO_2	I_3^-/I^-	$+0.33$	0.040	4.6 (1)	2.9	$+0.11$	$10^{6.7}$
	I_2/I_3^-	$+0.60$	0.033	2.3 (2)	2.9	$+0.71$	
	I_2/I^-	—				$+0.31$	
	Br_3^-/Br^-	$+0.70$	0.054	22 (1)	8.3	$+0.51$	$10^{7.3}$
	Br_2/Br_3^-	$+1.07$	0.051	12 (2)	8.3	$+1.17$	
	Br_2/Br^-	—				$+0.73$	
	Cl_3^-/Cl^-	$+1.03$	0.067	9.0 (1)	2.4	$+0.81$	
	Cl_2/Cl_3^-	$>+1.9$[d]				$>+2.0$	$>10^{13}$
 $CH_3\overset{\overset{O}{\Vert}}{C}CH_3$	I_3^-/I^-	$+0.28$	0.073	60 (1)	15	$+0.11$	
	I_2/I_3^-	$+0.77$	0.043	30 (2)	15	$+0.86$	$10^{8.3}$
	I_2/I^-	—				$+0.36$	
	Br_3^-/Br^-	$+0.88$	0.086	36 (1)	11	$+0.70$	
	Br_2/Br_3^-	$+1.44$	0.052	19 (2)	11	$+1.54$	$10^{9.3}$
	Br_2/Br^-	—				$+0.98$	
	Cl_3^-/Cl^-	$+0.98$	0.066	19 (1)	3.9	$+0.77$	
	Cl_2/Cl_3^-	$>+1.8$[d]				$>+1.9$	$>10^{12}$
$CH_3C\equiv N$	I_3^-/I^-[b]	$+0.25$[c]	—	—	7.8	$+0.06$	
	I_2/I_3^-[b]	$+0.55$[c]	—	—	7.8	$+0.65$	$10^{6.6}$
	I_2/I^-	—				$+0.26$	
	Br_3^-/Br^-	$+0.7$[e]	—	—	5	$+0.5$	
	Br_2/Br_3^-	$+1.0$[e]	—	—	5	$+1.1$	10^7
	Br_2/Br^-	—				$+0.7$	
	Cl_3^-/Cl^-	$+1.1$[e]	—	—	5	$+0.9$	
	Cl_2/Cl_3^-	$+1.7$[e]	—	—	5	$+1.8$	10^{10}
	Cl_2/Cl^-	—				$+1.2$	

[a] 0.1 *M* Et_4NClO_4 supporting electrolyte; [b] 0.1 *M* $NaClO_4$; [c] $E_{\frac{1}{2}}$ value from ref. 3; [d] background wave; [e] value from ref. 1.

$$E_{\frac{1}{2}(X_2,X_3^-)} = E^{\circ\prime}_{(X_2,X_3^-)} + \frac{0.059}{2}\log\frac{9}{16}C_{X^-} \tag{2}$$

Equations (1) and (2) were derived by first substituting into eqns. (3) and (4),

$$E = E^{\circ}_{(X_3^-,X^-)} - \frac{0.059}{2}\log\frac{\left(a^{\circ}_{X^-}\right)^3}{a^{\circ}_{X_3^-}} \tag{3}$$

$$E = E^{\circ}_{(X_2,X_3^-)} - \frac{0.059}{2}\log\frac{\left(a^{\circ}_{X_3^-}\right)^2}{\left(a^{\circ}_{X_2}\right)^3} \tag{4}$$

(which give the potential at any point on the two polarographic waves) $f_{X^-}C^{\circ}_{X^-}$ for

$a_{X^-}^\circ$, $f_{X_3^-}C_{X_3^-}^\circ$ for $a_{X_3^-}^\circ$, and $f_{X_2}C_{X_2}^\circ$ for $a_{X_2}^\circ$ (superscript o denotes activity or concentration at the electrode surface). This was followed by (i) replacement of $C_{X^-}^\circ$ by $(i_d-i)/k_{X^-}$, and $C_{X_3^-}^\circ$ or $[C_{X^-}-C_{X^-}^\circ]/3$ by $i/3k_{X_3^-}$ in eqn. (1); (ii) replacement of $C_{X_2}^\circ$ or $[3(C_{X_3^-}-C_{X_3^-}^\circ)]/2$ by $i/2k_{X_2}$ and $C_{X_3^-}^\circ$ by $(i_d-i)/3k_{X_3^-}$ in eqn. (2), and finally (iii) replacement of i_d by $k_{X^-}C_{X^-}$. The following check shows eqns. (1) and (2) to be stoichiometrically correct. At the half-wave potential for the oxidation of halide to trihalide, $[X^-] = {}^1/_2\, C_{X^-}$ and $[X_3^-] = {}^1/_3 \cdot {}^1/_2\, C_{X^-}$. Therefore $[X^-]^3/[X_3^-]$, equals $3/4\, C_X{}^2$. At the half-wave potential for the oxidation of trihalide to halogen, $[X_3^-] = {}^1/_2 \cdot {}^1/_3\, C_{X^-}$ and $[X_2] = {}^3/_2 \cdot {}^1/_3 \cdot {}^1/_2\, C_{X^-}$. $[X_2]^3/[X_3^-]^2$ is then equal to $9/16\, C_{X^-}$. The $E^{\circ\prime}$ values contain the activity coefficients f_{X^-} and $f_{X_3^-}$ or f_{X_2} and $f_{X_3^-}$, and the appropriate proportionality constants relating polarographic current to the concentrations of X^-, X_3^- and X_2 at the electrode surface.

The theoretical $0.059/n$ value for both the X_3^-/X^- and X_2/X_3^- couples is 0.030. The larger-than-predicted values obtained in nearly all cases for $0.059/n$ for the X_3^-/X^- and X_2/X_3^- couples in the different solvents, therefore, suggest that the electrode reactions are "irreversible". POPOV AND GESKE[2] also obtained slopes greater than the predicted values in the logarithmic analysis of the I_3^-/I^- and I_2/I_3^- waves in acetonitrile, but from the voltammetric data for iodide–triiodide and iodine–triiodide mixtures, concluded that the two electrode reactions are "reversible" and that the deviations from "reversibility" arise from electrode surface effects. It is possible, therefore, to use the equations above to describe the polarographic waves.

The $E^{\circ\prime}$ values of +0.06 V for the I_3^-/I^- couple and +0.65 V for the I_2/I_3^- couple in acetonitrile are in good agreement with the values +0.03 V and +0.69 V reported by POPOV AND GESKE[2].

$E^{\circ\prime}{}_{(X_2,\,X^-)}$ values were evaluated from the voltammetric formal potentials $E^{\circ\prime}{}_{(X_3^-,\,X^-)}$ and $E^{\circ\prime}{}_{(X_2,\,X_3^-)}$ by the standard method[10]. K_f values for the X_3^- species were obtained *via* the $E^{\circ\prime}$ values for the X_3^-,X^- and X_2 X_3^- couples, as follows:

$$\begin{array}{c}
2\,e + X_3^- = 3\,X^-;\ \overset{o\prime}{E}_{(X_3^-,X^-)} \\
2\,X_3^- = 3\,X_2 + 2\,e;\ \overset{o\prime}{E}_{(X_3^-,X_2)} \\
\hline
3\,X_3^- = 3\,X_2 + 3\,X^-;\ \overset{o\prime}{E}_{(X_3^-,X^-)} + \overset{o\prime}{E}_{(X_3,-X_2)}
\end{array}$$

$$(\overset{o\prime}{E}_{(X_3^-,X^-)} + \overset{o\prime}{E}_{(X_3^-,X_2)}) = \frac{0.059}{2}\log\frac{1}{K^3_{f(X_3^-)}}$$

The only $K_{f(X_3^-)}$ values in nitromethane, acetone, or acetonitrile reported in the literature are those for I_3^- in acetonitrile[4,11]. The reported values of $2.5 \cdot 10^7$ and $1 \cdot 10^7$ are in good agreement with the calculated value of $10^{6.6}$.

Because the half-wave potentials of the single waves for the oxidation of chloride ion in nitromethane and acetone are close to that of the first step for the oxidation of chloride ion in acetonitrile, the single voltammetric waves for chloride solutions of these two solvents have been attributed to the oxidation of chloride ion to trichloride ion. The second wave for the oxidation of chloride ion in nitromethane and in acetone must occur at a potential more positive than that at which the background wave appears. Lower limits for $E^{\circ\prime}{}_{(\mathrm{Cl_2},\,\mathrm{Cl_3^-})}$ and $K_{f(\mathrm{Cl_3^-})}$ based on this analysis of the current–~~voltage curves for the oxidation of chloride ion in nitromethane and in acetone have~~ been calculated.

The formation constants of the triiodide, tribromide, and trichloride ions in aqueous medium are $10^{2.9}$, $10^{1.2}$, and $10^{-0.7}$, respectively[12]. Because the acid strength, in the Lewis sense, of the three halogens is chlorine > bromine > iodine and the basic strength of the three halides is chloride > bromide > iodide, the stability constants of the trihalides at first glance appear to be incorrect. Water, however, is a stronger acid than chlorine and a stonger base than chloride ion: therefore, the hydration of ~~both X^- and X_2 increases from the triiodide system to the trichloride system and the~~ stability of the trihalides, accordingly, decreases in the order triiodide > tribromide > trichloride. Unfortunately, as it is too often the case, the above formation constants of the trihalides in water are taken by many as a measure of the general stability of the trihalides, resulting in a false notion that it is difficult to obtain the trichloride ion.

In aprotic solvents appreciably less acidic and less basic than water, such as acetonitrile, nitromethane, and acetone, the solvation energy of the halogens, in the Lewis acid–base sense, and the halides is much less than in water, and the stability of the trihalides is greatly increased. In fact, it is possible for the formation constants of the trihalides to show the expected order, $K_{f(\mathrm{Cl_3^-})} > K_{f(\mathrm{Br_3^-})} > K_{f(\mathrm{I_3^-})}$, as shown in Table 1, *i.e.*, the trichloride ion is more stable than the tribromide ion, and the tribromide ion is more stable than the triiodide ion.

ACKNOWLEDGEMENT

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SUMMARY

The formation constants of trichloride, tribromide, and triiodide ions in acetonitrile and tribromide and triiodide ions in nitromethane and in acetone have been evaluated from electrochemical data. In addition, lower limits for the formation constant of the trichloride ion in acetone and in nitromethane have been calculated. The order of stability of the trihalides in these three aprotic solvents is $\mathrm{Cl_3^-} > \mathrm{Br_3^-} > \mathrm{I_3^-}$, the reverse of that found in water.

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OSCILLOGRAPHIC POLAROGRAPHY OF INORGANIC POLYPHOSPHATES

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Alternating current oscillographic polarography has proved to be a very important and useful analytical tool. Apart from the study and quantitative analysis of depolarizers, it enables one to follow the behaviour of some non-reducible substances, which by virtue of being absorbed in a certain potential field on the dropping mercury electrode cause a change in the capacity of the electrode double-layer. This change manifests itself in a characteristic manner on the oscillopolarographic curve. This phenomenon is exhibited by several types of compounds *e.g.*, amino-acids, alkaloids, hormones, higher fatty acids etc.[1].

The possibilities of the application of oscillopolarographic studies to polymeric substances such as nucleic acids and proteins have already been examined in our Institute[2,3]. The present communication is an extension of this technique to the investigation of the behaviour of polyphosphates which have a unique status among polymeric substances, because they are of both synthetic and biological origin[9].

MATERIALS AND METHODS

Most of the measurements were carried out on an Oscillopolarograph P-576 (Křižík, Praha).

The position and depth of the indentations, see Fig. 1, were estimated quantitatively by measuring the curves photographed with an Exacta Varex camera, Biotar 1:2,

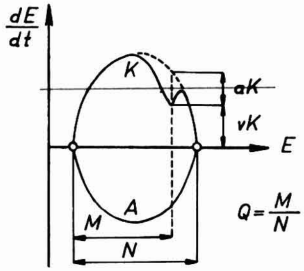

Fig. 1. Schematic illustration of function $dE/dt = f(E)$ and measurement of size and position of indentation.

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on Agfa ISS film, developed with Agfa-Final. Comparative measurements which are used for determining the kind of electrode process according to KALVODA[1], were also carried out on this oscillopolarograph. The registration of first curves and studies on the vibrating electrode were carried out on a universal oscillopolarograph constructed in the electronic laboratory of our Institute[8].

EXPERIMENTAL PROCEDURE AND RESULTS

(a) The electrolytes

It was found that higher polyphosphates (P_6 to P_{230}) produce indentations on the $dE/dt = f(E)$ curves in the following supporting electrolytes: sulphuric acid (Fig. 2), formic acid, acetic acid (Fig. 3), citric acid (Fig. 4), trichloroacetic acid, perchloric acid, ammonium formate of pH 3.8 and sodium acetate of pH 5–7 (1 *M* each). In the sodium acetate medium a turbidity appears. Monophosphates are inactive in all the electrolytes mentioned above. The highest sensitivity for the detection of polyphosphates is attained in organic acid medium. P_{16} produces an indentation even at a

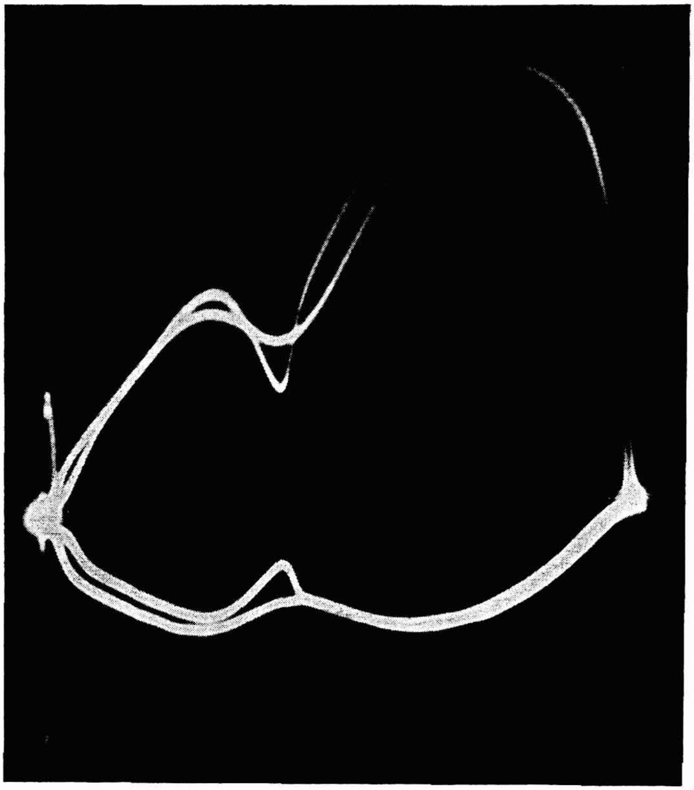

Fig. 2. Comparative measurement: $dE/dt = f(E)$ curves of polyphosphate P_{114}, 3.3mg/ml, and pure electrolyte 1 *N* H_2SO_4; $Q = 0.43$.

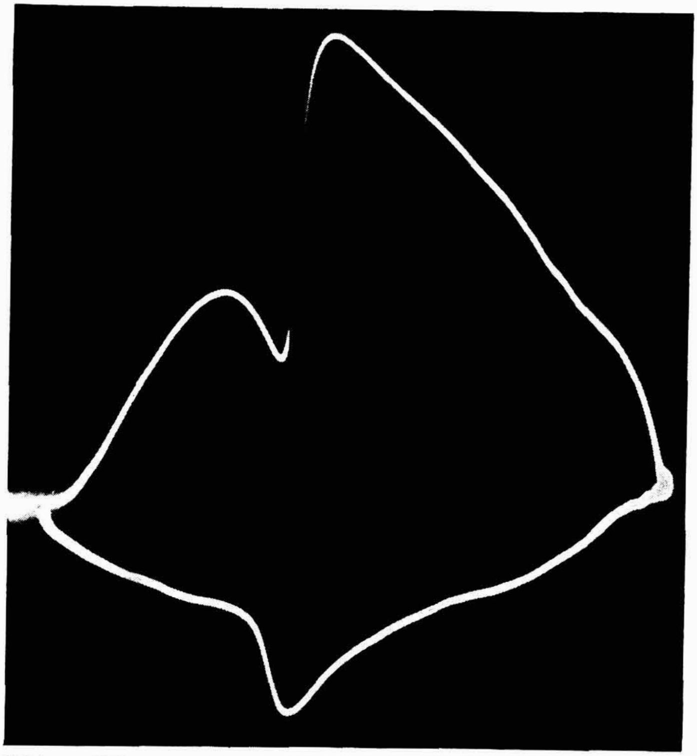

Fig. 3. $dE/dt = f(E)$ curve of P_{25}, 200 μg/ml, in 1 *M* CH_3COOH. Vibrating electrode.

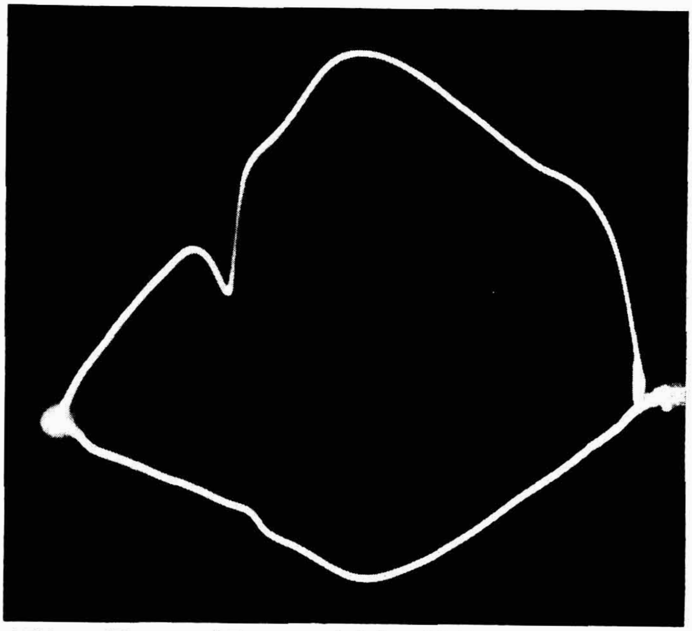

Fig. 4. $dE/dt = f(E)$ curve of P_{25}, 200 μg/ml, in 1 *M* citric acid. Vibrating electrode.

concentration of 15 μg/ml in 1 *M* citric acid medium (Table 1). In neutral and alkaline media (KCl, NH_4OH-NH_4Cl pH 9, KOH) polyphosphates do not give any indentation. The indentation of polyphosphate disappears after the addition of neutral salts (Na_2SO_4, NaCl) to the supporting electrolyte.

TABLE 1

THE SMALLEST QUANTITY OF POLYPHOSPHATES NEEDED FOR THE FORMATION OF AN INDENTATION IN *1 M* CITRIC ACID MEDIUM

Substance (see Table 2)	*Sensitivity (μg/ml)*
P_6	100
P_{12}	50
P_{16}	15
P_{25}–P_{230}	10

(*b*) *Elimination of the possibility of cations or impurities influencing the formation of the indentation*

These experiments were performed to examine whether the indentations were produced by polyphosphates *per se* and not by (i) any contaminants or (ii) Na^+ ions (arising from the Na salts in which form the polyphosphates were used).

(i) The various polyphosphates were subjected to hydrolysis in 1 *N* sulphuric acid at about 100° for 10 min. After this hydrolysis the indentation disappeared altogether. From this experiment we can conclude that the indentation is due to polyphosphates *per se* and is a specific property of the polymeric nature of these compounds.

(ii) To test the possible influence of Na^+ ions, the free acids of the alkali polyphosphates were prepared by the method of KATCHMAN[9] by passing the solution of a sodium polyphosphate through the catex column in the hydrogen cycle. Instead of Amberlite IR 112 catex quoted by these authors we used a Dowex 50 W catex, X-4, grade 200-mesh. A comparative measurement of the depth of the indentations showed that the sodium ions bound in the molecule in no way influenced the electrode process occurring, for the depth of the indentation was unchanged. These measurements were carried out with P_{16}, P_{25} and P_{230} in 1 *M* citric acid as supporting electrolyte.

(*c*) *Calibration curves*

For quantitative determinations a calibration curve is necessary. Calibration curves were prepared for all polyphosphates which yielded indentations in sulphuric, citric, and formic acid media. As a typical example we give only the calibration curve for the polyphosphates P_{230} in 1 *M* citric acid medium (Fig. 5). It can be seen from Fig. 5 that the steeper part of the curve lies approximately within the range 5–10 μg to 70–80 μg. The subsequent part of the curve expresses a much less marked change. Above 400 μg the curve attains a plateau.

(*d*) *The effect of the molecular weight* (*degree of condensation*) *of polyphosphates on the depth of indentation*

This relationship was studied in the following supporting electrolytes: sulphuric acid, formic acid, acetic acid, citric acid, in ammonium formate of pH 3.8. Equi-weight quantities of the different polyphosphates were employed in these experiments. Figure 6 shows the relationship of the depth of the indentations to the molecular weight of the polyphosphates, (*cf.* Table 2). The concentration used was 100 μg of the sodium salt of polyphosphates per ml and the supporting electrolyte was 1 *M* citric acid.

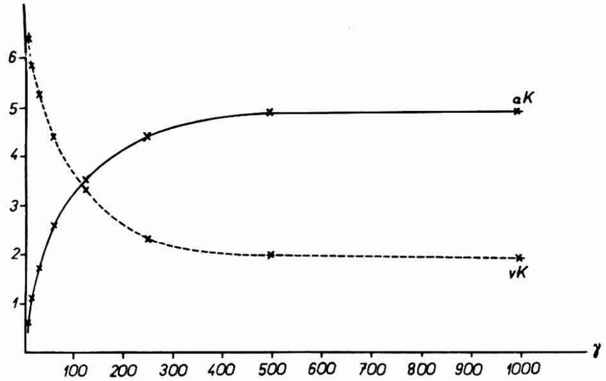

Fig. 5. Calibration curve for P_{230} in 1 *M* citric acid medium.

The results of this investigation show that an indentation first made an appearance with P_6; all the lower phosphates (P_2, P_3, P_4, M_3, M_4) were found to be inactive. The depth of an indentation increased progressively with increasing chain-length of the polyphosphates. At P_{25} it had reached almost a maximum value and for higher members of the series up to P_{230} it remained practically at the same level. Similar results were obtained using other electrolytes as supporting media. In these experiments it

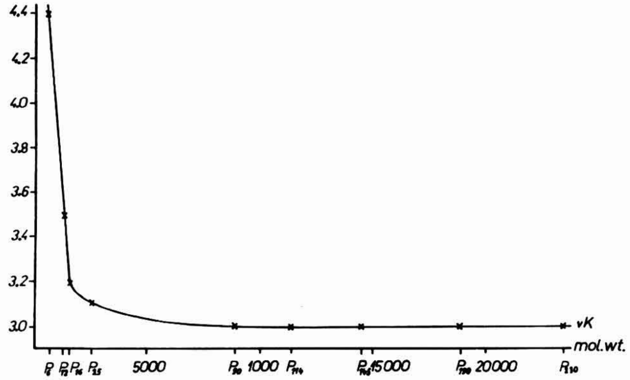

Fig. 6. Relationship of indentation depth to mol. wt. of polyphosphates at equi-weight quantities, 100 μg/ml. Supporting electrolyte 1 *M* citric acid.

TABLE 2

A LIST OF CHEMICALS USED

Name	*Abrev.*	*Mol. Wt*	*Manufacturer*
Trimetaphosphate	M_3	306	Dr. E. KARL KROUPA of
Tripolyphosphate	P_3	368	Monsanto Chemical Co., U.S.A.
Tetrametaphosphate	M_4	408	idem
Tetrapolyphosphate	P_4	470	idem
Polyphosphate	P_{12}	1,280	idem
Polyphosphate	P_{230}	23,500	idem
Polyphosphate	P_{90}	8,900	Dr. U. P. STRAUSS, U.S.A.
Polyphosphate	P_{114}	11,400	idem
Polyphosphate	P_{145}	14,500	idem
Polyphosphate	P_{190}	18,900	idem
Polyphosphate	P_{16}	1,690	Prof. E. THILO, Berlin
Calgon S	P_{12a}	1,280	Messrs. Albright and Wilson, London, U.K.
Calgon	P_{25}	2,600	idem
Hexametaphosphate	P_6	670	Judex Chemical Co., U.K.

[*] All condensed phosphates of synthetic origin were preparations in the form of sodium salts. The molecular weights given for the higher polyphosphates represent average values.

was important to choose a suitable electrolyte and a concentration which lay in the region of a steep rise of the calibration curve. All measurements were carried out within 5 min after the polyphosphates had been mixed with the supporting electrolyte, in order to eliminate as much as possible the hydrolysis which takes place at higher temperatures in acidic medium[4,5]. It can be seen from Fig. 6 that the maximum change in indentation depth lies in the range P_6–P_{16}, *i.e.*, 85.3% of the total number of polyphosphates tested. The change between P_{16} and P_{25} is very slow, *i.e.*, only about 7.1% of the total and is still more gradual between P_{25} and P_{90}, about 7.1%.

(*e*) *The elucidation of the type of electrode process*[1]

To investigate the type of electrode process the following experiments were carried out:

(*i*) *Effect of concentration of substances.* High concentrations of polyphosphates (10 mg/ml) did not cause any "cleaving" of the oscillopolarographic curve at the site of the indentation. This is commonly suggested to be a proof of a capacitive process.

(*ii*) *Comparative measurements of the supporting electrolyte curves and those for the same electrolyte with the substance added.* In the case of depolarizers the overall area of the curve diminishes, whereas with substances causing a change in the differential capacity, the area of the curve increases. In Fig. 2 a comparative measurement in 1 N H_2SO_4 is recorded. In the region of positive potentials the curve obtained with the phosphate was somewhat lower compared to that of the pure electrolyte; at more negative potentials a rise was distinctly visible.

(*iii*) *The effect of temperature on the size of the indentation.* It is characteristic of the capacity process that a rise of temperature reduces the size of indentation. The relationship of indentation to temperature in the case of polyphosphates is however, practically impossible to study, since in the acidic medium used hydrolytic decomposition sets in at higher temperatures. This causes a completely irreversible disappearance of the indentation as shown above.

(iv) The method of the first curve and work on the vibrating electrode. Since the indentations produced by polyphosphates were perceptible both on the first curve and on the vibrating electrode (partly replacing a streaming mercury electrode) it is certain that the indentations are not caused by an artefact.

In oscillopolarography it is well known that films of some organic solvents such as pyridine and butanol are capable of effectively eliminating the effect of bivalent and trivalent cations. These substances cause the disappearance of the characteristic indentation for cations from the cathodic arm of the oscillopolarographic curve (elimination of cations sets in at more negative potentials), while the indentation in the anodic arm remains intact[1].

We carried out experiments in which a polyphosphate was added to solutions of inorganic depolarizers and we followed the effect of this addition on the indentations caused by bivalent cations. Experiments with Zn^{2+} and Pb^{2+} in 1 *M* citric acid medium showed that only the higher polyphosphates caused the disappearance of the cathodic indentation of cations. The anodic indentation was a little reduced, but was

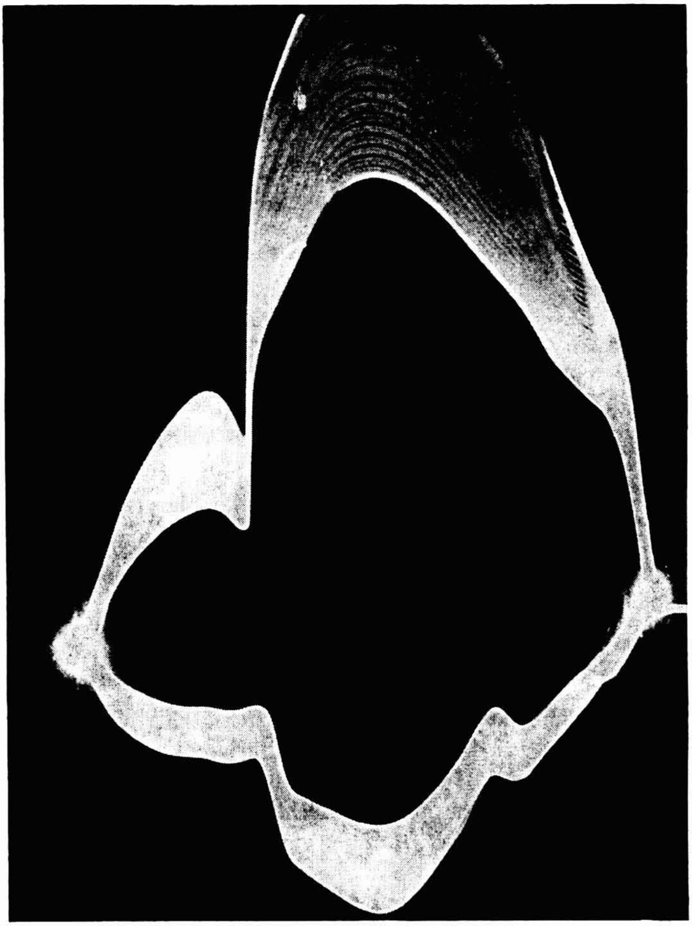

Fig. 7. $dE/dt = f(E)$ curve of P_{230}, 1 mg/ml + $5 \cdot 10^{-4}$ *M* $ZnSO_4$, in 1 *M* citric acid medium.

still perceptible. Figure 7 shows the oscillogram of $5 \cdot 10^{-4}$ *M* $ZnSO_4$ in 1 *M* citric acid after the addition of P_{230} (final concentration was 1 mg/ml).

Assessment of the results of these experiments is rendered more difficult by the well known fact that polyphosphates form complexes with cations, especially with Ca^{2+} and Mg^{2+}. This ability to form complexes is approximately proportional to the number of atoms of phosphorus present in the chain[19]. The interpretation of the electrode process which takes place in the presence of polyphosphates and bivalent cations will therefore probably be rather complicated. According to present-day views it seems that it is mainly the rate of adsorption of the surface active substances (which are subsequently desorbed at negative potentials from the surface of the dropping mercury electrode) which plays an important role.

An interesting phenomenon can be observed in 1 *M* formic and acetic acid media (see Fig. 8). The formation of the so-called "spikes" has so far been observed only in very dilute electrolytes, *e.g.*, concentration approximately 10^{-3} *M*[1]. Since this effect is evidently connected with the conductivity of electrolytes, we carried out measurements of this constant for the electrolytes used. For this purpose we used a Wheatstone bridge in conjunction with an immersion Pt electrode. The results showed that the conductivity of a 1 *M* organic acid is indeed comparable with that of 10^{-3} *M* H_2SO_4.

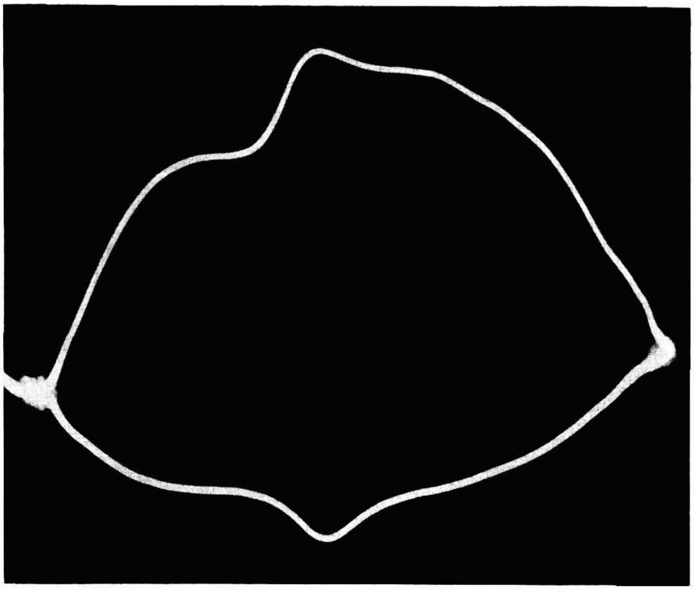

Fig. 8. $dE/dt = f(E)$ curve of supporting electrolyte 1 *M* HCOOH. Vibrating electrode.

DISCUSSION

The results of this investigation confirm the earlier report by SZYSZKO[7] on the oscillopolarographic inactivity of orthophosphates. Our data also show that the lower condensed phosphates — pyrophosphate P_2, tripolyphosphate P_3, tetrapolyphosphate P_4, trimetaphosphate M_3 and tetrametaphosphate M_4 — do not give any indentations in the several media studied.

With the higher phosphates, however, commencing from P_6, indentations are produced on the oscillopolarographic curves in some of the media tried. The indentation depth bears a direct relationship to the degree of polymerization of these polyanions *i.e.*, the aK value (Fig. 1) shows a progressive increase with an increase in the chain length of the poly-electrolytes. This change is very sharp (the curve is very steep) in the range P_6–P_{16}, and represents the major fraction (85%) of the total change in depth, whereas the change within the range P_{16}–P_{25} is less than 10% of the total change. The remaining small change in indentation depth is between P_{25} and approximately 10–15 chain lengths beyond P_{25}. The subsequent course of the curve lies along a plateau.

On the basis of these results we can safely conclude that the oscillopolarographic activity of sodium polyphosphates is not caused by Na^+ ions or by any contaminants present in these substances. On the other hand, evidence has been adduced to show that this property is an attribute of the polymeric and polyanionic character of polyphosphates. The inactivity shown by the lower members of the series and the first appearance of an indentation with P_6 also suggest that a polyphosphate molecule must possess a minimum chain length. The negative charge of the molecule must be suppressed by means of a suitable acid medium in order to give rise to an indentation.

Our data suggest that the electrode process responsible for the production of an indentation by polyphosphates is of capacity nature. It is a well known fact[1] that the depth of capacitive indentations greatly depends on the solubility of a given substance in the medium. As the solubility decreases, the indentation depth grows. This interpretation is also borne out by the fact that suppression of dissociation in acidic medium leads to a deepening of the indentation in the case of polyphosphates.

The relationship between the degree of polymerization of condensed phosphates and their oscillopolarographic activity as established in the present study, is worthy of note in view of several other physico-chemical studies available in the literature on these compounds. It is interesting to find several cases of analogy with the present observation. For example, while studying the metachromatic reaction given by polyphosphates with toluidine blue, TEWARI AND KRISHNAN[10] observed that the intensity of the metachromatic reaction was very low with metaphosphate of molecular weight 690, but increased with rising molecular weight and reached a maximum value at a molecular weight of 3600. It remained at this level for the molecular weight range 3600–20600. The results of a study of the intensity of metachromasy on filter paper with toluidine blue, and the binding capacity towards several basic compounds of biological importance (*e.g.*, Protamine, Neomycine, Viomycin, Polymyxin, Streptomycin, Quanidine etc.) as reported by SINGH for polyphosphates[11,12] show that these two properties progressively increase in value with increase in the chain-length of the polyanions up to P_{16}. From P_{16} onwards up to the highest phosphate studied, P_{230}, the two values are practically constant. The heparin equivalent of condensed phosphates as studied by the chemical method of casein precipitation according to FISCHER AND SCHMITZ (see ref. 13) (SINGH — unpublished work) also shows a similar behaviour in relation to the molecular weight of the inorganic polymer.

Studies on the diffusion coefficient behaviour of condensed phosphates according to KATCHMAN AND SMITH[9] have revealed that this constant progressively decrease in value with increasing chain-length up to P_{36}. This is followed by a unique plateau with increasing molecular weight of the polyanion.

One more property of polyphosphates which has a bearing on their degree of polymerization may also be mentioned. KATCHMAN AND VAN WAZER[14] have shown that the amount of polyphosphate precipitated with albumin in an acid medium increases with increasing number of average chain-length of the polyanions, such that Kurrol's salt with an average chain-length of 1600 is completely precipitated.

The binding of sodium by the long-chain phosphates has been studied by a number of different techniques (electrolyte transference-number measurements and ion activity measurements with cation exchange membranes[16,17,18]). The amount of sodium closely associated with the phosphate chain increases rapidly with the length of the chain in the region below chain-lengths of about 30. Above this value, the fraction of the total sodium which is bound to the phosphate chain increases slowly with increasing chain-length. Similarly polarographic data[19] indicate an increase in the binding of barium with the chain-length of the phosphate ($pK = 4.5$ for the pyrophosphate and 6.5 for an average chain length of 75). The long-chain phosphates are well known as peptizing, deflocculating and dispersing agents by virtue of their ability to exert strong influence on colloids. These properties are also a function of the chain-length of these poly-electrolytes, the longer chains being always more effective in this respect[20,21].

Studies on the electrical, optical and mechanical properties of condensed phosphates indicate that changes in the optical and electrical anisotropy, equivalent conductance, intrinsic viscosity etc. are a function of their molecular weight[22–29].

The need for developing a simple and a reliable method for the detection and characterization of polyphosphates can hardly be over-emphasized; it may be mentioned in passing that polyphosphates are of great biological and biochemical significance [4,5,6]. The present method affords such a technique which is quite sensitive and is capable of differentiating lower phosphates from the higher ones.

In addition, according to our previous results[15] the method is also applicable to acid polysaccharides such as hyaluronate, heparin, dextran sulphates, chondroitin sulphate etc. By choosing suitable experimental conditions it may be possible to differentiate them from one another as well as from the inorganic polymers.

It may also be possible by using this method, to follow the kinetics of the decomposition of polyphosphates under the influence of heat, pH, etc.

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It is a pleasure to acknowledge the helpful and critical interest which Dr. E. PALEČEK and Dr. K. MICKA have shown in this work. One of the authors (Ch. S.) is indebted to the ČSAV for a research fellowship and also to Professor F. HERČÍK for kindly making available all the necessary facilities at this Institute for the completion of this work.

We also wish to thank the authors and manufacturers quoted in Table 2 for generously providing the samples of polyphosphates. Finally, we express our thanks to Mrs. H. HELÁNOVÁ for assistance in carrying out the technical work.

SUMMARY

A sensitive oscillopolarographic method has been worked out for the detection

and quantitative analysis of inorganic condensed phosphates.

A relationship has been established between the depths of indentations and the molecular weight of polyphosphates.

The principal factor responsible for the production of an indentation is the polymeric nature of polyphosphates.

The electrode process is of capacity nature.

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INVESTIGATION OF THE ELECTROCHEMICAL GENERATION AND THE VISIBLE SPECTRA OF FREE RADICAL ANIONS OF THE MONO-NITRONAPHTHALENES AND NITROMESITYLENE, IN DIMETHYLFORMAMIDE

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The formation of free radical anions was postulated, to explain the formation of one-electron, reversible waves obtained in the polarographic investigation of aromatic nitro-compounds in aprotic solvents such as dimethylformamide or acetonitrile[1-6]. Free radical anions can be generated in larger quantities by electrolysis in aprotic solvents and MAKI AND GESKE[2,3] and also ADAMS *et al.*[7,8] applied the method of electrolytic generation in their investigation of EPR spectra of free radical anions of aromatic nitro-compounds.

Recently we have improved the method of investigation of electrolytically-generated nitrobenzene free radical anion in dimethylformamide[9-11], by measuring its concentration as a polarographic oxidation current[9]. Using a special electrolytic, and at the same time spectrophotometric, cell we determined the visible absorption spectrum of the nitrobenzene free radical anion[10,11]. Chemical methods for the generation of nitrobenzene free radical anion in solution together with an investigation of its optical absorption have been described[12]. The spectrum of electrolytically-generated nitrobenzene free radical anion was also investigated by ADAMS[13] and KASTENING[14].

We have extended the previously developed method of electrochemical generation and determination of the absorption spectra to the investigation of the free radical anions of the mono-nitronaphthalenes and nitromesitylene. Using the results obtained an attempt was made to interpret the visible spectra of the free radical anions of these aromatic nitro-compounds.

EXPERIMENTAL

A base electrolyte 0.2 N solution of $NaNO_3$ in dimethylformamide was used in the investigation[15]. For polarographic determinations we used a Radiometer PO-4 polarograph. The characteristics of the polarographic capillary in the 0.2 N solution of $NaNO_3$ in dimethylformamide were: drop time, $t = 4.6$ sec; rate of flow of mercury, $m = 0.98$ mg/sec for a height of mercury column, $h = 520$ mm (temp. 20°).

The free radical anions were generated in the base electrolyte solution on a mercury pool cathode against an aqueous saturated calomel electrode (S.C.E.) in a small electrolytic cell (20-cm³ volume), equipped with a polarographic dropping electrode[9].

A compact filter-paper plug moistened with the base electrolyte solution separated the cell from the working calomel electrode. A second reference saturated calomel electrode was connected with the cell through an electrolytic bridge. The solution was de-aerated and also mixed during electrolyses by a stream of very pure hydrogen purified from trace amounts of oxygen by a catalytic apparatus[16]. The applied potential of the electrolysis was controlled against the reference S.C.E. and kept constant manually.

For investigating the spectra of the free radical anions we used the method described for nitrobenzene[10,11]. The free radical anions were generated by electrolysis in a quartz electrolytic (and simultaneously spectrophotometric) cell equipped with the dropping mercury electrode, placed inside the optical chamber of a single-beam Optica-Milano CF-4 spectrophotometer. After the generation of the free radical anions, the extinctions of the solutions were measured at different wavelengths against air. The extinctions of the free radical anions were obtained from the results by subtracting the extinction (measured against air) of the solution in the cell after the free radical anions had been decomposed by the action of oxygen. The concentrations of the free radical anions during the individual extinction measurements were obtained from the heights of the polarographic oxidation current of the free radical anions, registered simultaneously at a constant potential, -0.7 and -0.9 V *vs.* S.C.E. for the free radical anions of the mono-nitronaphthalenes and nitromesitylene respectively. From these data the extinction coefficients were calculated for several wavelengths and the spectra were traced from their average values. The concentrations of the solutions of the nitro-compounds investigated were $2\text{–}3 \cdot 10^{-3}$ *M*. The optical length of the cell was 35 mm.

The dimethylformamide used was purified by drying over anhydrous K_2CO_3 for one day and distillation through two *dephlegmators*, at reduced pressure (70 mm Hg) to diminish the possibility of decomposition during the process.

RESULTS

Polarography

α- and β-nitronaphthalenes are reduced in the 0.2 *N* solution of $NaNO_3$ in di-

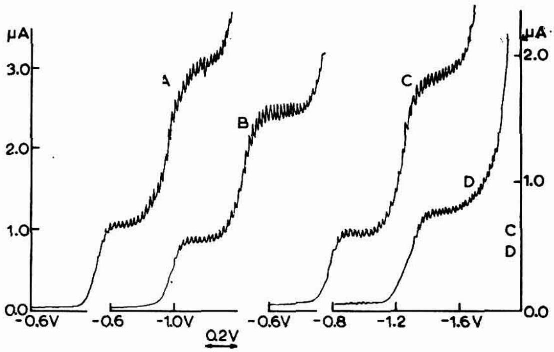

Fig. 1. Polarograms in a 0.2 *N* solution of $NaNO_3$ in dimethylformamide. (A), 3.0×10^{-4} *M* nitrobenzene; (B), 3.0×10^{-4} *M* α-nitronaphthalene; (C), 2.0×10^{-4} *M* β-nitronaphthalene; (D), 2.2×10^{-4} *M* nitromesitylene. The current intensity scale for polarograms (C) and (D) is on the right-hand side. Potentials *vs.* S.C.E.

methylformamide in two polarographic waves, similarly to nitrobenzene. Nitromesitylene has only one reduction wave, as the second wave coincides with the reduction curve of the base electrolyte (Fig. 1). The characteristics of the polarographic waves of the nitro-compounds are given in Table 1.

TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF NITRO-COMPOUNDS IN THE 0.2 *N* SOLUTION OF $NaNO_3$ IN DIMETHYLFORMAMIDE (TEMP. 20°)

Compound	*First wave*		*Second wave*	
	$E_{1/2}$	I	$E_{1/2}$	I
Nitrobenzene*	-1.01	2.35 ± 0.1	-1.44	5.1 ± 0.1
α-Nitronaphthalene	-0.97	1.9	-1.41	3.9
β-Nitronaphthalene	-0.98	1.9	-1.42	4.3
Nitromesitylene	-1.26	2.0		

Half-wave potentials, $E_{1/2}$, in V *vs.* S.C.E.; diffusion current constants, I, in μAsec $^{1/2}$/mmol · mg$^{2/3}$
*Data taken from ref. 5.

Like those of nitrobenzene, the first reduction waves of the mono-nitronaphthalenes ~~and nitromesitylene are of one-electron height.~~ Their diffusion current constants are somewhat smaller than that of nitrobenzene, as a result of their larger molecular size and consequently smaller diffusion coefficients. At the potentials of the first one-electron reduction waves of the nitro-compounds, stable free radical anions are formed:

$$R-NO_2 + e = (R-NO_2)^-$$

Electrolysis

The free radical anions of the nitro-compounds can be generated in the 0.2 *N* solution of $NaNO_3$ in dimethylformamide by electrolysis at a mercury pool cathode, at potentials of their first, one-electron polarographic waves. The free radical anions generated initially, react with trace amounts of proton-active impurities in the dimethylformamide solution and undergo further reduction, which causes a slight decrease in the initial concentration of the nitro-compound. After a few minutes of electrolysis the proton-active impurities in the solution are exhausted and the free radical anions then formed are stable in the solution. They are coloured in solution; the free radical anions of the mono-nitronaphthalenes $(C_{10}H_7-NO_2)^-$ are green, those of nitromesitylene $(C_9H_{11}-NO_2)^-$ are pinkish-red.

The free radical anions give a one-electron polarographic oxidation wave (Fig. 2, B) corresponding to their oxidation to the nitro-compounds:

$$(R-NO_2)^- - e = R-NO_2$$

The polarographic oxidation wave can be used for the determination of the concentrations of free radical anions in the solution, if one assumes approximate equality of the diffusion coefficients of the free radical anions and their corresponding nitro-compounds. The intensity (I_o) of the oxidation wave of the free radical anions is a sum of the intensities of the anodic wave (I_a) and the cathodic condenser current (I_o) at a given potential.

The free radical anions are relatively stable in the solution. Nevertheless they decay slowly in time with restoration of the original nitro-compound. The decay can be followed by recording their oxidation currents as a function of time at constant potential (Fig. 2, D). Under our experimental conditions the full decay of the generated free radical anions took 2–3 h and was not influenced by intensity of light.

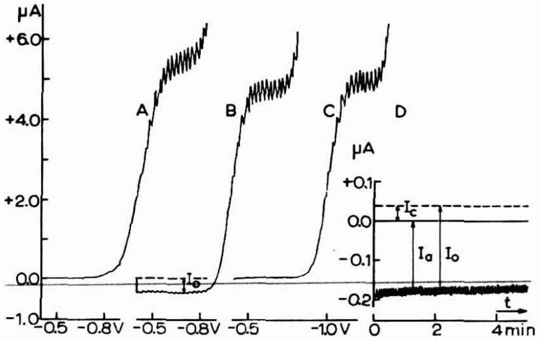

Fig. 2. Electrolysis of 2.3×10^{-3} *M* α-nitronaphthalene in a 0.2 *N* solution of $NaNO_3$ in dimethylformamide. (A), first reduction wave of α-nitronaphthalene before electrolysis; (B), the same reduction wave after electrolysis, the oxidation current of the free radical anions can be seen; (C), the same reduction wave after decomposition of the free radical anions by oxygen; (D), variation of anodic oxidation current of the α-nitronaphthalene free radical anion with time at constant potential, −0.7 V *vs.* S.C.E. The height of the oxidation current corresponds to a concentration of the free radical anion of about 9×10^{-5} *M*.

Oxygen, because of its more positive half-wave potential ($E_{1/2} = -0.63$ V *vs.* S.C.E.), accepts electrons from the free radical anions and converts them into the original nitro-compounds. It is possible to compare the height of the oxidation wave (I_o) of the free radical anions with the increase of the height of the one-electron reduction wave after the full conversion of the free radical anions into the original nitro-compounds by the action of oxygen (Fig. 2, B, C). From this comparison it is confirmed that there is practically no difference between the diffusion coefficients of the nitro-compounds investigated and their free radical anions.

Spectra

The visible absorption spectra of the free radical anions of the mono-nitronaphthalenes and nitromesitylene in the 0.2 *N* solution of $NaNO_3$ in dimethylformamide are represented in Figs. 3 and 4. During the light absorption measurements the concentrations of the free radical anions were about $1 \cdot 10^{-4}$ *M* for α-nitronaphthalene and about $2 \cdot 10^{-4}$ *M* for β-nitronaphthalene and nitromesitylene. The broad absorption band of the nitromesitylene free radical anion is probably composed of two close bands. The curves II in the figures represent the spectra of the solutions before the electrolyses and curves III the spectra of the solutions after the electrolyses and the decay of the free radical anions under the influence of oxygen from air introduced into the cell at the end of the measurements. At shorter wavelengths, curves III are somewhat higher than curves II, probably because of the formation of coloured reduction products of the nitro-compounds caused by proton-donor impurities in the solvent, especially at the beginning of the electrolyses.

In the range of concentrations of the free radical anions investigated, Beer's law is obeyed (Fig. 5). The concentrations of free radical anions were taken from their oxidation current at constant potential. The similar dependence of the extinctions of the two absorption maxima of α-nitronaphthalene on the oxidation current

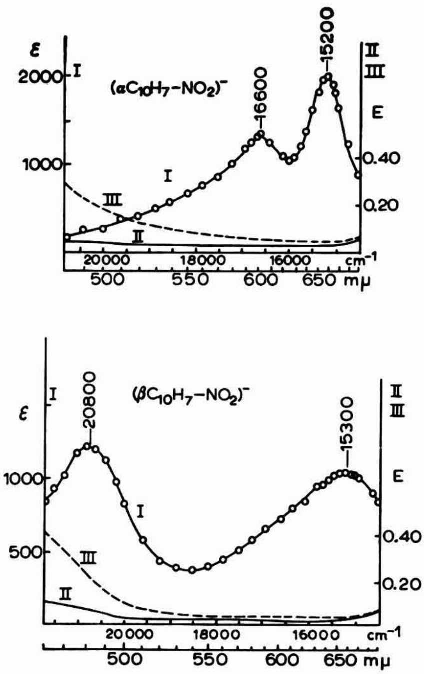

Fig. 3. The absorption spectra of the free radical anions of α-nitronaphthalene (upper picture, curve I) and β-nitronaphthalene (lower picture, curve I) in the 0.2 N solution of $NaNO_3$ in dimethylformamide. Curves II, spectra of the solutions before the electrolysis; curves III, spectra of the same solutions after the electrolysis and the decomposition of the free radical anions. ε, molar extinction coefficient; E, extinction.

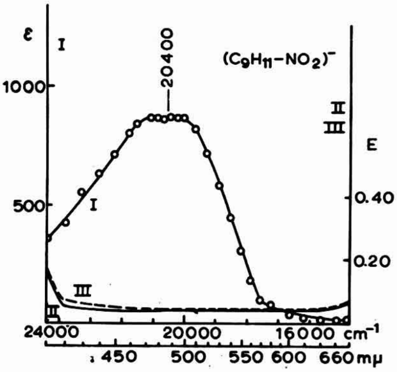

Fig. 4. The absorption spectrum of nitromesitylene free radical anion (curve I) in the 0.2 N solution of $NaNO_3$ in dimethylformamide. Curve II, spectrum of the solution before electrolysis; curve III, spectrum of the solution after electrolysis and decomposition of the free radical anions.

intensity, indicates that both bands belong to the same free radical anion $(C_{10}H_7—NO_2)^-$. This is also the case for both absorption bands of β-nitronaphthalene, and also of nitrobenzene.

The nitro-compounds do not themselves absorb light in the visible region. They absorb in the u.v. region and their u.v. absorption spectra are given in Fig. 6.

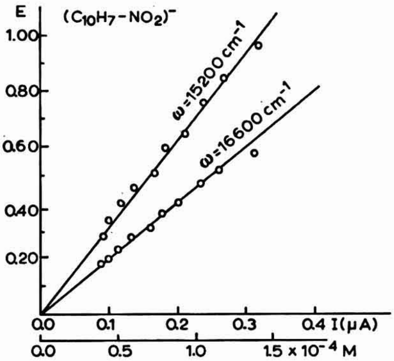

Fig. 5. The dependence of the extinction of the α-nitronaphthalene free radical anion in the 0.2 N solution of $NaNO_3$ in dimethylformamide from the intensity of its oxidation current recorded at constant potential −0.7 V *vs.* S.C.E. The lower scale represents the concentrations of the free radical anion corresponding to the oxidation current intensities.

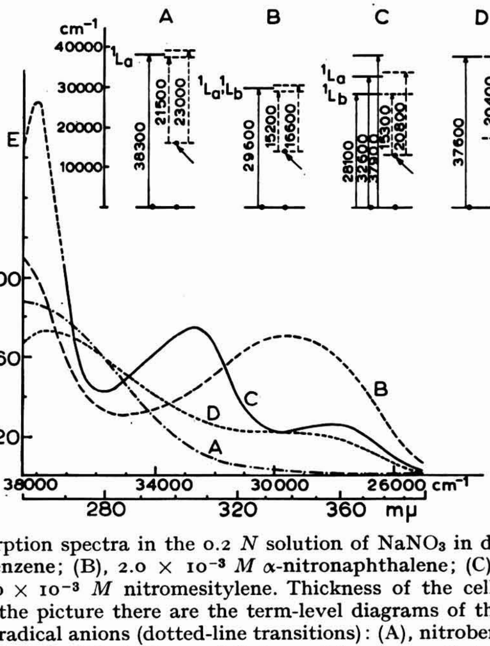

Fig. 6. The u.v. absorption spectra in the 0.2 N solution of $NaNO_3$ in dimethylformamide. (A), 1.0×10^{-3} M nitrobenzene; (B), 2.0×10^{-3} M α-nitronaphthalene; (C) 1.0×10^{-3} M β-nitronaphthalene; (D), 4.0×10^{-3} M nitromesitylene. Thickness of the cell, 0.1 cm; E, extinction. In the upper part of the picture there are the term-level diagrams of the respective nitro-compounds and their free radical anions (dotted-line transitions): (A), nitrobenzene; (B), α-nitronaphthalene; (C), β-nitronaphthalene; (D), nitromesitylene.

DISCUSSION

The formation of the free radical anions of aromatic hydrocarbons has been interpreted by means of molecular-orbital theory. The odd electron occupies the first π anti-bonding molecular orbital of the hydrocarbon. The energy of this anti-bonding molecular orbital (MO) is characterised by the frequency of light of the $V_1 \leftarrow N$ electronic transition from the last occupied bonding MO to the first anti-bonding MO. The frequency, ν of this transition is related to the half-wave potential, $E_{1/2}$, of the one-electron polarographic wave corresponding to formation of free radical anions, by means of the Watson and Matson equation:

$$-E_{1/2} = 1/2\ h\nu + \text{const.}^{17,18,19}.$$

Assuming that entropy changes during the formation of the various stable free radical anions can be neglected, the half-wave potentials, $E_{1/2}$ of one-electron polarographic waves are a comparative measure of the energy required to form a free radical anion.

The half-wave potentials of the one-electron polarographic waves of aromatic nitro-compounds are much less negative than the half-wave potentials of unsubstituted aromatic hydrocarbons. For example, $E_{1/2}$ of naphthalene in dimethylformamide is more negative than -2 V[20]. This indicates that during the formation of a free radical anion of an aromatic nitro-compound the electron is introduced to an orbital of lower energy than in case of formation of free radical anion of unsubstituted aromatic hydrocarbon.

The half-wave potentials of nitrobenzene and the mono-nitronaphthalenes are similar, although there exists a rather great difference in the extension of the aromatic systems of the compounds. The half-wave potential of nitromesitylene is only 0.25 V more negative than the half-wave potential of nitrobenzene, although in the nitromesitylene molecule sterically-induced de-coupling of the π electron systems of the aromatic ring and the nitro-group can be postulated[21,22]. This would indicate that the energy of the orbital to which electron is introduced is dependent rather on the nitro-group than on the aromatic ring.

It can be seen from the EPR investigation of free radical anions of aromatic nitro-compounds by MAKI AND GESKE[2,3] and ADAMS *et al.*[7,8,22], that the unpaired electron is located mainly on the nitro-group.

To account for these facts, we assume, that in the formation of free radical anions of aromatic nitro-compounds, the electron is introduced into a local π anti-bonding orbital of the nitro-group attached to the ring. This orbital is a *low-energy* orbital. Its energy is considerably lower than that of the first π anti-bonding MO of the aromatic nucleus, and also lower than the energy of the orbitals to which u.v. optical transitions take place in the nitro-compounds. The half-wave potentials of the nitro-compounds depend on the energy of this local orbital.

The observed absorption bands, in the visible spectra, of the free radical anions correspond to the excitations of the unpaired electron from this *low-energy* orbital of the nitro-group to higher molecular orbitals. The molecular orbitals can be assumed—in the first approximation—to be the same as in the nitro-compounds.

The proposed term-level diagrams (Fig. 6) of the nitro-compounds and their free radical anions were constructed on these suppositions and also on the presumption, that the observed u.v. absorption bands of the nitro-compounds correspond to transitions of electrons from the energetically highest, filled molecular orbital. The dotted line transitions correspond to the visible absorption bands of the free radical anions, and the solid line transitions to the u.v. bands of the nitro-compounds.

According to the proposed term-level diagram A (Fig. 6), the two bands of the nitrobenzene free radical anion arise from the unpaired electron transitions from the *low-energy* orbital of the nitro-group to the double-energy level corresponding to the 38300 cm^{-1} band of nitrobenzene. The level may also be double in nitrobenzene, as the 38300 cm^{-1} band is broad, and is supposed to correspond to ^1L_a, and perhaps also ^1L_b, bands of benzene in the Platt nomenclature[23].

The rather big difference between the spectra of the free radical anions of α-nitronaphthalene and β-nitronaphthalene can be discussed on the basis of the term-level diagrams of the nitro-compounds (Fig. 6, term-level diagrams B and C).

The difference between the u.v. absorption spectra of α-nitronaphthalene and β-nitronaphthalene and consequently their free radical anions may be caused by different transverse or longitudinal extensions of conjugation of the naphthalene nucleus by the nitro-group. The extension of conjugation would enhance and shift to longer wavelengths, the absorption bands of the naphthalene nucleus polarised in this direction, in a similar manner to that indicated in the case of the spectra of α- and β-aminonaphthalenes[24]. According to the Platt nomenclature, the 29600 cm^{-1} band of α-nitronaphthalene would correspond to fused ^1L_a and ^1L_b bands of naphthalene, and the 28100 cm^{-1} and 32600 cm^{-1} bands of β-nitronaphthalene to the red-shifted ^1L_b band, and ^1L_a band respectively of naphthalene.

In α-nitronaphthalene there might be hydrogen-bonding interaction between the peri H-atom and oxygen of the nitrogroup, especially as this would lead to another six-membered ring.

The two bands of the α-nitronaphthalene free radical anion can arise from transitions of the unpaired electron to two close energy levels corresponding to the 29600 cm^{-1} band of the α-nitronaphthalene (Fig. 6, term-level diagram B). The energy level may also be double in the nitro-compound as the 29600 cm^{-1} band is broad and may correspond to the ^1L_a and ^1L_b bands of naphthalene.

In the spectrum of β-nitronaphthalene there are three absorption bands (Fig. 6, curve C) and these can correspond to three different energy levels. The two wide-apart absorption bands of the β-nitronaphthalene free radical anion can arise from promotions of the unpaired electron to two of the three levels (Fig. 6, term-level diagram, C,). The second energy level of the free radical anion in the diagram (dotted level), is of somewhat higher energy than the corresponding level in the nitro-compound.

The results obtained by us in the investigation of the free radical anions of the aromatic nitro-compounds, particularly the determinations of the concentrations of the free radical anions by means of their oxidation currents, and the method of investigation of the spectra, can be applied generally to the investigation of other free radical anions in aprotic solvents.

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SUMMARY

As a result of certain polarographic investigations, the free radical anions of α- and β-nitronaphthalenes and nitromesitylene were generated by electrolysis in a 0.2 *N* solution of $NaNO_3$ in dimethylformamide. The free radical anions of the mono-nitronaphthalenes were green in solution and those of nitromesitylene pinkish-red. The visible spectra of the free radical anions were determined, using their polarographic oxidation current as a measure of their concentration.

The interpretation of the spectra of the free radical anions and nitrobenzene free radical anion, and their correlation with the u.v. spectra of the nitro-compounds has been discussed.

It has been suggested that in the free radical anions of the aromatic nitro-compounds, the unpaired electron occupies a *low-energy* orbital of the nitro-group. The visible absorption bands of the free radical anions correspond to transitions of the unpaired electron from this orbital to higher molecular orbitals.

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Short Communications

The use of programmed current chronopotentiometry in studies of adsorption

The presence of a surface excess, Γ, of an electroactive species at an electrode surface is revealed in chronopotentiometric transition time data by an increase of the characteristic chronopotentiometric constant over the normal diffusional value. This increase is more pronounced at increased applied currents. There are four reasonably distinct mechanisms whereby the absorbed species produces this effect:

(*i*) *Equilibrium mechanism.* The solution reactant, SR, and the adsorbed reactant, AR, are coupled by a rapid equilibration process, and are simultaneously depleted at the transition time. A common simplifying assumption is that $\Gamma/C = K$, a constant.

(*ii*) *AR, SR mechanism.* The species AR is coulometrically depleted prior to the reaction of any SR. The implied double wave may not be resolved; the present discussion refers to this less easily recognized situation. In this mechanism, and in the two below, no equilibration between SR and AR occurs (other than that at $t = 0$).

(*iii*) *SR, AR mechanism.* The surface concentration of SR is reduced to zero prior to the reaction of AR.

(*iv*) *SAR mechanism.* The species SR and AR react and are depleted simultaneously; each consumes a fixed fraction of the applied current throughout the chronopotentiogram.

The constant current chronopotentiometric relationships for all of the above mechanisms are available in the chemical literature[1,2]. These relationships show that the dependency of the characteristic constant current $i\tau^{\frac{1}{2}}$ value on i is a function of the adsorption mechanism. It is thus necessary to ascertain the mechanism most closely appropriate to the experimental case in order to obtain meaningful values for Γ. This is accomplished in the constant-current technique by a careful comparison of the form of the experimental current–transition time variation with the several theoretical expressions. Because the actual differences between the various mechanisms are not extremely large, a reasonably wide range of transition time values must be employed.

The form of the chronopotentiometric relationship between current and transition time is also a function of the type of current control employed. It might be reasonably expected that the use of appropriate current programs could produce an additional and useful dispersion in the chronopotentiometric behavior of the various adsorption mechanisms. The theoretical characteristics of two types of current programs have been found to display useful diagnostic properties. The pertinent theory of these techniques and their application as mechanistic tests are discussed below.

Ramp current chronopotentiometry

The use of ramp current ($i = \beta t$) chronopotentiometry as a diagnostic test is based upon an examination of the relative increases (arising from adsorption) of the ramp current constant, $\beta\tau^{\frac{3}{2}}$, and the constant current $i\tau^{\frac{1}{2}}$, at a common transition time value. The diffusion-only values of these constants are related by the expression $2\beta\tau^{3/2}/3i\tau^{1/2} = 1 = \theta$. If the ramp current technique displays a greater sensitivity toward the presence of a particular adsorption mechanism, then the *relative sensitivity factor* $\theta > 1$; if the reverse is true, then $\theta < 1$.

It is obvious that the AR, SR mechanism produces a $\theta > 1$, as the species AR reacts in the low current region of the ramp current program and requires a relatively larger portion of the total transition time for its depletion. This qualitative observation is verified by consideration of the exact chronopotentiometric relation for this case. If τ_a corresponds to the time for depletion of AR, then by integration

$$\beta\tau_a^2 = 2nFA\Gamma \tag{1}$$

The current program applied to the simple diffusional depletion of SR is then a step current, $\beta\tau_a$, plus the ramp current, βt, both initiated at time τ_a. Utilization of the response function additivity principle[3] then yields at τ (total transition time)

$$\tau = \frac{3nFAD^{1/2}\pi^{1/2}C^\circ}{4\beta(\tau - \tau_a)^{1/2}} - \frac{\tau_a}{2} \tag{2}$$

Theoretical calculations were performed on eqn. (2) and the corresponding constant current relation[1] using an assumed set of typical values for the quantities involved. Some representative numbers are given in Table 1, and it can be seen that the ramp current technique exhibits a measurably greater relative sensitivity.

It is obvious that the above situation is reversed in the case of the SR, AR mechanism, and $\theta < 1$.

Examination of the behavior of θ for the equilibrium and SAR mechanisms necessitates inspection of the respective ramp current chronopotentiometric relations. For the equilibrium mechanism, Laplacian solution of Fick's Law under the appropriate boundary conditions (assuming $\Gamma_t/C_{(0,t)} = K$) yields at the transition time

$$\tau^{3/2} - \frac{3\pi^{1/2}\tau K}{4D^{1/2}} + \frac{3\tau^{1/2}K^2}{2D} + \frac{3\pi^{1/2}K^3\phi(\tau)}{4D^{3/2}} = \frac{3nFA\pi^{1/2}D^{1/2}C^\circ}{4\beta} + \frac{3\pi^{1/2}K^3}{4D^{3/2}} \tag{3}$$

where $\phi(\tau) = \exp[D\tau K^2]\ \mathrm{erfc}[(D\tau)^{1/2}K]$. For the SAR mechanism, division of β into fixed fractions for consumption by AR and SR allows separate solutions for the transition time relation for each species. Because the τ in both equations is the same, they may be readily combined to give the final relation

$$\beta\tau^{3/2} = \frac{2nFA\Gamma}{\tau^{1/2}} + \frac{3nFAD^{1/2}\pi^{1/2}C^\circ}{4} \tag{4}$$

The results of theoretical computations of the behavior of eqns. (3) and (4) are given in Table 1. Both mechanisms result in $\theta > 1$.

An experimental determination of the value of θ, using values of β and i adjusted to produce the same τ for both ramp and constant current techniques, thus allows a very simple means of inspection for the presence of the SR, AR mechanism, as it alone yields $\theta < 1$. It is obvious from Table 1 that the test is more reliable at short transition time values.

It is interesting that the relative sensitivity of any two power of time current ($i = \beta t^r$) techniques provides an analogous differentiation of the SR, AR mechanism from the other three mechanisms. It can be shown that for two methods having the time powers r_1 and r_2, the applicable relative sensitivity factor $\theta(r_1/r_2)$ for SR, AR

TABLE 1

THEORETICAL VALUES OF RELATIVE SENSITIVITY FACTOR

Mechanism	τ	$(\beta\tau^{\frac{1}{2}})_{ads}/(\beta\tau^{\frac{1}{2}})_{diff}$	$(i\tau^{\frac{1}{2}})_{ads}/(i\tau^{\frac{1}{2}})_{diff}$	θ
AR, SR	1.0	1.13	1.10	1.03
AR, SR	0.1	1.55	1.42	1.09
AR, SR	0.01	3.28	2.60	1.26
Equil.	1.0	1.28	1.19	1.08
Equil.	0.1	1.90	1.62	1.17
Equil.	0.01	4.00	3.15	1.27
SAR	1.0	1.30	1.23	1.06
SAR	0.1	1.94	1.70	1.14
SAR	0.01	4.02	3.26	1.23

Values assumed: $n = 1$, $A = 0.1$ cm², $C° = 5 \cdot 10^{-4}$ M, $\Gamma = 5 \cdot 10^{-10}$ mole/cm², $D^{\frac{1}{2}} = 5 \cdot 10^{-3}$, $K = 10^{-3}$

is < 1 for $r_1 > r_2$, and is > 1 for $r_2 > r_1$. The reverse is true for the remaining three mechanisms. The case of $r_1 = 1$ compared to $r_2 = 0$ discussed above is simplest mathematically and experimentally, and yields neither more nor less mechanistic information than would any other pair of power of time techniques similarly employed.

Step current chronopotentiometry

In the AR, SR mechanism the species AR is coulometrically depleted prior to the reaction of SR. A specific test for this mechanism can be based on the fact that the sequential depletions of AR and SR are essentially independent processes and need not be carried out at the same constant current values. Consider the application of current i_1 at $t = 0$ followed at $t = \tau_a$ by a step change to a different constant current i_2, where $i_2 >$ or $< i_1$ but > 0. The values i_1 and τ_a are selected to produce depletion of AR at τ_a; *i.e.*, $i_1\tau_a = nFA\Gamma$. The current i_2 and the additional time required to reach the total transition time, $\tau - \tau_a$, then correspond to the occurrence of a diffusional process (reaction of SR) and therefore $i_2(\tau-\tau_a)^{\frac{1}{2}} = nFAD^{\frac{1}{2}}\pi^{\frac{1}{2}}C°/2$.
Variation of the current i_2 over a wide range of values (using a constant $i_1\tau_a$) with a constant value of $i_2(\tau-\tau_a)^{\frac{1}{2}}$ resulting, then provides a positive identification of the AR, SR mechanism. As the value of $i_1\tau_a$ corresponding to the surface excess Γ is not known *a priori*, a practical application of this test would best follow an examination by the simple constant current technique which had resulted in a suspicion of the presence of the AR, SR mechanism and an approximate value of Γ. In a practical sense, it is therefore a confirmatory rather than a primary diagnostic test.

Because in the equilibrium and SAR mechanisms the reaction of AR would occur during the time $\tau - \tau_a$ as well during τ_a, even if $i_1\tau_a$ were selected by chance to correspond to $nFA\Gamma$ the experimental values of $i_2(\tau-\tau_a)^{\frac{1}{2}}$ would not be constant but would increase with increasing values of i_2. This qualitative expectation has been confirmed by theoretical computations using the appropriate theoretical expressions for these two mechanisms and a step current program in which $i_1\tau_a = nFA\Gamma$. The calculations indicate that several values of i_1 (but constant $i_1\tau_a$) should be employed for most positive elimination of these mechanisms by observance of a trend in $i_2(\tau-\tau_a)^{\frac{1}{2}}$.

Applications of the above diagnostic tests in experimental studies of adsorption mechanisms will be reported in future publications.

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A simple electronic-scan, controlled-potential polarograph

Several methods have been employed to compensate for the *iR* drop encountered in the polarographic analysis of high resistance solutions[1–8]. The all-electronic polarograph built by KELLEY, FISHER AND JONES[6] at the Oak Ridge National Laboratory has proved quite effective and reliable. This polarograph is a highly sophisticated device with many features in addition to the electronic scan and potential control.

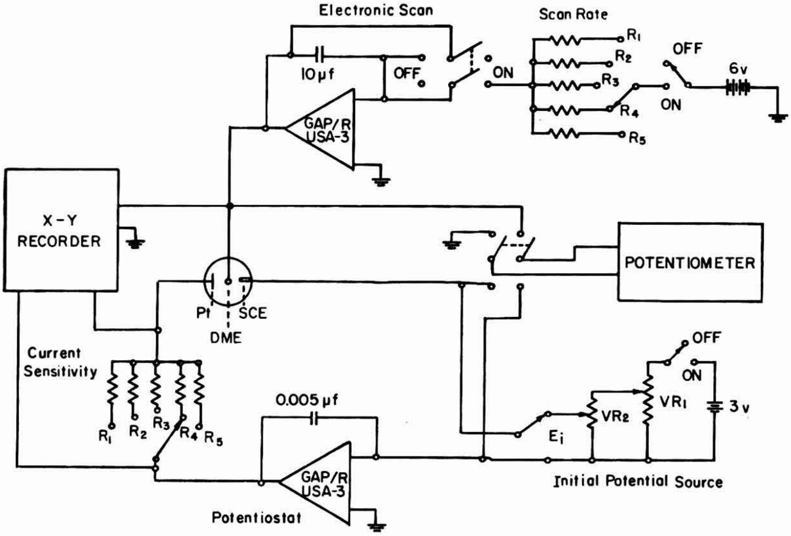

Fig. 1. Circuit diagram. Scan-rate resistors: R_1 = 720 MΩ; R_2 = 360 MΩ; R_3 = 140 MΩ; R_4 = 72 MΩ; R_5 = open. Current sensitivity resistors: R_1 = 400 Ω; R_2 = 1 KΩ; R_3 = 2 KΩ; R_4 = 10 KΩ; R_5 = 100 KΩ. The power supply, a Philbrick R-100 B, is not shown. VR_1 = 25 kΩ; VR_2 = 50 Ω.

In 1961, a relatively simple polarograph was designed and constructed at the Massachusetts Institute of Technology using two high-gain, chopper-stabilized operational amplifiers of the GAP/R model USA-3 type* for electronic potential control and scan. This polarograph is similar in design to the ORNL instrument but has certain modifications and simplifications. Because the applications of the instrument at M.I.T. are primarily concerned with the measurement of half-wave potentials, several of the features of the ORNL polarograph including the linear residual current compensator, the parallel-T RC filter for average current polarograms, the peak follower for maximum current polarograms, and the differentiating circuit for derivative polarograms were considered unnecessary and therefore were not included.

Basically, the polarograph consists of two operational amplifier circuits, a three-electrode system, and an X-Y recorder. The arrangement of these components is shown in the schematic diagram (Fig. 1). One of the amplifiers operates as a potentiostat to control the potential between the reference and working electrodes while the second amplifier is used as an integrator for electronic potential scan and applies this potential directly to the dropping mercury electrode (D.M.E.).

In the ORNL instrument, the D.M.E. is not connected to the electronic-scan amplifier as in the M.I.T. polarograph but, instead, the scan potential is applied to the second input of the potential control amplifier, which must be modified internally to operate as a difference amplifier. The over-all action of the potential control system is to force the e.m.f. between the polarized electrode and the reference electrode to equal the sum of the potentials of the initial potential source and the scan potential source independently of the value of the cell resistance[6].

In the M.I.T. polarograph, the necessity of modifying the internal circuit of the operational amplifier is avoided by connecting the scan amplifier output to the D.M.E. instead of to the second input of the potential control amplifier. Because the input of an operational amplifier is held at virtual ground potential by negative feed-back of voltage from the working electrode to the input, the initial potential of the D.M.E. will be equal to the potential of the reference electrode (S.C.E.) plus any voltage applied by the initial potential source between the S.C.E. and potentiostat. If a negative potential is applied to the D.M.E. by the electronic scan, the solution potential becomes negative with respect to instrument ground. This is sensed by the S.C.E. and the negative error signal which appears at the input of the potentiostat is inverted by the operational amplifier, and a positive potential of such magnitude as is necessary to eliminate the error signal is applied to the platinum electrode. Because no current flows through the circuit loop that includes the S.C.E., the system causes the potential difference to be identical with the effective potential between the reference electrode and the D.M.E. independently of the magnitude of the circuit and cell resistances, as in the Kelley–Fisher–Jones instrument. By the use of resistances in series with the polarographic cell and solutions of high resistance, *e.g.*, glacial acetic acid, it was found that as much as 10 MΩ had little effect on the polarographic wave. The half-wave potential was not detectably shifted, and the observed diffusion current was decreased only by about 1%.

A linear potential scan is obtained from the output of an operational amplifier which is being used as a constant current integrator, charging a bank of high-quality

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Mylar capacitors. The scan-rate is adjusted by selecting various resistors which are connected in series with the voltage source and the input of the integrator[6]. Because the scan rate is E/RC where E is the value of the voltage source (6 V), C is the size of the capacitor (10 μF), and R is the resistance, a simple calculation determines the size of resistor necessary for any particular scan-rate. The resistors indicated in Fig. 1 should give rates in the range of 50–500 mV/min. By means of the switch between the voltage source and the resistors, it is possible to stop the scan and hold the potential constant at any desired value for as long as 30 min. The scan-switch consists of a double-pole double-throw switch which charges the capacitor by a constant current in the *ON* position and discharges the capacitor in the *OFF* position. It is possible to scan in either direction by reversing the polarity of the connections to the voltage source. A decided advantage of the electronic scan over the usual motor-driven potentiometer is that it produces much less electrical noise.

The polarograms are recorded on a Houston Instrument Co. HR-92 X-Y recorder with a maximum sensitivity of 1 mV/in. on both axes and a maximum pen speed of 7.5 in./sec. By this means it is possible to record current *vs.* scan potential directly rather than current *vs.* time. The pen maintains its position on the potential axis when the electronic scan is stopped. The X-Y recorder has the additional advantages of having built-in, continuously variable sensitivity controls for each axis and zero controls for positioning the pen at any point on the chart.

As can be seen from the schematic diagram, current is measured on the recorder Y-axis by the voltage drop across the precision resistors between the platinum working electrode and the output of the amplifier in the potentiostat circuit. The iR drop which occurs across these resistors is therefore compensated by the potentiostat and does not cause an error in the observed potential. The resistors indicated in Fig. 1 give sensitivities from 0.01–2.5 μA/mV.

The inputs for the X-axis of the recorder are connected to the output of the scan amplifier and to ground so that this channel of the recorder records the potential applied to the D.M.E. and is unaffected by the initial potential. It is possible to scan any reasonable potential range adjusting the recorder sensitivity so that the polarogram for this range will make full use of the graph paper to give the optimal sensitivity for determining the half-wave potential. While the use of an X-Y recorder is a convenience, it is by no means a necessity. Entirely satisfactory results may be obtained with a conventional single channel 1 mV recorder to register current *vs.* time, or a 10 mV recorder if the current sensitivity resistors are increased correspondingly.

The initial potential source consists of a three-volt battery and two one-turn potentiometers, which allow the initial potential to be set at any value between ± 3.0 V to within ± 0.2 mV. A potentiometer accurate to ± 0.1 mV (Rubicon Instruments Model 2700) was used to measure the initial potential and to monitor the electronic scan. The potentiometer is set for the scan-range and when the galvanometer needle passes through the null point, the polarogram is stopped. In this way, it is possible to establish the final potential very exactly. The half-wave potential is then obtained by interpolation between the initial and final potentials. Reproducibility of the half-wave potentials is excellent; the standard deviation of a series of 20 measurements of the half-wave potential of cadmium in 1 *M* chloride medium was 0.98 mV.

The basic instrument described here may be simply constructed in most chemical laboratories since the components required, including the operational amplifiers and their power supply, are readily available. The maintenance of this type of all-electronic polarograph has been found to be minimal. In more than two years of operation, there have been no difficulties encountered with the polarograph itself, and it has been necessary only to replace periodically the batteries in the polarograph and recorder. Because of the reliability and convenience of operation of this type of polarograph, a unit based on these principles is highly to be recommended even for applications in which high cell resistance is not a problem.

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Transference numbers in concentrated sodium perchlorate solutions

In order to evaluate the Planck and Henderson equations[1] for the junction potential between relatively concentrated sodium perchlorate solutions, it was found necessary to determine transference numbers in these solutions for concentrations in the range 4–10 molal (m). The only experimental technique which proved to be readily applicable to such concentrated solutions was that of e.m.f. measurement on concentration cells[2,3].

For a concentration cell (reversible, with transference) of the general type

$$\mathrm{M} \mid \underset{a_1}{\mathrm{MA(aq)}} \parallel \underset{a_2}{\mathrm{MA(aq)}} \mid \mathrm{M}$$

the e.m.f. is given by

$$E_t = \frac{ztRT}{nF} \ln \frac{a_1}{a_2}$$

where z is the total number of ions produced by dissociation of one molecule of the salt, and t is the transference number of the ion not involved in the electrode reaction. For a cell without transference,

$$\mathrm{M} \mid \underset{a_1}{\mathrm{MA(aq)}} \mid \mathrm{A} \mid \underset{a_2}{\mathrm{MA(aq)}} \mid \mathrm{M}$$

the e.m.f. is

$$E = \frac{zRT}{nF} \ln \frac{a_1}{a_2}.$$

Where the e.m.f.'s of both cells are determinable, the transference number is obtainable from the relation $t = E_t/E$. This value applies to a concentration which is the average of the two cells if the change in transference number may be assumed to be a linear function of concentration in the range involved.

In the case of sodium perchlorate, a concentration cell with transference can be made with identical sodium amalgam electrodes. It is not possible to determine experimentally the e.m.f. of a cell without transference for this system because there is no reversible perchlorate-ion electrode. The potential of the hypothetical cell

$$\mathrm{Na(Hg)} \mid \underset{a_1}{\mathrm{NaClO_4(aq)}} \mid \mathrm{M} \mid \underset{a_2}{\mathrm{NaClO_4(aq)}} \mid \mathrm{Na(Hg)}$$

(in which M is an electrode reversible to the perchlorate ion) can, however, be calculated from known values of the activity coefficient of sodium perchlorate[4,5].

EXPERIMENTAL

The sodium amalgam to be used in the concentration cell was prepared by the constant current electrolysis of a concentrated solution of sodium hydroxide between a mercury cathode and platinum anode. The solution was de-aerated with nitrogen before and during electrolysis and the mercury surface was stirred with a glass-covered magnetic stirring bar. The amalgam was made approximately 0.05% sodium by weight. The actual concentration of sodium is not critical because e.m.f. is independent of the amalgam concentration, if it is the same in both halves of the cell. The amalgam was stored under a layer of benzene and a nitrogen atmosphere. Transfers were made under benzene and by nitrogen pressure.

The final form of the concentration cell used is shown in Fig. 1. The two halves of the cell were identical. Each consisted of a 500-ml, three-necked flask in which were mounted a fritted-glass nitrogen bubbler for de-aeration and stirring, a sodium amalgam trap to prevent the amalgam from reacting with the solution, a nitrogen vent, and a streaming sodium amalgam electrode. The streaming electrode was made from a 25-ml separating funnel connected to a piece of 1-mm i.d. capillary tubing drawn out to a fine tip to produce a continuous sodium amalgam stream approximately 1.5 cm long. Electrical contact between the amalgam and the measuring potentiometer was made by means of a platinum wire sealed into the streaming electrode.

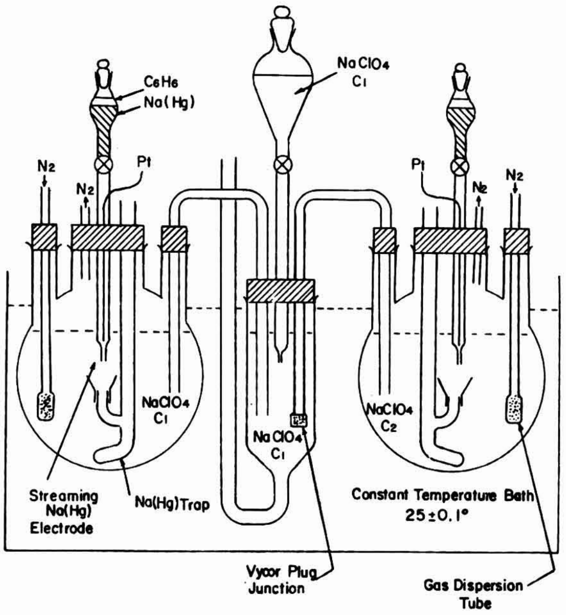

Fig. 1. Streaming sodium amalgam cell with transference.

The ~~amalgam in the separating~~ funnels was covered by a layer of dry benzene to minimize air oxidation of the sodium. Each flask was connected by a solution bridge to a third container in which the actual junction was formed. The solution in the center cell was the same as in one of the flasks, and the bridge connecting them was open. The other flask was connected by a bridge closed by an unfused-Vycor plug across which the boundary exists. The separating funnel and vacuum line attached to this middle cell were used for levelling the solutions and emptying the cell. The entire apparatus was immersed in a constant temperature water bath held at 25±0.1°.

The sodium amalgam traps were found necessary because the sodium amalgam

TABLE 1

RESULTS OF TRANSFERENCE NUMBER MEASUREMENTS

$NaClO_4$ concn. (m)			E_t[a]	E[b]	t_-
Cell No. 1	*Cell No. 2*	*Average*			
3.0	5.0	4.0	0.0146	0.0292	0.500
4.0	7.0	5.5	0.0193	0.0349	0.553
5.0	6.0	5.5	0.0062	0.0112	0.554
4.0	10.0	7.0	0.0365	0.0600	0.609
6.0	8.0	7.0	0.0110	0.0191	0.576
7.0	10.0	8.5	0.0172	0.0251	0.685
9.0	11.0	10.0	0.0118	0.0151	0.782

[a] E_t is the measured e.m.f. of the concentration cell with transference.

[b] E is the e.m.f. calculated from activity data for a cell without transference.

reacted with water to form sodium hydroxide which disrupted the e.m.f. readings. With this arrangement, however, it was possible to get e.m.f. measurements which were stable to 0.1 mV for at least 5 min, after which time the traps overflowed and the amalgam reacted with the solution. In actual operation, the solutions in the flasks were de-aerated for about 1 h before the streaming amalgam electrodes were turned on and the e.m.f. measurements made. The results are summarized in Table I. It can be seen from Fig. 2, where the transference number of the perchlorate ion is plotted against the concentration of sodium perchlorate, that the total change in the transference number over the range 4–10 *m* is 0.28. Using these values of the transference number in conjunction with the activities of sodium perchlorate, junction potentials can be determined by the graphical integration of the Planck and Henderson equations.

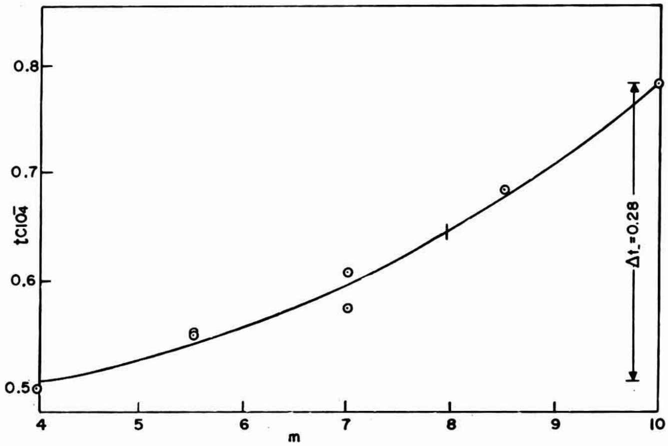

Fig. 2. Transference number of perchlorate ion as a function of sodium perchlorate concentration.

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Book Review

Electrochemistry, by G. MILAZZO, Elsevier Publishing Co., Amsterdam, London and New York, 1963, xv + 708 pages, £5.10.0.

This expensive book is beautifully produced. It is a pity that it cannot be recommended. The reviewer's irritation with it diminished as he reached the later chapters. These are largely concerned with the technological details of industrial electrolytic processes in both aqueous and molten salt solutions, and of primary cells and storage batteries. There is here a wealth of information in readable form. These chapters on industrial electrochemistry are preceded by chapters on analysis and on colloid chemistry; both these topics are adequately treated in several other text books.

The first 180 pages of the book are devoted to a discussion of electrolyte solutions and galvanic cells (pH, buffer solutions, and indicators are not dealt with). The kindest thing that can be said about this part is that it would have been better if it had never been written. It simply does not bear comparison with books such as those of MACINNES, ROBINSON AND STOKES, and KORTÜM. To condense the material given in books such as these into 180 pages is a formidable task and the author has not succeeded. A detailed critique would run to several pages. The text contains erroneous and misleading statements dealing with such fundamental and elementary topics as the definition of concentration (p. 14) and of rational activity coefficients (p. 150). The Debye–Hückel theory is identified with total dissociation (p. 86), and the entire treatment of the effects of coulombic interaction on the behaviour of solutions of strong and weak electrolytes is unsatisfactory. A well-defined potential for a hydrogen electrode is stated to depend on the validity of Henry's Law for the solubility of gaseous hydrogen in platinum (p. 124). The discussions of experimental methods of measuring conductance (pp. 49–51) and e.m.f. (pp. 99–106) are both inadequate and misleading, and there is no proper discussion of how to analyse results. The nomenclature recommended by C.I.T.C.E. is used in a thoroughly confusing way. Indeed, the first part of the book can be guaranteed to confuse anyone.

J. E. PRUE, University of Reading

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