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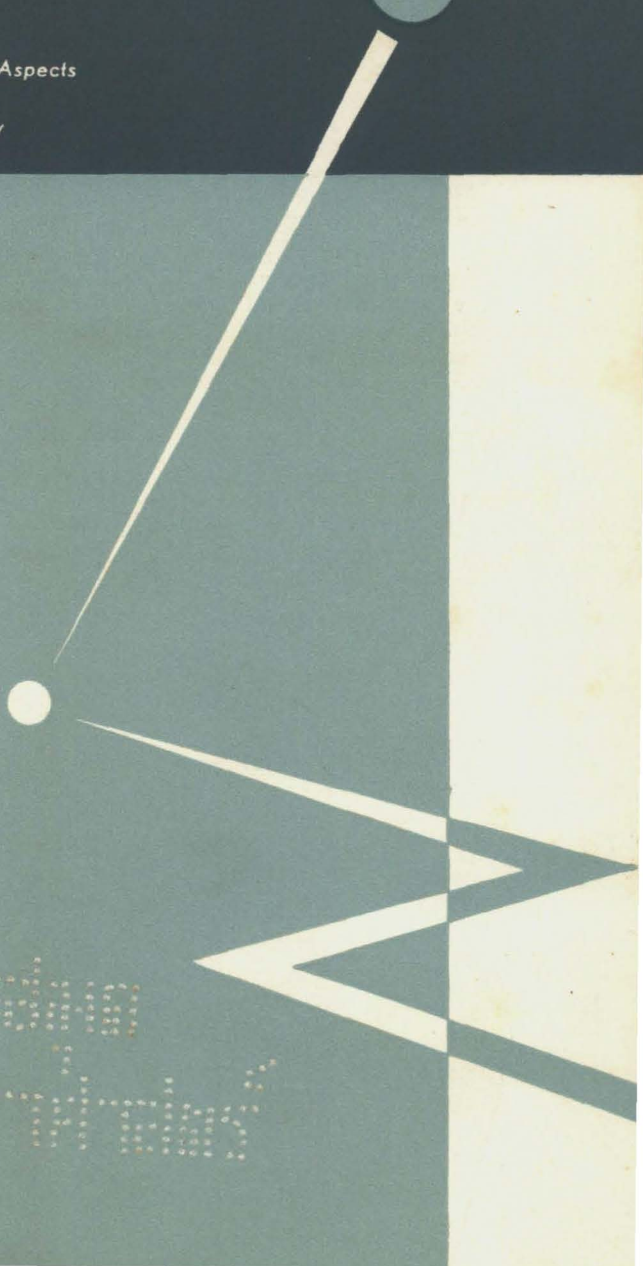

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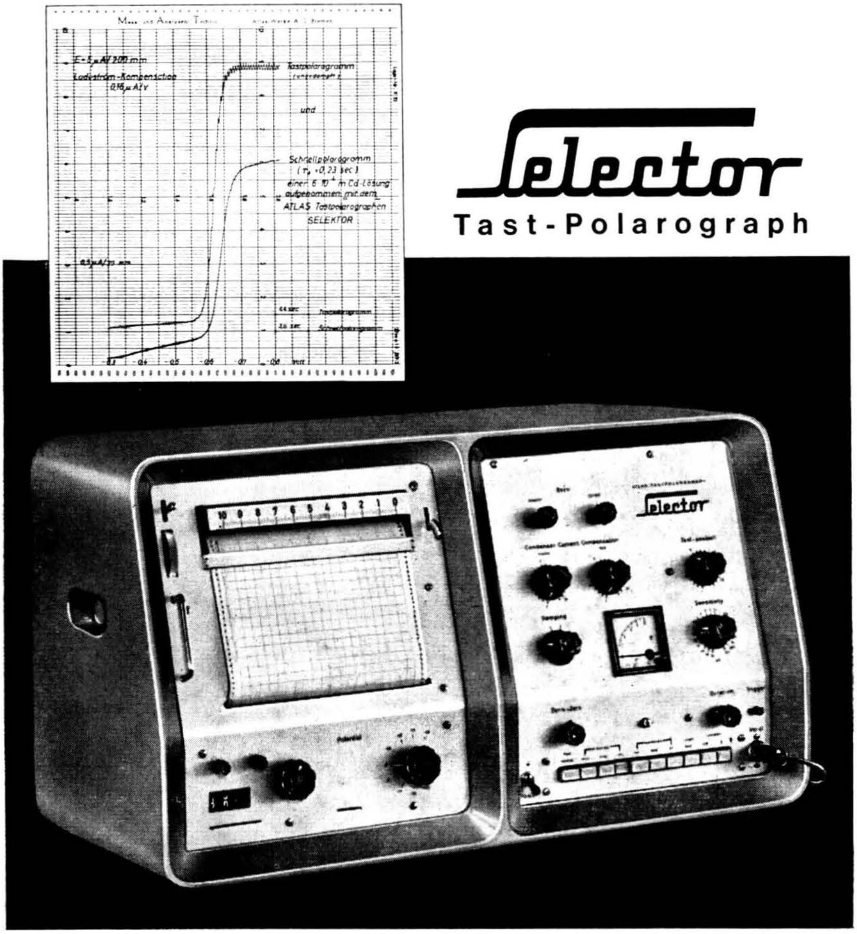

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The abstracts are for convenience divided into ten sections as follows:

1. Fundamental electrochemistry
2. Apparatus and accessories
3. Polarography
4. Potentiometry
5. Conductometry
6. Electrolysis
7. Coulometry
8. Electrophoresis
9. Other methods
10. Related topics

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REVIEW

CONDUCTOMETRY AND OSCILLOMETRY

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(Received January 30th, 1962)

Of the instrumental methods used in analytical chemistry, conductometric titrations were among the first. From Kohlrausch's law, it can readily be understood, that when changes occur in the type and quantity of ions in solution during the titration, the conductance of the solution also changes. Conductance can be measured using metal plates immersed in the solution, and this procedure is called conductometry. Another method is to observe a physical quantity related to the conductance, in an electrode-free system. This can be carried out in such a way, that for the actual measurement a low frequency, or eventually a high frequency, method is applied. In the latter case, the method is called oscillometry.

THEORETICAL FUNDAMENTALS

Changes in the conductance of solutions during titration serve as common bases for both conductometric and oscillometric titrations. In the case of acid–base titrations, and of other titrations connected with conductance changes, the changes can be calculated on the basis of the mobilities of all the ions participating in the reaction. In recent years, the solution of problems connected with the titration curves of weak acids has been approached, to a great extent, by the investigations of GILBERT[1], who unambiguously stated that, for conductometric titrations, the concept of strong and weak acids is related to the problem of the concentration of the solution. A hyperbolic relation proved to exist between the conductance of the solution and the degree (ξ) to which the acid had been titrated*. The minimum of the titration curves actually coincides with the peak of the hyperbola. It was found further, that the salt line is the asymptote of the titration curve measurable with weak acids.

GILBERT also succeeded in evolving a method for the calculation of minimum conductances of various concentrations of acids of different strengths. For this purpose, the following formula is suggested:

$$\xi_{\min} = \frac{K}{C} + (\Lambda_H - \Lambda_A - 2\Lambda_B)\sqrt{\frac{1}{(\Lambda_A + \Lambda_B)(\Lambda_H - \Lambda_B)}\,\frac{K}{C}}$$

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* The degree of the titration is defined as the ratio between the volume (V) of titrant added to the solution to be titrated, and the volume of the titrant added to the solution to reach the end-point (V_e), *i.e.* V/V_e.

where K is the thermodynamic dissociation constant of the acid*, C the original concentration of the acid to be titrated and Λ the equivalent conductance, while A, B and H denote acid anions, base cations and hydrogen ions, respectively.

The above formula holds for every acid, provided we accept that the minimum value is virtual at a $\xi_{\min}$ value exceeding unity. In this case, on titrating an acid with a strong base, a V-shaped curve is obtained, *i.e.* a titration curve characteristic of strong acids.

The determination of two or more acids in the presence of each other is affected to a great extent by the minimum conductance mentioned already. It was found that on titrating multi-basic acids, either by conductometry or by oscillometry, the first point of inflexion does not correspond to the expected equivalence point. Measurements of this type are presented in Fig. 1, indicating that the site of the first point of inflexion migrates with changes in the dielectric constant of the medium[2], while that of the second point of inflexion remains the same.

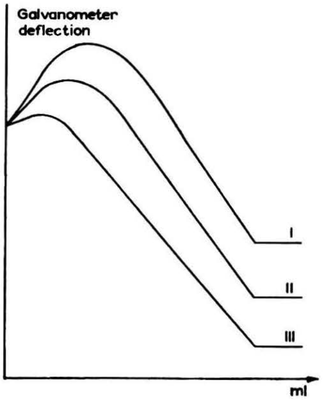

Fig. 1. Titration of dibasic acid with NH_4OH; (1), water solution; (2), 25% ethanol–water solution; (3), 50% ethanol–water solution.

It is not possible to carry out the titration of hydrochloric acid and acetic acid in the presence of each other without an end-point error, because the minimum conductance of acetic acid appears as the end-point of the titration. The accuracy of the measurement can be increased by decreasing the dielectric constant of the medium, or by increasing the concentration of acetic acid[3]. These statements are in unequivocal accordance with the GILBERT theory.

The method of end-point determination presents a problem common to both conductometry and oscillometry. This is of particular importance in the titration of weak acids and bases, where, on approaching the end-point, the reaction rate decreases[4], and thus, at the end-point instead of a point of inflexion, a transitional section along a curve appears. This problem has been elucidated by GRÜNWALD[5]. He presents a method, based on theoretical fundamentals, by which it is possible to calculate from three arbitrarily chosen values of measurement, a fourth value. With the aid of this

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* The above equation predicts that the conductance minimum varies with the strength of the acids and their concentrations.

fourth value, the required two straight lines intersecting each other can be constructed. For the simple reaction,

$$A + B \rightleftarrows C + D$$

the formula for calculation is as follows:

$$\frac{\xi'_1 + \xi_1 - 2\xi_1\xi'_1}{(1 - \xi'_1)(1 - \xi_1)} = \frac{\xi'_2 + \xi_2 - 2}{(\xi_2 - 1)(\xi'_2 - 1)}$$

where ξ_1 is the degree of titration, and ξ_2 the degree of over-titration*.

For titrations carried out on the basis of conductance measurements, an appreciable advance was made by a publication of GASLINI AND NAHUM[6,7] who presented a solution of the problem of titration of weak acids and bases. It has already been mentioned earlier that weak acids react slowly in the vicinity of the end-point. Thus, in general, the region ± 15% from the end-point is unsuitable for the evaluation of acid–base titrations. In this connection, for the measurement of very weak acids (where K values are below 10^{-8}) and for the determination of very weak bases (K values are below 10^{-8}), respectively, GASLINI AND NAHUM suggest in a very ingenious way, that first the salts of the very weak base and acid with a weak electrolyte should be formed, and subsequently, a displacement titration should be carried out. On measuring weak acids, the acid is dissolved in about 1.0 *M* ammonia, then the acid component is titrated with lithium hydroxide. In the case of very weak bases, acetic acid, similarly about 1.0 *M* concentration, may be used as solvent and titration can be carried out with trichloroacetic acid. With extremely weak electrolytes (where K reaches below 10^{-12}), determination is made difficult in an aqueous medium, even by this method, due to hydrolysis. According to GASLINI AND NAHUM, in this case, satisfactory results can be attained in a medium of 50% ethanol and water.

When one of the components is a strong electrolyte in displacement titrations, a negative error appears at the end-point. As an example, the displacement titration of borax with hydrochloric acid can be mentioned[8]. The dissociation constant of borax is $7.3 \cdot 10^{-10}$ at 20°. When, in addition to borax, free boric acid is also present, the negative error of titration increases, as shown by the data in Table I

TABLE I

TITRATION OF BORAX IN THE PRESENCE OF EXCESS BORIC ACID

Concentration of excess boric acid (mole/l)	*Amount of 0.1 N HCl consumed (ml)*	*Difference between calculated and measured consumption (ml)*
—	10.40	—
$3.3 \cdot 10^{-3}$	10.35	0.05
$1.0 \cdot 10^{-2}$	10.30	0.10
$2.0 \cdot 10^{-2}$	10.22	0.18
$3.3 \cdot 10^{-2}$	10.17	0.23
$4.0 \cdot 10^{-2}$	10.15	0.25
$5.0 \cdot 10^{-2}$	10.12	0.28

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* The degree of over-titration is defined in the same way as the degree of titration, taking as numerator the entire volume of titrant added until the actual point being measured is reached, in the case of over-titration.

Oscillometric measurements, besides the general theoretical advances, have been successfully extended in many new directions. Statements of prominent theoretical importance, concerning the fundamental principles of capacitative and inductive measurements carried out using conductance and susceptibility methods, are mainly merited by CRUSE and his co-workers[9–14]. Within the framework of these, the research of RIECKE AND CRUSE in recent years gave results of the greatest significance, in that they solved the problem of describing capacitative measuring cells theoretically.

APPARATUS AND TECHNIQUE OF MEASUREMENTS

In conventional conductometric measurements, two electrodes are used. The position of these electrodes in relation to each other, the areas of their surface etc., raise a number of problems, (Parker effect, Shedlovsky effect, and polarisation phenomena). In order to prevent polarisation phenomena, platinization of the platinum electrodes proved to be practical. Side circuits were ingeniously eliminated by NICHOL AND FUOSS[15], by using electrodes which were cylindrically symmetrical, and further improvements were made by SCHMIDTS AND BARTSCHER[16], who carried out conductance measurements using three electrodes, placed in a capillary in such a way that both extreme electrodes were maintained at an identical potential. Obviously, owing to the presence of this capillary, only very low current intensities are permissible in this system, to avoid overheating the liquid in the capillary.

As in all fields of instrumental analysis, the application of these methods in automation and in automatic analysis has become increasingly important in recent years. The bridge method in conductometry has, in this respect, the disadvantage of making a so-called zero-compensation necessary. Therefore, direct measurements came into prominence within the sphere of conductometry proper, and the so-called four-electrode conductometers have been evolved. Instruments of this type have been constructed both for direct current[17–21], (in some cases with two electrodes[22]), and for alternating current[23–24]. The method of operation, in principle, is as follows. Current is led through two so-called primary electrodes, and the fall of potential occurring between them is measured by a "sonde", *i.e.* two other electrodes located in the cir-

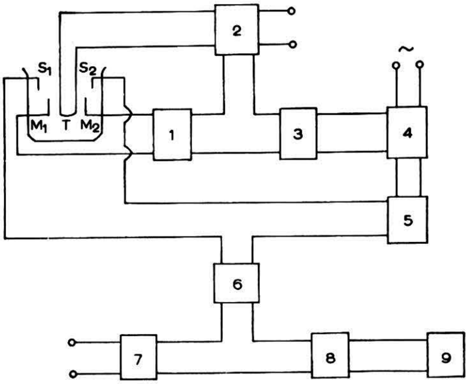

Fig. 2. S_1 and S_2, primary electrodes; M_1 and M_2, secondary electrodes; T, thermistor; 1, a.c. amplifier and rectifier; 2, correction equipment, which uses the thermistor; 3, d.c. amplifier; 4, magnetic amplifier; 5, transformer; 6, current transformer and rectifier; 7, d.c. controller; 8, d.c. amplifier; 9, registration unit.

cuit. The fall of potential on the latter electrodes is proportional to the resistance of the solution. Also, non-polarisable electrodes prepared from common metal plates were applied with success.

The communication of BARENDRECHT AND JANSSEN[24] presents examples of direct methods of measurement. A block diagram of the apparatus suggested by these authors is shown in Fig. 2. The a.c. potential taken from the measuring electrodes M_1 and M_2 is corrected, subsequent to amplification and rectification, in the d.c. section of the apparatus. This correction is carried out by the thermistor. Eventual fluctuations of the temperature of the cell leading to changes in resistance are then compensated by a suitably chosen thermistor.

The differences in signs (*i.e.* of potential) developed in this way are then amplified by a d.c. amplifier; a magnetic amplifier is governed by the d.c. potential, adequately amplified. The current feeding the two primary electrodes S_1 and S_2, (of the four electrodes of the cell) flows through the magnetic amplifier. This current is adjusted with the aid of the magnetic amplifier in such a way that the potential drop between the electrodes M_1 and M_2 remains constant, even when the resistance of the cell changes. Consequently, the current passing the electrodes S_1 and S_2 shows, according to Ohm's law, a linear change with the resistance of the measuring cell. Thus, an inverse relationship exists between the intensity of the rectified current after transformer (6) and the resistance of the solution. The magnitude of the potential received by the detector is controlled by unit (7) in such a way that a part of the potential existing after rectification is compensated.

This apparatus is suitable for long-period measurements of conductance, due to its stable construction. After establishing the amplifying factors (units (6) and (8)), the registering unit can be calibrated in ohms, or mhos (reciprocal ohms, Siemens).

In the apparatus based on the bridge method, attempts were made to evolve zero indications of increased sensitivity. The telephone transmitter method has been replaced by zero indication, first with a magic eye, and later with an oscilloscope. In conductometric titrations, great accuracy in conductance measurements is not needed, and thus, in addition to precision bridges, also less precise, cheaper conductometers were brought into commercial use. In one of these types, the simple principle that the reference resistance and the resistance to be measured are represented separately by the grid resistances of two separate triodes is used, and an a.c. of a frequency deviating from that of the mains is applied to these two resistances. The governing voltage generated in this way affects the anodic current of the valves, and on the common anodic loading resistance, a point can be found at which, on coupling one of the tubes, the voltage generated by the other tube can be reduced to zero. On applying zero indication using a magic eye, this point of the potentiometer, which is constructed in a helipot-like shape, can quickly be found during the titration, and the evaluation of end-point indication of titrations can be established on the basis of the helipot position calibrated for μ ohms.

When a.c. bridges are used for measurements, low frequencies are applied. In general, frequencies not exceeding 5 kc/s are used. As we have seen, electrodes with direct galvanic couplings can be applied successfully in this region of frequencies. Recently, some ingenious attempts were made to make operations possible at low frequencies without the use of electrodes. In this field, the research of GRIFFITHS[25–27] made a marked advance. The instrument which he used for this purpose was constructed in such a way, that the solution to be measured was placed in a glass cell located in the core of the transformer.

The techniques of oscillometric, or under another name, of high frequency measurements can be classified from various aspects. The most practical classification is based on measurements made during actual high frequency titrations. This system is based on the distinction, that the total admittance, or only a real or imaginary part of it, may be measured. For the first category, the methods of measurement used by BLAKE are characteristic[28–32]. The methods of conductometry are based on measuring and following the changes of conductance[33–51], while susceptibility can be followed by the frequency drifts of the oscillating circuit[9, 52–54]. In both latter groups, a number of instruments have been constructed in the last decade.

In most of the instruments applied today, the solution under investigation is placed in the field of a condenser[55–63] or of an inductance coil[10,34,36–39,46,64–66], and thus, it forms a part of the oscillating circuit proper. The frequency of the oscillating circuit shifts to an extent proportional to the change in the imaginary portion of the a.c. conductivity: this is a measure of the susceptibility. Between this latter and the d.c. resistance of the solution the following relation exists using a capacitative cell

$$A_i = \frac{\omega C_1 + \omega^3 R^2 C_1 C_2 (C_1 + C_2)}{1 + \omega^2 R^2 (C_1 + C_2)^2} \qquad (1)$$

where the values of C_1 and C_2, and also of R can be obtained from the circuit shown in Fig. 3, which replaces the cell, in the case of a capacitative measuring cell, while $\omega = 2\pi\nu$ is the frequency of the circuit concerned.

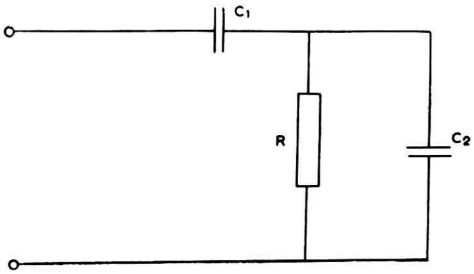

Fig 3. Equivalent circuit which can be used to replace a capacitative measuring cell.

A linear correlation exists between the concentration of the solution and its d.c. conductance. Thus, in the functional relation, d.c. conductance can be replaced by the concentration of the solution. On plotting susceptibility against the logarithmic values of the concentration of solution, (according to CRUSE AND HUBER[67]), curves of the type shown in Fig. 4 are obtained. Consequently, if titrations are performed using observations of the susceptibility values, the titration curves alter with changes in concentration only in such a way that the sensitivity of the determination appears at the point of inflexion of the susceptibility diagram shown in Fig. 4.

The simplest way to determine the imaginary component of the a.c. conductivity is to compare the frequency of the oscillating circuit containing the solution to be measured, with the frequency of the standard oscillating circuit. Of the instruments evolved so far, that of CRUSE and co-workers[9] is the most ingenious. This is operated at two frequencies, with two oscillating circuits at each frequency. One of the oscillating circuits contains the solution to be measured, in a capacitative cell, while the other is in an inductive cell. Cruse's instrument also lends itself to registration and derivation of the titration curves. The derived titration curves have sharp inflexion points suitable for precise evaluation[68].

The real portion of admittance, conductance, can be followed by the Q-factor of the oscillating circuit. The anodic current or the grid current of the electronic valve in the oscillating circuit can be measured. The anodic current increases, while the grid cur-

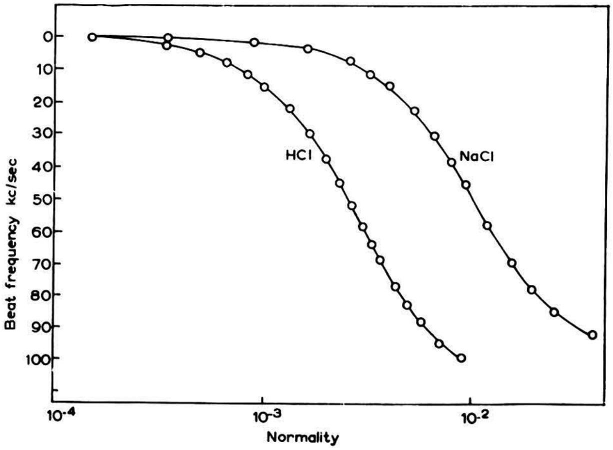

Fig. 4. Calibration diagram for susceptibility measurements (after BLAEDEL AND MALMSTADT[53])

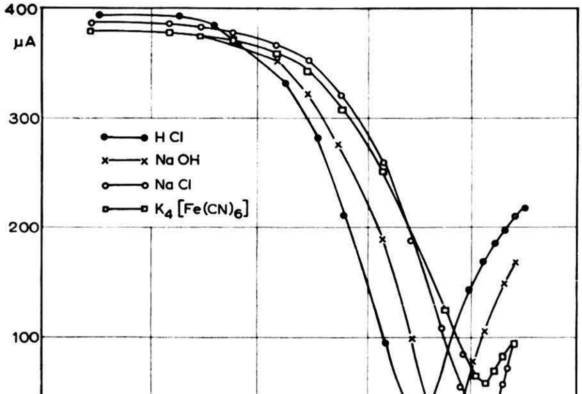

Fig. 5. Calibration diagram for conductance measurements.

rent decreases with the decrease of Q-factor. The correlation between conductance and d.c. resistance can be expressed by the following formula:

$$K = \frac{\omega^2 R C_1^2}{1 + \omega^2 R^2 (C_1 + C_2)^2} \qquad (2)$$

where the symbols have the same significance as in eqn. (1)

It appears from eqn. (2) that a rather complicated relation exists between conductance and d.c. conductivity, and the concentration of the solution, as already explained above. As shown by Fig. 5, a correlation of an extreme curve type exists between the logarithmic value of concentration and conductance. When grid current is used, a minimum appears. From this it follows that in the case of the same reaction, titration curves may have different shapes on both sides of the maximum value. This is indicated by Fig. 6 for the case of curves measured during the titration of hydrochloric acid and sodium hydroxide. The only difference between these titration curves appears in their initial concentrations.

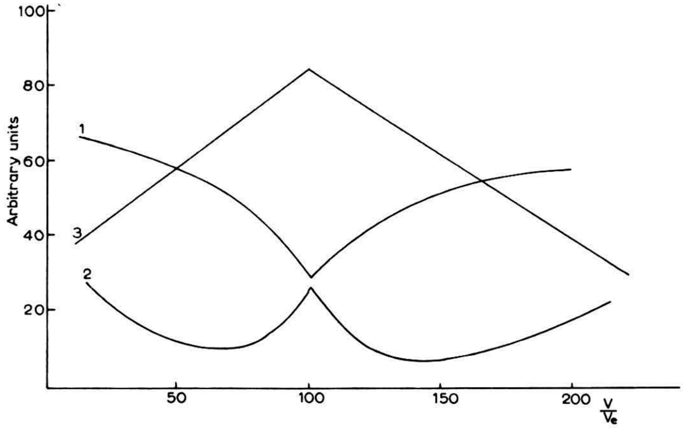

Fig. 6. Titration curves in a capacitative cell with an oscillo-titrator of 130 Mc/s, for the case of HCl–NaOH: 1), 5 ml of 10 N HCl titrated with 10 N NaOH; 2), 5 ml of N HCl titrated with N NaOH; 3), 5 ml of 0.1 N HCl titrated with 0.1 N NaOH.

The Q-factor of the oscillating circuit can be followed by an instrument, where the oscillating circuit is not operated at a forced frequency[45], though devices can also be constructed where a forced frequency[49] is applied in the oscillating circuit. In the latter case, a value proportional to the apparent Q-factor is obtained.

As we have seen in the discussion, high frequency investigations can be carried out both in capacitative and in inductive cells. When applying the frequency shift method, a high frequency is necessary for the investigation of systems of high conductance, as calculated by the formula,

$$\frac{1}{K} = \frac{1}{\omega(C_1 + C_2)} \sqrt{\frac{\frac{1}{\omega^2} - \frac{1}{\omega_0^2}}{\frac{1}{\omega_\infty^2} - \frac{1}{\omega^2}}} \qquad (3)$$

where ω_0 corresponds to the values for $R = 0$, and ω_∞ to those for $R = \infty$. On using inductive cells instead of capacitative cells, the reverse case exists, *i.e.* the frequency values can be reduced with increasing conductance. *E.g.* when the method of investigation suggested by CRUSE[10] is used for plotting phase diagrams using a high frequency method, it is practical to use inductive measuring cells. In this case, the correlation of frequency shifts is expressed by the formula,

$$\frac{1}{K} = \frac{\omega}{k\left(1 + \frac{L_1}{L_2}\right)} \sqrt{\frac{\omega_\infty - \omega^2}{\omega^2 - \omega_0^2}} \tag{4}$$

In eqn. (4) k is a constant depending on the shape of the cell, while L_1 and L_2 are the enclosing and measuring self induction coils.

In the case of a capacitative measuring cell, the frequency for methods based on following the frequency shift and Q-factor can be found from the relation shown in Fig. 7, on the basis of work done by TARNAY AND JUHÁSZ[69]. It must be noted that the curves of susceptibility against the logarithmic values of concentrations, and of conductance against the logarithmic values of concentrations, respectively, are characterized by the fact that in the case of identical frequencies, the inflexion point of the first curve coincides with the maximum of the conductance curve.

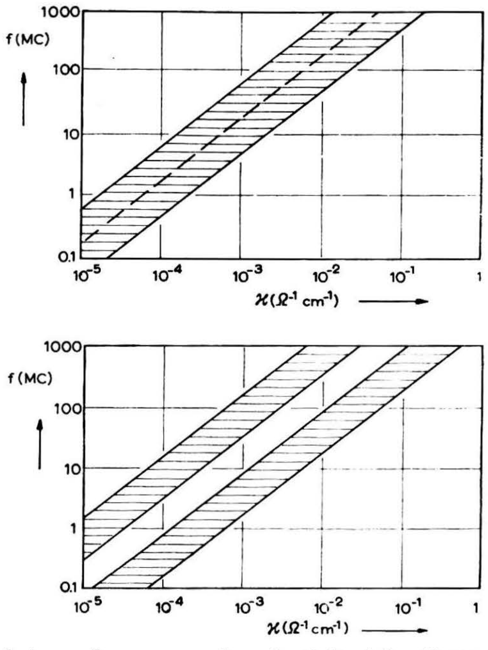

Fig. 7. Correlation between frequency and conductivity (after TARNAY AND JUHÁSZ[69]).

PRACTICAL APPLICATION OF CONDUCTOMETRIC AND OSCILLOMETRIC MEASUREMENTS

Acid-base titrations

In conductometry and oscillometry, acid–base titrations and determination of acids and bases in the presence of each other have already been discussed in the theoretical survey. With suitable conditions, two or even more acids can be determined by measuring their conductance, using either conductometric or oscillometric methods, with satisfactory accuracy. From a practical aspect, conductometric and oscillometric measurements are suggested mainly for use in cases where end-point indication by coloured indicators cannot be used, or, when the dissociation constant of the electrolyte in question is so low that potentiometric titration does not appear to be promising.

The conductometric method can be applied with success for determining free acid in the presence of metals which hydrolyse (PEPKOVITZ and co-workers[70], and MUNAMORI[71]). This method has been evolved with the use of sodium fluoride. GUPTA[72,73] successfully measured the amount of hydrogen ion dissociating from micelles of colloidal substances, using barium hydroxide. MORTLAND AND TIMNICK[74] measured the hydrogen capacity of zeolites using oscillometric methods.

In the determination of very weak acids, *e.g.* for the measurement of phenols by the method of GASLINI AND NAHUM[7], direct and indirect methods can be applied. KOLTHOFF[75] titrates phenols by conductometry with sodium hydroxide, while lithium hydroxide as titrant has been suggested by JAMIESON[76] and mainly by SARKANEN AND SCHNERCH[77]. In the indirect method, excess lithium hydroxide is added to the solution, and the excess is titrated with hydrochloric acid.

Very weak bases can be titrated using the method of GASLINI AND NAHUM[6]. A procedure which is also suitable for the measurement of certain weak bases is the combined use of acid–base and precipitation reactions. Thus, the displacement–precipitation titration of alkaloids dissolved in acetic acid has been carried out using silico-tungstic acid[78].

Displacement titrations in aqueous media were recently utilized in the determination of sodium carbonate in mixtures with sodium bicarbonate[79], and of the aluminium content of aluminate liquors[80–81].

A considerable number of communications[82–100] published in the field of conductometric and oscillometric acid–base titrations discuss acid–base measurements in non-aqueous media. Here, mainly ethanol–benzene, glacial acetic acid, pyridine and dimethyl formamide have been used as solvents. Perchloric acid (dissolved in glacial acetic acid), sodium ethylate (dissolved in a benzene–methanol mixture and used as an alkali in the solvents benzene–methanol and dimethyl formamide), sodium acetate (dissolved in glacial acetic acid, and used as a base in glacial acetic acid titrations), potassium hydroxide (dissolved in ethanol, and used as a base in pyridine solution) have been suggested as titrants. From the aspect of acid measurements in non-aqueous media, VAN MEURS'[90] research is of fundamental importance, because it establishes the following criteria for evaluated titration curves.

1). The components to be measured can be solvated by the solvents only to a small extent.

2). The dielectric constant of the solution should be below 20, if this is possible.

3). The base cation applied in the titrations should preferably possess a small volume.

4). The titrations should preferably be carried out at high temperature.

The investigations of KARRMAN AND JOHANSSON[41], and DEAN AND CAIN[83] must be mentioned, in reference to the technique of oscillometric acid–base measurements in non-aqueous media. These further the fundamental research which has meant an appreciable advance in the theory of non-aqueous solutions (SPANDAU AND BRUNNECK[89], PAUL AND JOHAR[91], JANDER AND WINKLER[93], etc.). Through this research, our knowledge of the properties of the solvents thionyl chloride and benzoyl chloride was extended.

The investigations of VAN MEURS AND DAHMEN[98], WAGNER AND KAUFFMANN[95], and LIPPINCOTT AND TIMNICK[97] contributed to an appreciable extent to the advance in the determination of nitrogen bases in non-aqueous solvents, mainly in glacial acetic acid.

In a glacial acetic acid medium, OEHME[99,100] found that amino acids can be titrated in the presence of peptides, using oscillometric methods. Further, he evolved a method for the oscillometric determination of various antibiotics (terramycin, actinomycin) in a glacial acetic acid medium.

Precipitation titrations

Besides the argentimetric haloid determinations[2], conductometric and oscillometric methods can be used in an ethanolic medium for determination of sulphanilamide[10], and in a neutral medium for determination of sulphathiazole[102], mercaptan, mercapto-benzthiazole, sulphide[103], etc.

Sulphate can be determined using a barium salt. However, in this case, the formation of centres of crystallization must be promoted by addition of barium sulphate crystals, and, on adding ethanol, the solubility of barium sulphate is reduced[2].

Also, the fact that the majority of bi- and tri-valent ions form precipitates with hydroxyl ions, can be utilized for precipitation titrations. Thus, *e.g.* magnesium can be titrated with barium hydroxide if carbon dioxide is excluded[104]. In order to prevent the adsorption of barium hydroxide on the surface of the precipitate, *p*-nitrophenyl-azo-1-naphthol is added to the solution.

In addition, precipitations by oxalate can be used in precipitation titrations. In this way, thorium and calcium can be determined[105]. Bismuth and uranium(VI) can be measured by titrations with pyrophosphate[106].

Fluoride can be determined by precipitation titration. The principle of this method is that fluoride is separated from the substance to be analyzed by distillation as hydrogen silico-fluoride, and this latter is then titrated with lanthanum acetate[107,108]. Fluoride can also be determined by titration with thorium nitrate[109].

An ingenious method has been evolved by CALMAR for the conductometric measurement of substances insoluble in water but capable of complex formation[110]. As an example, he mentions the determination of silver iodide. Here, silver iodide is dissolved in potassium cyanide, then the solution is titrated with hydrochloric acid. Three sections of the titration curve can be distinguished. The first represents titration of excess potassium cyanide, the second represents precipitation of silver iodide, due to decomposition of the complex, and the third shows accumulation of excess acid.

Titrations based on complex formation

In the field of conductometry, the greatest advance has been brought about by the work of SPECKER AND JACKWERTH[111] who suggested titrations based on complex formation with mono-functional ligands. The principle of their method is to transfer the metal from the aqueous phase into the non-aqueous phase (immiscible with water), by using complex forming agents. Conductance is then measured in the non-aqueous phase. For example, in the titration of iron with sulphocyanide, the iron–sulphocyanide complex formed is transferred, by shaking, into the cyclo-hexanone solution. In addition to its analytical significance, this method is also of importance from the aspect of complex chemistry, particularly with regard to the application of the JOB method[112]. However, on using this latter, one must take into account the fact, pointed out by TATE AND JONES[113], that in the course of the JOB method, the maximum of conductance coincides with the maximum concentration of the component bound as a complex only in the case where no changes of ionic strength occur during the constant variation.

From an analytical aspect, titrations using EDTA are of particular importance [114–120]. In this field, methods have been evolved for the determination of copper, iron, lead, cadmium, cobalt, nickel, thorium, lanthanum and uranyl ions. All of these, excepting uranyl ions, form 1 : 1 complexes, while uranyl ions bind the complexone only in a ratio of 1 : 0.5.

Also, oxy-tetracycline can be determined by complexometric titration[121]. In this case, displacement complex titrations can be carried out as well.

Titrations based on redox reactions

On systematically reviewing redox–conductometric titrations, CEAUSESCU[122] states that, in the main, those redox reactions can be used for conductometric (oscillometric) titrations where hydrogen ions are generated or hydrogen ions and hydroxyl ions respectively, disappear. Methods were evolved for the titrations of sulphite, arsenite and antimonite with a methanolic solution of iodine[123].

Use in chromatography

In chromatographic processes, the use of conductance measurements for the purpose of indication seems to be possible. Conductometric methods have been applied with success in the measurement of the exchange capacity of columns filled with ion exchangers, and in evaluating the surface of spots in paper chromatography. The use of conductometry in this latter field has been greatly extended recently, particularly by the work of BLAKE who evolved the method of so-called electrostatic discharge[124–125], for the measurement of the surface of spots in paper chromatograms.

Other possibilities of application

CRUSE and co-workers evolved oscillometric methods for plotting phase diagrams[10], and for the measurement of the rate of crystallization[12].

Also, procedures were developed for the investigation of drugs in ampoules during storage, without opening the ampoules. In this way, it was possible to follow the decomposition reactions taking place during storage in injections of chlorpromazin[126] and vitamin C.

Oscillometric methods can also be advantageously applied for the kinetic investigation of reactions which occur at moderately fast rates. Besides esterification and hydrolyzing reactions, the reactions by which complexes are formed with complexone(III) and complexone(IV), for various central atoms in the complex, have been followed kinetically, and possibilities of this process were investigated[127].

Conductometric methods can also be used for investigating systems of very low conductance, *e.g.* the recycle water of power stations.

The oscillometric method, in turn, lends itself to rapid determination of the salt content of natural water, a useful help in their evaluation.

Conductometric and oscillometric methods represent fields of instrumental analysis, which have developed in recent years at a fast rate. Particularly, oscillometric methods are expected to play a significant role in automation of the chemical industry.

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DETERMINATION OF TRACE AMOUNTS OF OXYGEN USING THE ALUMINIUM ELECTRODE. II

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INTRODUCTION

In order to establish suitable experimental conditions for using the aluminium electrode in the determination of trace amounts of oxygen, electric tension–time curves of the open galvanic cell, Cu | Al | solution | KCl agar bridge | S.C.E. | Cu, were determined:

using aluminium electrodes prepared from 99.99% pure metal and undergoing a mechanical treatment either alone or followed by an electrolytic treatment of anodization;

in distilled water;

in a 10^{-6} M $CuCl_2$ solution;

in electrolytically purified distilled water.

During determinations, the solution in the cell was saturated with purified hydrogen or with air and was thoroughly and continuously stirred at a constant rate.

MATERIALS, APPARATUS AND PROCEDURE

The electrodes, their preparation, mechanical and electrolytic treatments, apparatus and hydrogen purification were described in previous papers[1-3].

The anodization of the electrodes was performed at 20 V for 30 sec or at 60 V for 60 sec.

The distilled water was purified by means of electrolysis at controlled electric tension with a mercury cathode, according to the usual technique[4]; but care was taken to keep the stirrer close to the mercury but outside of it, in order to prevent contamination of the water by mercury.

Experiments were made with 100 ml of solution, using a cell similar to that previously described[3], but smaller. The solution was constantly stirred throughout the experiment. In the experiments in deoxygenated media, purified hydrogen continuously flowed through the solution at a rate of 20–30 ml/min.

RESULTS

Electric tension–time curves

The experimental conditions for the U–t curves determinations are shown in Table I.

In experiment No. 6, air was either bubbled into the cell (No. 6a) or not (No. 6b). Each experiment was run several times; curves differed, sometimes markedly, especially those of experiment No. 2 (mainly in the early part); however, they were close to each other and distinctive enough to distinguish them from those resulting from the other experiments. Typical curves are shown in Figs. 1 and 2.

TABLE I

Experiment No.	*Electrode treatment**	*Solution**	*Solution saturated with**
1	*m*	H_2O	H_2 *p*
2	*m,e* (20 V)	H_2O	H_2 *p*
3	*m,e* (60 V)	H_2O	H_2 *p*
4	*m,e* (20 V)	H_2O *p*	H_2 *p*
5	*m,e* (20 V)	10^{-6} *M* $CuCl_2$	H_2 *p*
6	*m,e* (20 V)	H_2O	air

* *m* = mechanical; *e* = electrolytic; *p* = purified.

Experiment No. 2 was run several times using the same portion of solution; the successive curves were found to shift gradually towards more negative values of tension.

In experiment No. 2, by adding small amounts of Cu^{2+} (so as not to bring the concentration to beyond 10^{-6} *M*) where the curve was poorly inclined, a stable rise of electric tension was obtained.

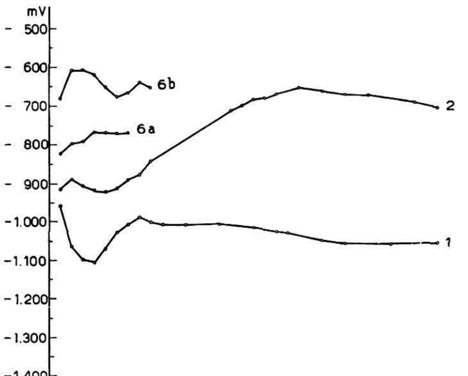

Fig. 1. Experiments Nos. 1, 2, 6a and 6b.

At the end of experiment No. 5, it was noted that the electrodes faintly stained filter paper, when rubbed on their active surface.

In experiments Nos. 1, 2, 3 and 4, the electric tension was usually stable within a

1 mV range, slight oscillations being seen at the minimum and maximum of the curves. In experiments Nos. 5 and 6, oscillations were found more frequently and were wider. Variations of stirring intensity caused the electric tension also to show variations, particularly where oscillations had previously occurred.

In experiments Nos. 2 and 3, by shifting the flow of hydrogen from the bulk of the solution over its surface, the electric tension increased and became stable within 10–20 min at more positive values; turning back the flow of gas into the bulk of the solution, the electric tension decreased and became stable within 10–20 min. These variations of the electric tension were wider in experiment No. 3, while in experiment No. 2, changes of the electric tension were limited, especially several hours after it had been started.

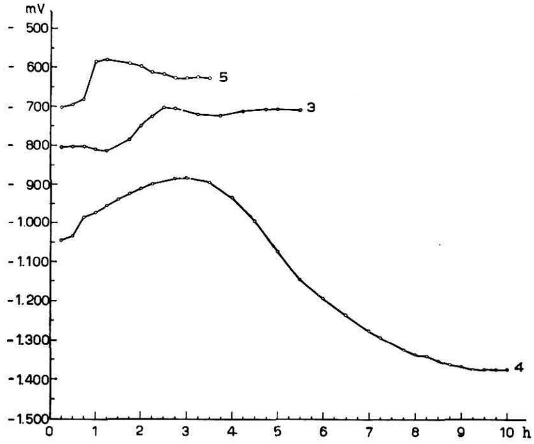

Fig. 2. Experiments Nos. 3, 4 and 5.

Influence of $[O_2]$ *variation*

In experiments Nos. 1, 3 and 4, coincidently with the portion of the curves showing a stable electric tension, and in experiments Nos. 2 and 5, at the slightly inclined sections of the curves, 0.1 or 1 ml of air were introduced into a vacuum rubber tube, inserted in the hydrogen pipe with a syringe, and carried by the hydrogen flow into the solution. Within a few seconds the electric tension increased, reached a maximum after 1–2 min, then decreased and became stable again within 10–20 min, to a value:

coincident or close to the previous one, in experiments Nos. 4, 3 and 2;
more positive or more negative, in experiment No. 1;
more negative, in experiment No. 5.

In experiments Nos. 1 and 2, the repeated additions of air caused the electric tension to shift permanently and markedly towards more negative values.

The immediate positive variation of the electric tension increased with the amount of air and was dependent on the hydrogen flow. It was highest in experiment No. 1 and lowest in experiments Nos. 5 and 4.

By bubbling purified hydrogen through the solution, coincidently with the slightly inclined portion of the curve in experiment No. 6b, the electric tension decreased to a minimum in about 45 min, then rose again; when air was bubbled through the solution, the electric tension dropped promptly and became stable at a more negative value.

DISCUSSION

The aluminium electrode is a corrosion polielectrode[5]. In nearly neutral solutions the corrosion results from many local operating galvanic cells. Corrosion is limited by an insoluble oxide film, covering the whole electrode surface, showing a different composition, structure and thickness. The film permits the passage of Al^{3+} and electrons but adsorbs H_2 and O_2.

This film may be compact or porous. A compact film may result from an anodization treatment[6], such as used for the herein reported experiments. A porous film, on the other hand, may spontaneously form in aqueous solutions. A more compact and thick film provides a better protection against corrosion. A more porous and thick film retains a greater amount of solution, so that the electrode poorly reflects the variations of the latter.

The anodes of the local cells are sites that can be reached more easily by Al^{3+} released from the metal. At the interphase, Al^{3+} turns into $Al(OH)_3$, which builds up a new porous film on the older one, either porous or compact. It may happen that $Al(OH)_3$ is detached by stirring.

The cathodes are sites more easily reached by electrons. They include I, H and O cathodes.

The I cathodes are the sites where ionic metallic impurities are reduced to metal, because of the low overtension (cementation of copper, iron, etc.).

The H cathodes are the sites where reduction of H^+ to H_2 occurs, because of the low hydrogen overtension. They are mostly metals, such as Cu and Fe. Their number increases with cementation and decreases as they are covered by a gradually spreading and thickening film[7].

The O cathodes are the sites where O_2 is reduced to H_2O_2 or H_2O, because of the high content of adsorbed oxygen. They increase in number and efficiency as $[O_2]$ increases. When the solution undergoes deoxygenation, a part of the oxygen passes back into the solution and a part is wasted in the corrosion process.

The correlation between the total electrode corrosion and the cathodic processes can be expressed as follows:

$$i = i_{\mathrm{I}} + i_{\mathrm{H}} + i_{\mathrm{O}} \tag{1}$$

where i is the total corrosion current and i_{I}, i_{H} and i_{O} are parts of it depending on the reduction of the metallic ions, H^+ and O_2.

The I cathodes can be considered as electrodes of copper, iron, etc.

The H and O cathodes can be considered as hydrogen and oxygen electrodes. These are, theoretically, the same electrode, as indicated by the identity of the following expressions:

$$U_{H_2} = -0.0591\ \mathrm{pH} - 0.0295 \log p_{H_2} \tag{2}$$

$$U_{O_2} = 1.228 - 0.0591\ \mathrm{pH} + 0.0148 \log p_{O_2} \tag{3}$$

correlated by:

$$(p_{H_2})^2(p_{O_2}) = 10^{-83} \tag{4}$$

concerning the following equilibrium:

$$2\ H_2 + O_2 \rightleftharpoons 2\ H_2O \tag{5}$$

Actually, since reaction (5) does not take place at room temperature, p_{H_2} and p_{O_2} lack correlation but indicate the partial pressure of both gases in the gaseous phase in equilibrium with the solution.

For the aluminium electrode, under the experimental conditions described above, p_{H_2} is constant and possibly equal to 1 atmosphere, while p_{O_2} is variable. The value of p_{O_2} in purified hydrogen is $4 \cdot 10^{-7}$ atmospheres[8]; this value corresponds to a concentration of about $5 \cdot 10^{-10}$ *M* in water saturated with purified hydrogen.

Both H and O cathodes, therefore, can coexist on the electrode surface, since: (1) sites are found with chemical and physical differentiations, showing aptness for either reduction process; (2) p_{H_2} and p_{O_2} are independent. When $[O_2]$ is increasing, the possible transformation of H cathodes into O cathodes cannot be discarded.

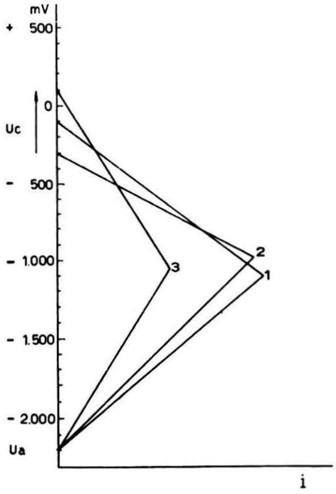

Fig. 3. Electrode states and their changes in experiment No. 1: 1, at 1 h; 2, at 2 h; 3, at 7 h.

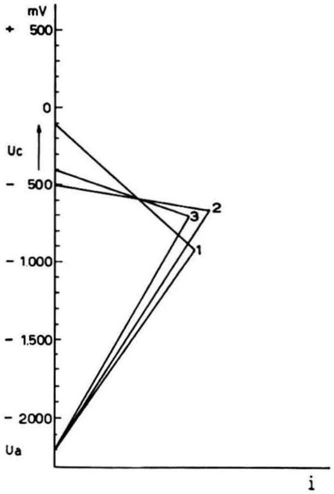

Fig. 4. Electrode states and their changes in experiment No. 2: 1, at 1 h; 2, at $5\frac{3}{4}$ h; 3, at $8\frac{1}{2}$ h.

Many different electrodic states are possible, to each of which a different electrode tension is correlated; a given electric tension being correlated with several electrodic states. The electrodic state, however, is continuously changing because of developing corrosion; the electric tension, therefore, is variable.

The electrodic state, its changes and correlation with the electrode tension can be represented and interpreted with EVANS diagrams[9] (Figs. 3–6). In the EVANS diagrams there are related: the electric tension of the anodic area at zero current, *i.e.* the anodic thermodynamic electric tension, U_a; the cathodic thermodynamic electric tension, U_c; the anodic and cathodic electric tensions when the corrosion current is flowing; the anodic polarization, *i.e.* the difference between the anodic thermodynamic electric tension and the anodic corrosion tension; the cathodic polarization; the anodic and the cathodic polarizability, or specific polarization; the corrosion current.

U_a is calculated from a POURBAIX diagram for the reversible aluminium electrode[10], when the pH = 7.

U_c could be calculated from NERNST equations for electrodes of copper, iron, etc., and for hydrogen and oxygen ones from the values of $[Cu^{2+}]$, $[Fe^{2+}]$, pH, p_{H_2}, p_{O_2}, etc. and from the ratios of the areas of the different cathodes. Since several of these data are unknown, U_c can be only roughly calculated.

With pH = 7, $p_{H_2} = 1$ atmosphere, $p_{O_2} = 4 \cdot 10^{-7}$ atmospheres, $[Cu^{2+}] = [Fe^{2+}] = 10^{-6}$ M (disregarding other cementing metals), the electric tensions (*vs.* S.C.E.) found for the different electrodes are as follows: $U_{O_2} = +474$ mV; $U_{Cu} = -82$ mV; $U_{H_2} = -660$ mV; $U_{Fe} = -860$ mV.

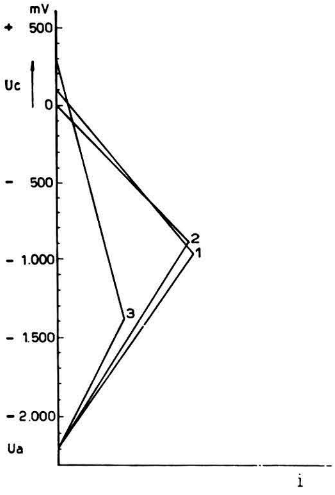

Fig. 5. Electrode states and their changes in experiment No. 4: 1, at 1 h; 2, at 3 h; 3, at 10 h.

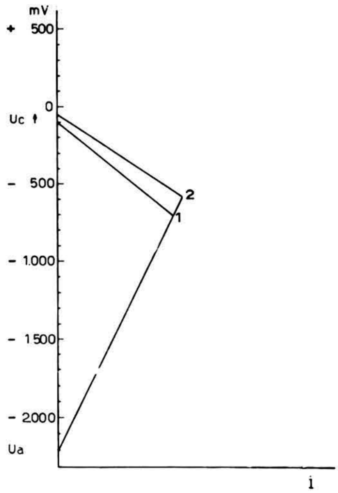

Fig. 6. Effect of oxygen in experiment No. 3: 1, in the absence of oxygen; 2, in the presence of oxygen.

U_c lies among the above values and is closer to the electric tension of the cathode which has the largest area. In view of the identity of Fe and Cu cathodes with H ones only U_{H_2} and U_{O_2} are considered; thus, U_c falls between −660 mV and +474 mV, shifting towards the former value following cementation, and towards the latter as a result of the inactivation of H cathodes.

Following p_{O_2} variations, U_c shifts to more positive values especially when the $[O_2]$ variation is larger (Fig. 6).

The electric tension of the aluminium electrode, defined as the electric tension of the open galvanic cell, Cu | Al | solution | KCl agar bridge | S.C.E. | Cu, corresponds to the intersection of the two polarization lines. The ordinate of the intersection point gives the anodic and the cathodic electric tensions at corrosion current. The slope of the polarization lines expresses the polarizability.

The polarizability of the anodic area increases in proportion to the resistance to Al^{3+} passage; it is, therefore, higher with anodized electrodes, reaching its highest value with those anodized at 60 V. It increases as corrosion goes on, because of the increasing thickness of the film; such an increase is remarkable for unanodized electrodes, limited for those anodized at 20 V and negligible for electrodes anodized at 60 V.

The polarizability of the cathodic area decreases as the total number of cathodes increases, *i.e.* as the ratio of the total cathodic area to the anodic area becomes higher. It decreases following both cementation and an increase of $[O_2]$. When U_c and the anodic and cathodic polarizability vary, due to the causes indicated, the corrosion current also varies, as well as the electric tension of the electrode.

Briefly, the factors causing electric tension variations are: cementation; inactivation of H cathodes caused by coating or by other processes; variations of $[O_2]$; growth of the film; removal of the film caused by the stirring. These processes may occur simultaneously, causing positive or negative variations of the electric tension, or producing no change at all.

Figs. 3, 4 and 5 show some states and changes concerning the $U-t$ curves. Fig. 6 shows the influence of oxygen on experiment No. 3. In these figures, the total corrosion current values are purely indicative, and the relative values are logically deduced; on the contrary, the values of the electric tension at the intersection points are experimental.

Other experimental data can be interpreted without the aid of EVANS diagrams.

The relative lack of reproducibility of the $U-t$ curves may be caused by: deoxygenation, which does not always occur in the same way; uncontrollable differences in the stirring close to the electrode surface; different amounts of metallic impurities in the distilled water; variability of the early electrode state.

The initial portions of the curves 1, 2, 3, 4 and 5 (disregarding the very first part, where the influence of deoxygenation is very strong), up to the maximum, are characterized by the prevailing cementation process; the second portions of the curves 2, 4 and 5 are characterized by the prevailing H cathodes' inactivation processes.

Curves 4 and 5 are the limits between which curve 2 should occur; the uncertain position of the latter is due mostly to the variable content of metallic impurities in distilled water, even though this is less than 10^{-6} M, (it is easy to establish that the impurity content increases during pre-experiment manipulations).

Water is partly purified from metallic impurities by the aluminium electrode through cementation[2] (negative shift of successive curves in experiment No. 2 recorded on the same portion of the solution). When the amount of impurities increases, the electric tension shifts to positive values because of the larger number of H cathodes. When the cemented impurities are very abundant on the electrode, the latter stains filter paper.

The anodization effect of increasing the anodic polarizability is apparent when curves 1 and 2 are compared.

The oscillations should be referred to irregular stirring and to prevailing anodic or cathodic variations of polarization (or depolarization) or the reverse. Obviously they reach a maximum when, for different causes, the corrosion current is high (experiments Nos. 5 and 6).

The portions of the curves showing slight inclination result from the cementation counterbalancing the inactivation of the H cathodes. The portions showing a steady electric tension, in experiments Nos. 3 and 4, should also be referred to a limited corrosion resulting, for the former, from highly efficient protection provided by the film and, for the latter, from the small number of I and H cathodes, since this solution was extremely pure.

The rise of the electric tension following the deviation of the flow of purified hydrogen is difficult to explain in experiments Nos. 2 and 3. Possible causes are the adding of trace amounts of oxygen into the solution and the effect of decreased hydrogen pressure.

The immediate effect of adding oxygen to the solution originates from the drop of the cathode polarizability for the more extensive total cathode area (Fig. 6).

The permanent effects of adding oxygen should be ascribed to a stronger corrosion: the negative shift of the electric tension results from the inactivation of H cathodes, while the positive shift comes from the rise of anode polarizability following the growth of the film. When neither shift occurs, it has to be put either to the counterbalancing effects of both processes, or to the fact that they are very limited.

The situation of the curve 6a, being more negative than 6b, should be ascribed to stronger H cathodes inactivation, resulting from greater amounts of available oxygen. In experiment No. 6b, the drop of the electric tension after air is bubbled, is due to the H cathodes inactivation. In experiment No. 6b, the bubbling of purified hydrogen causes a decrease of the electric tension during 45 min, corresponding to the period of time required for deoxygenation; later the electric tension shifts to positive values because of the prevailing cementation process.

The high sensitivity to oxygen found under the conditions of experiment No. 1 is probably due to the high permeability and limited thickness of the porous film causing a high degree of corrosion; by adding oxygen, a decrease of polarizability of the cathodic area occurs with an increase of polarizability of the anodic area, both acting on the electric tension with accumulative effects. The low sensitivity to oxygen shown under the conditions of experiment No. 4 results mainly from the porous film developed several hours after the experiment is run and acting as a barrier between the electrode and the solution.

From the behavior reported above, it is apparent that the best conditions for oxygen determination are found when the electrode tension is steady and no permanent effect follows addition of oxygen. Such conditions are increasingly fulfilled, coincidently with the portions of the curves showing steady electric tension, in experiments Nos. 2, 4 and 3.

In the next paper determinations performed under experiment No. 3 conditions, which guarantee high sensitivity, reproducibility and saving of time, will be dealt with.

SUMMARY

The experimental conditions for determining trace amounts of oxygen using the aluminium electrode have been investigated by means of electric tension–time curves of the open galvanic cell, Cu | Al | solution | KCl agar bridge | S.C.E. | Cu, in nearly neutral solutions.

The aluminium electrode acts as a corrosion polielectrode, by means of anodic processes such as dissolution of metal, formation of $Al(OH)_3$ and growth of the film,

and by means of three different cathodic reactions: reduction of ionic metallic impurities to the metal (cementation), of H^+ to H_2 and O_2 to H_2O. Cementation causes the electric tension to rise, while the film growth gradually coats the cemented metals causing the electric tension to decrease.

When both processes are limited, the changes of the electric tension are dependent on the $[O_2]$ variations only and result from the last two cathodic reactions counterbalancing each other.

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THE REDUCTION WAVES OF NICKEL ION IN SOME SUPPORTING ELECTROLYTES

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INTRODUCTION

Studies on the reduction wave of nickel ion in perchlorate as a supporting electrolyte have shown that it consists of one wave, whose wave height is independent of the concentration of perchlorate.

R. H. SANBORN[1] reported that the wave height in the reduction of nickel ion depends upon the concentration of an electrolyte such as sodium chloride or potassium chloride, and concluded that this result was due to the formation of Ni(I) ion. Furthermore, A. A. VLCEK[2] considered the reduction wave of nickel in sodium chloride to be accompanied by a kinetic current. The present paper shows that the reduction waves of nickel ion in potassium nitrate, potassium bromide and potassium sulfate, as well as potassium nitrite, depend on the concentration of the supporting electrolyte, and that except in the case of potassium nitrate, two waves are formed.

APPARATUS

The details of d.c. and a.c. polarographs have already been reported[3,4]. The a.c. voltage of 10 mV was superimposed on the applied d.c. voltage, and the standard

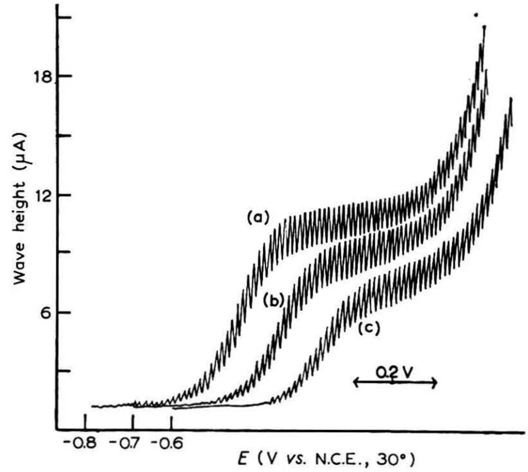

Fig. 1. D.c. polarograms of 1 mM nickel ion in potassium nitrate at various concentrations (30°): (a), 0.5 M KNO_3; (b), 1.0 M KNO_3; (c), 1.8 M KNO_3.

capacity (C_s) was 0.2 μF. An agar-agar bridge connected the reference electrode (1 N calomel) and the polarographic cell, from which oxygen was removed by passing hydrogen.

The dropping mercury electrode used had the following properties: $m = 2.77$ mg/sec, $t = 3.6$ sec, (—1.2 V *vs.* N.C.E. in 0.5 M potassium nitrate).

Potassium nitrate as a supporting electrolyte

The reduction wave of nickel has one wave in 0.5 M potassium nitrate, having a half-wave potential at —1.08 V (30°). Figure 1 shows the d.c. polarograms of 1 mM nickel ion in potassium nitrate at various concentrations.

The wave height decreases with increasing potassium nitrate concentration, and is independent of the addition of 0.005% gelatine. Figure 2 shows the a.c. polarograms of nickel ion in both the presence and absence of dissolved oxygen. The two wave polarogram, registered in the presence of dissolved oxygen, changes to a one wave

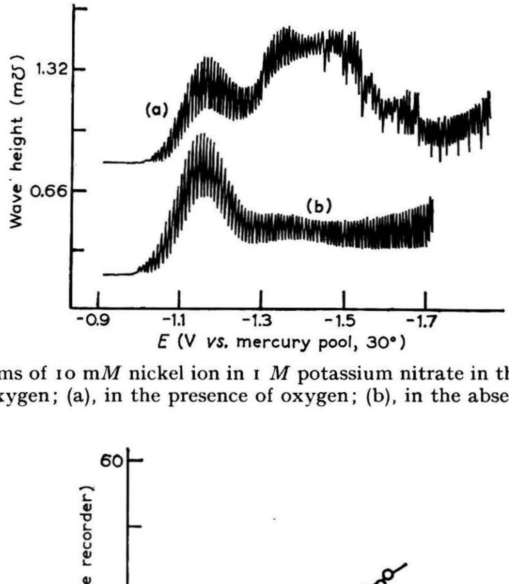

Fig. 2. A.c. polarograms of 10 mM nickel ion in 1 M potassium nitrate in the presence or absence of dissolved oxygen; (a), in the presence of oxygen; (b), in the absence of oxygen.

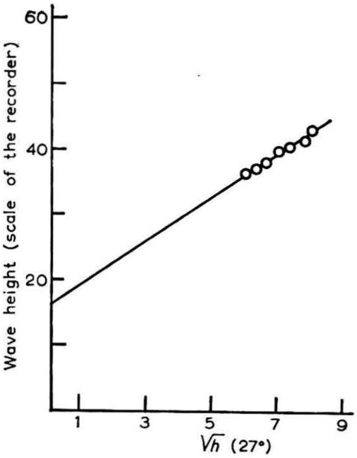

Fig. 3. Relationship between the wave height of 1 mM nickel ion and $\sqrt{h}$ in 1.8 M potassium nitrate.

polarogram when the dissolved oxygen is removed. The disappearance of this wave is presumed to be due to the reduction of $Ni(OH)^+$ or $Ni(OH)_2$ formed by reaction with OH^- ion, which is produced by dissolved oxygen on the surface of the electrode.

Figure 3 gives the relationship between the wave height and $\sqrt{h}$ in 1.8 M potassium nitrate. The graph does not pass through the origin, indicating the presence of a kinetic current in the limiting current.

Potassium bromide as a supporting electrolyte

The shape of the reduction wave of nickel ion changes with the concentration of potassium bromide used as a supporting electrolyte.

In Fig. 4, the d.c. polarogram shows two distinct waves in 0.8 M potassium bromide, but the second wave seems to disappear at a concentration of 1.8 M, as is shown by (c). The half-wave potential of the first wave is —1.07 V (30°) in 0.5 M potassium bromide. The second wave also disappears if 0.005% gelatine is added to the supporting

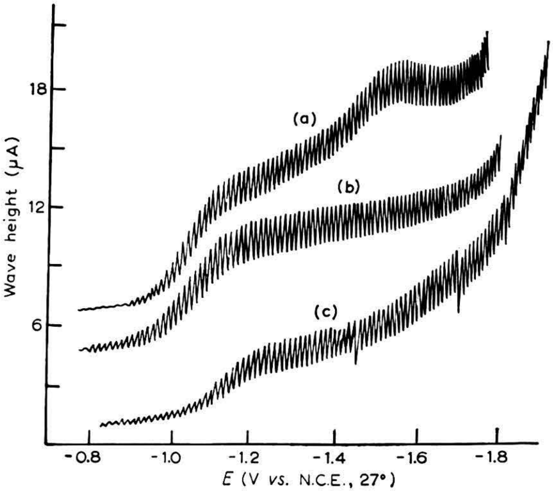

Fig. 4. D.c. polarograms of 1 mM nickel ion in potassium bromide: (a), in 0.8 M KBr; (b), in 0.8 M KBr containing 0.005% gelatine; (c), in 1.8 M KBr.

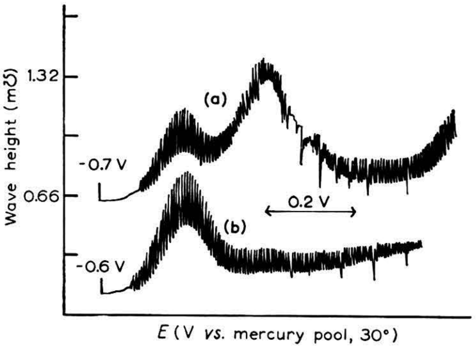

Fig. 5. A.c. polarograms of 10 mM nickel ion in 0.8 M potassium bromide: (a), in the presence of oxygen; (b), in the absence of oxygen.

electrolyte solution, as can be seen from Fig. 4(b). Similarly, the appearance of the second wave was confirmed in the presence of dissolved oxygen, in the absence of which it disappeared, as can be seen from Fig. 5.

Figure 6 gives the relationship between the wave height of the first wave and $\sqrt{h}$ in a d.c. polarogram of 1 m*M* nickel ion in 0.8 *M* potassium bromide, in which the line (b) does not pass the origin, indicating the presence of a kinetic current. Furthermore, the existence of a kinetic current was also found in the d.c. polarogram (c) of nickel ion in 0.8 *M* potassium bromide containing 0.005% gelatine, (as shown in Fig. 6), and in 1.8 *M* potassium bromide (not shown in the Figure). But the line expressing the relationship between the total wave height and $\sqrt{h}$ passes through the origin (line (a)), showing that the limiting current is controlled by the diffusion rate.

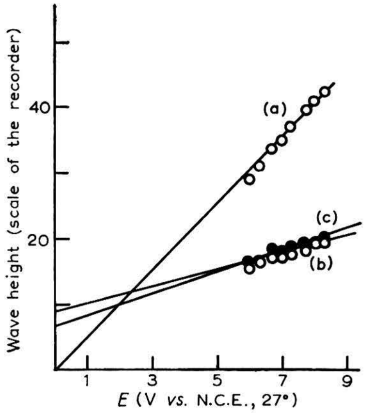

Fig. 6. Relationship between the wave height of 1 m*M* nickel ion and $\sqrt{h}$ in 0.8 *M* potassium bromide (27°): (a), sum of the first and second waves; (b), the first wave; (c), the first wave in the presence of 0.005% gelatine.

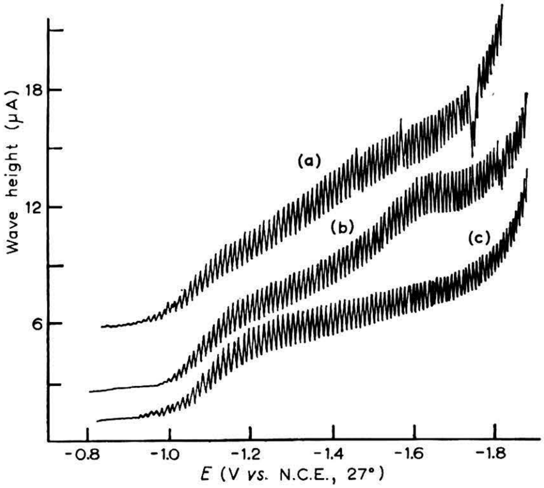

Fig. 7. D.c. polarograms of 1 m*M* nickel ion in potassium sulfate at various concentrations: (a), in 0.45 *M* K_2SO_4; (b), in 0.3 *M* K_2SO_4; (c), in 0.3 *M* K_2SO_4 containing 0.005% gelatine.

Potassium sulfate as a supporting electrolyte

Figure 7 shows the d.c. polarogram of 1 m*M* nickel ion in 0.45 *M* (a) or 0.3 *M* (b) potassium sulfate. The shape of the wave changes with the concentration of potassium sulfate, and the addition of 0.005% gelatine makes the second wave disappear, as the polarogram (c) in 0.3 *M* potassium sulfate shows. The half-wave potential is —1.12 V (30°) in 0.3 *M* potassium sulfate. The a.c. polarogram of nickel ion in the presence of dissolved oxygen is given in Fig. 8, which shows two waves, the second wave disappearing in the absence of dissolved oxygen.

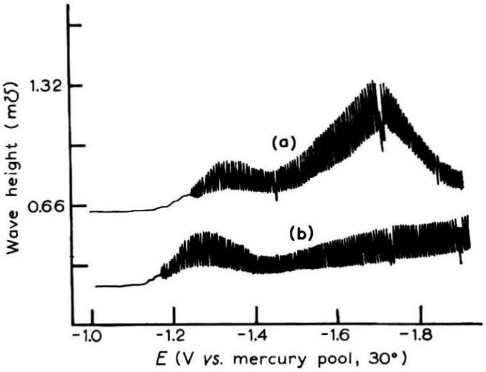

Fig. 8. A.c. polarograms of 10 m*M* nickel ion in 0.5 *M* potassium sulfate: (a), in the presence of dissolved oxygen; (b), in the absence of dissolved oxygen.

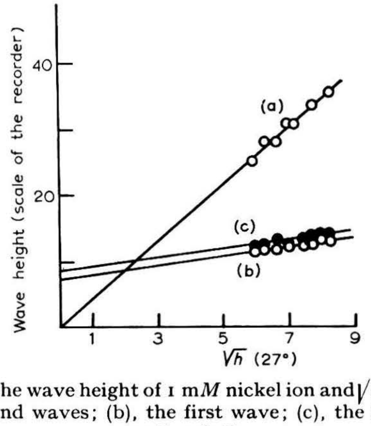

Fig. 9. Relationship between the wave height of 1 m*M* nickel ion and $\sqrt{h}$ in 0.3 *M* potassium sulfate: (a), sum of the first and second waves; (b), the first wave; (c), the first wave in the presence of 0.005% gelatine.

The relationship between the wave height of the first wave and $\sqrt{h}$ in the d.c. polarogram in 0.3 *M* potassium sulfate is shown in Fig. 9, in which the line (b) does not pass through the origin, indicating the presence of a kinetic current. Since line (c) also does not pass through the origin after the addition of 0.005% gelatine, the wave height is partly dependent on kinetic current. But the limiting current containing the first and second waves is controlled by the diffusion rate, because the line (a) expressing the relationship between the total wave height and $\sqrt{h}$ passes through the origin.

Potassium nitrite as a supporting electrolyte

The d.c. polarogram of nickel ion in 0.5 *M* and 1 *M* potassium nitrite gives two waves as shown in (a) and (b) in Fig. 10, but with an increase in the concentration of potassium nitrite, the first wave height seems to increase and the second wave height decreases, although only slightly. The half-wave potential of the first wave is —0.85 V (30°) and that of the second wave —1.09 V (30°) in 0.5 *M* potassium nitrite. The latter potential[5] equals the half-wave potential of $Ni(H_2O)_6^{2+}$.

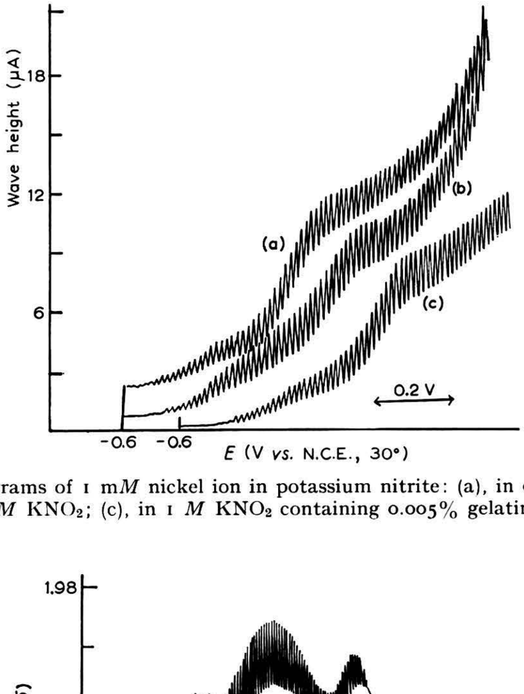

Fig. 10. D.c. polarograms of 1 m*M* nickel ion in potassium nitrite: (a), in 0.5 *M* KNO_2; (b), in 1 *M* KNO_2; (c), in 1 *M* KNO_2 containing 0.005% gelatine.

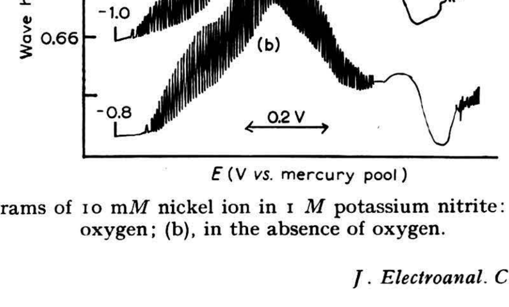

Fig. 11. A.c. polarograms of 10 m*M* nickel ion in 1 *M* potassium nitrite: (a), in the presence of oxygen; (b), in the absence of oxygen.

The a.c. polarogram in 1 *M* potassium nitrite containing dissolved oxygen is given Fig. 11, which shows three waves in the presence of dissolved oxygen, although the third wave disappears after removal of the oxygen. It is not certain that the first wave is controlled by the diffusion rate, because it is difficult to determine the relationship between the wave height and $\sqrt{h}$, as the first wave approaches the second wave. But the total wave height obtained by combining the first and second waves passes through the origin, indicating that the total limiting current is controlled by the diffusion rate, as can be seen from Fig. 12.

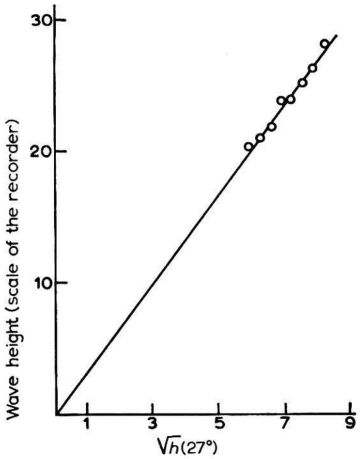

Fig. 12. Relationship between the wave height of 1 m*M* nickel ion and $\sqrt{h}$ in 0.5 potassium nitrite (27°).

DISCUSSION

Of the two waves of nickel ion in potassium sulfate and potassium bromide, the first wave accompanies the kinetic current. Therefore, it is considered that the reduction of nickel ion is the electrode reaction, for compounds which are in mutual equilibrium. Here, the first wave equals the half-wave potential of $Ni(H_2O)_6{}^{2+}$, so the first wave is probably due to the reduction of $Ni(H_2O)_6{}^{2+}$. But the second wave appearing in the presence of dissolved oxygen occurs at a potential —0.2 V more negative than that of the first wave, and it disappears in the absence of dissolved oxygen, so that it is perhaps due to the reduction of $Ni(OH)^+$ or $Ni(OH)_2$ formed between nickel ion and OH^- ion, which is produced by reduction of the dissolved oxygen. The second wave appearing in the absence of dissolved oxygen occurs at a potential —0.4 to —0.5 V more negative than that of the first wave, so that it is probably not due to the reduction of any compound co-ordinated by an OH^- group. But such a second wave is considered to be due to the reduction of a compound co-ordinated by $SO_4{}^-$ or Br^- ions of the supporting electrolyte, because the second wave height depends upon the concentration of the supporting electrolyte. According to I. M. KOLTHOFF AND J. J. LINGANE[5], nickel ion exists as $Ni(H_2O)_2{}^{2+}$ in potassium nitrate solution. But the present study showed a decrease in the wave height of nickel ion with increased (0.5 *M* →

1 *M* → 1.8 *M*) potassium nitrate concentration, and a combination of kinetic current into its wave height. Therefore, it is evident that in potassium nitrate there is not only $Ni(H_2O)_6^{2+}$, but also a compound co-ordinated by NO_3^-. These compounds are mutually in a state of equilibrium, the latter compound not being reduced until the applied d.c. voltage reaches the potential of the final increase of the polarographic current.

In potassium nitrite, nickel ion exists as two complexes, *i.e.*, as $Ni(H_2O)_6^{2+}$ and the complex co-ordinated by NO_2^-. The first wave is caused by the reduction of the latter and the second wave by the reduction of $Ni(H_2O)_6^{2+}$.

The authors have considered the results of R. H. SANBORN[1] regarding the interdependence of wave height and the concentration of the supporting electrolyte, as follows. Nickel ion perhaps occurs as $Ni(H_2O)_6^{2+}$, even in large concentrations of perchlorate, because perchlorate ions do not complex with metallic ions. In sodium chloride solution, two complexes, *i.e.*, $Ni(H_2O)_6^{2+}$ and a compound co-ordinated with Cl^- co-exist, and the former may be more reactive to the reduction than the latter. Therefore, the concentration of $Ni(H_2O)_6^{2+}$ decreases with increase of Cl^- ion, resulting in a lower wave height in large concentrations of sodium chloride than that occurring in small concentrations.

SUMMARY

The reduction wave of nickel ion in potassium sulfate, bromide or nitrite shows two waves and the first wave is accompanied by a kinetic current, so that $Ni(H_2O)_6^{2+}$ and a compound co-ordinated with the anion of the supporting electrolyte are mutually in a state of equilibrium, the former being responsible for the first wave and the latter for the second wave.

In potassium nitrate supporting electrolyte, $Ni(H_2O)_6^{2+}$ and another complex are in equilibrium, and it was concluded from the half-wave potential that the latter is responsible for the reduction wave.

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MICRODOSAGE RAPIDE DU ZINC DANS LE SANG, AU POLAROGRAPHE A RAYONS CATHODIQUES

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(Reçu le 19 mai 1961)

INTRODUCTION

Le zinc, comme tout oligo-élément, intervient dans les processus enzymatiques[1], il est indispensable à l'activité de plusieurs déshydrogénases hépatiques, notamment la déshydrogénase de l'alcool et la déshydrogénase glutamique. Les perturbations sériques du zinc apparaissent très nettement dans la cirrhose de Laënnec; on peut observer également des diminutions du taux de zinc dans d'autres affections hépatiques, mais elles sont moins importantes. L'excrétion urinaire du zinc, très élevée dans les cirrhoses modérées, diminue progressivement au cours de la maladie et devient anormalement basse en phase terminale.

D'autre part, il a été constaté[2] que des variations significatives de la teneur en zinc dans les différents constituants du sang se produisent, notamment en cas de leucémie et d'anémie pernicieuse (mais non dans les anémies par carence en fer), en cas d'infarctus du myocarde, d'ictères par occlusion, d'hémoblastoses et autres néoplasmes malins et pour diverses maladies infectieuses.

L'étude du métabolisme du zinc dans les organismes humains et animaux nécessite une méthode de dosage sensible, permettant de travailler sur de faibles prises de substance (sang ou plasma) de manière à réduire la durée des opérations de minéralisation et de séparation. Les méthodes proposées mettent en oeuvre principalement des déterminations colorimétriques, polarographiques, turbidimétriques et même gravimétriques.

Un excellent procédé est décrit par VALLÉE ET GIBSON[3] pour doser des quantités de zinc de 2 à 30 μg dans le sang et les tissus. La prise est calcinée dans un creuset de platine durant 12–24 h à 600°, puis dissoute dans l'acide chlorhydrique et additionnée de tartrate, de thiosulfate et de cyanure. On extrait ensuite au pH de 5.5 par une solution de dithizone dans le tétrachlorure de carbone et on mesure l'extinction de la phase organique à deux longueurs d'onde de manière à éviter toute interférence due à l'excès de réactif. Une modification de cette méthode, consistant à faire une triple précipitation des protéines à l'aide d'acide trichloracétique, a été proposée[4], elle permet d'éviter la calcination de la prise mais elle est délicate et doit être effectuée avec grand soin.

Pour leur part, WEITZEL ET FRETZDORFF[5] effectuent une minéralisation par voie humide à l'aide d'acide sulfurique et de perhydrol, après traitement du produit à 90–120° durant 12 à 48 h. Après extraction à la dithizone, ils minéralisent le dithizonate de zinc. La détermination se fait ensuite par polarographie, en présence d'un tampon tartrique de pH 5.5. La méthode est applicable pour des teneurs en Zn de 2 à 20 μg.

RÄKER[6] effectue une minéralisation (par voie sèche ou humide) sur des prises contenant de 10 à 100 μg de Zn puis une extraction au moyen de dithizone en milieu CCl_4. Le dithizonate de Zn est minéralisé et le Zn est polarographié en présence de ClLi 0.1 N et de gélatine.

Nous avons pour notre part étudié un procédé permettant de doser rapidement le Zn dans le sang en partant d'une petite prise (0.2 à 0.5 ml) qu'on minéralise par voie humide (ce qui est plus rapide et plus sûr qu'une calcination). On extrait ensuite par la dithizone en milieu chloroformique à pH 8.5 et on décompose le dithizonate de Zn formé par de l'acide nitrique dilué, de manière à éviter la minéralisation du réactif (opération plus longue et source supplémentaire de pertes); le Zn repasse donc dans la phase aqueuse et, après élimination de l'acide par évaporation, on polarographie en présence de KCl 0.01 N comme solution de base. Cette manière d'opérer est simple et rapide (du fait de la petite quantité de sang à minéraliser) et, pour peu que l'on opère avec soin, la contamination en Zn, qu'il est pratiquement impossible d'éviter complètement, se trouve réduite au minimum.

Les différentes étapes de l'analyse ont été contrôlées par l'emploi de ^{65}Zn radioactif de manière à déterminer les pertes moyennes qui se produisent à chaque stade de l'analyse. Une série d'essais à blanc permet d'autre part de déterminer la contamination moyenne en Zn. Il est bien entendu que si on utilise le marquage radioactif pour les analyses courantes, la rapidité et la précision des dosages s'en trouvent notablement augmentées.

APPAREILLAGE

Polarographe à rayons cathodiques de Southern Instruments (Camberley) type „Polarotrace K 1000" avec électrode à goutte de mercure. Echelle décadique „Tracerlab", type SC-33A avec sonde à scintillation P-20B équipée d'un cristal NaI(Tl) à puits.

RÉACTIFS ET SOLUTIONS

(Produits Merck pro anal).

Acides perchlorique, chlorhydrique et nitrique concentrés; acide nitrique à 1%; acide chlorydrique 4 N.

Soude caustique 4 N et 0.1 N.

Solution de KCl 0.1 et 0.01 N.

Chloroforme.

Solution de dithizone à 0.01% dans le chloroforme.

Tartrate sodico-potassique à 20%, amené au pH 8.5 par NaOH 0.1 N.

Solution de ^{65}Zn ayant une activité de 0.065 μC/ml et une concentration de 0.62 μg/m de Zn (provenance Harwell).

Purification des réactifs

Etant donné qu'un essai à blanc est toujours effectué parallèlement à une série d'analyses, on peut éventuellement utiliser les réactifs tels qu'ils viennent d'être préparés. Mais il est évident qu'il est préférable d'avoir dans les blancs effectués, des teneurs aussi faibles que possible en zinc; la précision des dosages fait sur des échantillons de sang en est d'autant meilleure. Nous utilisons pour toutes les opérations de l'eau bidistillée dans un appareil en quartz.

Solutions de KCl 0.1 et 0.01 N. On utilise pour en éliminer le Zn, une colonne échangeur d'ions contenant de la résine Dowex 1-X8 sur une hauteur de 2 cm, pour un diamètre intérieur de colonne de 0.8 cm. Cette colonne est lavée avec 20 ml de HCl 0.01 *N*, puis on fait passer, à vitesse de 1 ml par minute environ, une solution de KCl 1 *N* dont on rejette les premiers 5 ml. La solution qui s'écoule ensuite est diluée 10 fois et 100 fois pour obtenir les solutions 0.1 et 0.01 *N* nécessaires à l'analyse. Ces solutions sont conservées dans des flacons de polyéthylène, elles sont pratiquement exemptes de zinc (moins que 0.01 μg/ml).

Solution de tartrate sodico-potassique. Elle est purifiée par agitation énergique en présence de la solution de dithizone qu'on utilise pour l'analyse. Pour 100 ml de solution tartrique placés dans une ampoule à robinet, 2 à 3 extractions avec des portions de 5 ml de dithizone suffisent; la dernière extraction ne doit plus présenter de changement de teinte. Cette solution doit également être conservée dans un flacon de polyéthylène.

Acides concentrés. Les acides chlorhydrique et nitrique peuvent être distillés sous vide dans un appareil en quartz. Mais les expériences faites nous ont montré que si l'on utilise des acides „Merck" de qualité pro anal, l'amélioration obtenue est faible et ne justifie pas ce surcroit de travail, aussi avons nous utilisé ces acides tels qu'ils sont livrés par le fabriquant. Il en est de même pour l'acide perchlorique dont la purification est très délicate et qui malheureusement renferme une quantité appréciable de Zn.

NETTOYAGE DE LA VERRERIE

La contamination des récipients par le zinc n'est pas négligeable, aussi toutes précautions utiles doivent être prises pour la réduire au minimum. On préparera à l'avance la verrerie nécessaire pour une série d'analyses en la laissant tremper, après l'avoir bien dégraissée, pendant une nuit dans de l'acide nitrique concentré. On la rince ensuite soigneusement à l'eau courante, puis à l'eau bidistillée. On la sèche et la conserve ensuite à l'abri des poussières jusqu'au moment de l'emploi. En ce qui concerne les ampoules à robinet, on les rince avec la solution de dithizone dans $CHCl_3$ après avoir enduit robinets et bouchons d'un peu de graisse de silicone. Le dernier lavage ne doit plus présenter de changement de teinte.

MODE OPÉRATOIRE

Minéralisation du sang

Nous avons utilisé pour la minéralisation du sang des béchers philips de 50 ml recouverts d'un verre de montre. Les parois de ces béchers sont suffisamment hautes pour assurer un reflux convenable des vapeurs d'acide et prolonger ainsi leur action; il est en effet nécessaire, pour réduire les contaminations, d'utiliser des quantités aussi faibles que possible de réactifs. Le volume de ces béchers est tel que, même s'il se produit des soubresauts au cours de l'ébullition, il n'y a pratiquement pas de risques de pertes par projections. La minéralisation du sang se fait de la manière suivante:

(1) Placer dans le bécher: 0.2 ml de sang; 1.0 ml de solution de KCl 0.1 *N* comme support pour éviter les phénomènes d'adsorption; 1.0 ml de la solution de ^{65}Zn

comme traceur; 2.0 ml d'acide nitrique concentré. Porter le contenu du bécher à douce ébullition sur une plaque chauffante, après avoir recouvert d'un verre de montre. Continuer le chauffage jusqu'à évaporation totale du contenu.

2. Laisser refroidir un instant et verser sur le résidu 1 ml de NO_3H et 0.5 ml de ClO_4H. Porter à nouveau à douce ébullition et après 30 min, enlever le verre de montre pour laisser évaporer à sec. Laisser refroidir un peu et ajouter 0.5 ml de ClH concentré en inclinant le bécher pour bien humecter tout le résidu. Chauffer à nouveau pour chasser l'acide. On obtient de cette manière une minéralisation totale laissant un résidu tout à fait blanc.

3. Ce résidu est repris par 5 ml d'eau en chauffant. Après transvasement, on ajoute encore 1 ml de HCl 4 *N*, chauffe à nouveau et dilue avec 3 ml d'eau. On ajoute cette solution à celle précédement recueillie et neutralise avec 1 ml de NaOH 4 *N*. En procédant de cette manière on assure une récupération pratiquement totale du Zn, il ne reste aucun dépôt adhérent au fond du bécher.

4. On ajoute à la solution obtenue, 5 ml de tartrate sodico-potassique à 20% et amène le pH à 8.5 à l'aide d'un peu de NaOH 0.1 *N*. La solution n'est pas tamponnée mais il ne se produit pratiquement pas de variation de pH durant l'extraction.

Séparation du zinc

Nous avons effectué la séparation du zinc en utilisant l'extraction à la dithizone en milieu chloroformique. Cette méthode est excellente par son rendement et sa rapidité. L'emploi du ^{65}Zn nous a permis de déterminer les conditions de travail les meilleures, elles sont les suivantes:

1. La solution obtenue après minéralisation est placée dans une ampoule à robinet de 50 ml et on effectue l'extraction au moyen de 2 ml de dithizone en agitant énergiquement durant 2 min. On répète deux fois cette extraction dans les mêmes conditions. On termine par un lavage avec 2 ml de chloroforme pur.

2. La phase organique est ensuite lavée avec 2 ml d'eau bidistillée amenée au pH d'environ 8.5 par une trace de NaOH 0.1 *N*. On y ajoute alors 2 ml d'acide nitrique à 1% et, après deux minutes d'agitation, le dithizonate est décomposé et le Zn repasse en solution aqueuse. On renouvelle deux fois l'opération.

3. La phase aqueuse acide est ensuite soigneusement lavée deux fois avec 2 ml de chloroforme pour éliminer les résidus organiques qui pourraient gêner les mesures polarographiques (le chloroforme résultant du deuxième lavage doit être incolore, si ce n'est pas le cas, répéter l'opération).

4. On verse cette solution dans une capsule et y ajoute 1 ml de solution de KCl 0.01 *N*. On place sous une calotte chauffante et évapore à sec. On ajoute 1 à 2 ml d'eau bidistillée et évapore à nouveau pour chasser les dernières traces d'acide.

Détermination polarographique

On reprend le résidu par 1 ml d'eau bidistillée, transvase quantitativement dans une petite éprouvette et mesure l'activité à l'aide du compteur à scintillation. (On mesure de même l'activité de 1 ml de la solution de ^{65}Zn ayant servi au marquage.) La solution est ensuite placée dans une semi-microcuve polarographique; on fait passer un courant d'azote pur durant 10 min et on polarographie en maintenant la solution à l'abri de l'air. Le saut de réduction du Zn se produit à $E_{\frac{1}{2}} = -1.25$ V par rapport à la surface mercure/solution.

Si la séparation a été bien faite, les résultats que l'on obtient en ce qui concerne la qualité de la courbe sont comparables à ceux que donnent des solutions témoins de zinc pur.

Contrôle des analyses

Dans le but de contrôler la bonne marche d'une série d'analyses, il peut être utile, surtout si l'on ne dispose pas du matériel permet tant d'appliquer la méthode des traceurs, d'effectuer en plus de la détermination du blanc une analyse par étalon interne en ajoutant au sang une quantité connue de zinc. L'augmentation de la hauteur du saut polarographique permet de déterminer avec une précision accrue la teneur en Zn du sang.

La bonne reproductibilité du saut de réduction polarographique du zinc permet naturellement aussi de se reporter directement à une courbe d'étalonnage.

ÉTUDE DES PERTES

L'emploi de ^{65}Zn nous a permis une étude précise des pertes survenant au cours des différentes phases de l'analyse. Quelles que soient les précautions prises, les pertes sont en effet inévitables dans les analyses de ce genre. Nous avons pu constater que pour des analyses faites dans les mêmes conditions, les pertes sont toujours du même ordre de grandeur de sorte que si on ne peut utiliser un traceur, il est possible de déterminer un facteur de correction. Les valeurs obtenues sont données dans le Tableau I.

TABLEAU I

ÉTUDE DES PERTES

	Pertes(%)	*Zn restant(%)*
Prise	—	100
Minéralisation	5	95
Extraction à la dithizone	2	93
Extraction par NO_3H à 1%	5	88
Evaporation, reprise par 1 ml d'eau	5	83
Pertes mécaniques diverses; ordre de	3	80

Lors des analyses que nous avons faites (pour des quantités de Zn de l'ordre de 1 à 2 µg), nous avons eu des pertes comprises entre 15 et 24%. Le résultat d'un dosage doit donc être multiplié par le facteur 1.25.

ÉTUDE DES CONTAMINATIONS

La contamination en zinc des solutions se produit avec une extrême facilité et si on ne prend pas des précautions suffisantes pour les prévenir, la quantité de cet élément trouvé dans les essais à blanc est souvent supérieure à celle que renferme la prise de sang. Ces contaminations se produisent tout au long de l'analyse et nous avons fait une série de contrôles pour nous rendre compte de leur importance relative.

Tous les réactifs contiennent une quantité plus ou moins grande de zinc, même après purification (les indications à ce sujet sont données sur p. 322). C'est la raison pour laquelle nous avons évité de tamponné (avant extraction) la solution provenant de la minéralisation du sang. Le zinc étranger au dosage provient essentiellement des acides que l'on utilise pour la minéralisation. On veillera donc à en utiliser des quantités égales (et provenant des mêmes flacons) pour tous les essais d'une série et en quantité aussi faible que possible.

Une autre cause de contamination est constituée par les évaporations à sec sous calotte chauffante. Il se produit alors une forte circulation d'air (et par conséquent de poussières) autour des capsules et les solutions peuvent s'enrichir en zinc. La solution idéale consiste à travailler sous enceinte fermée[7] dans laquelle on provoque une circulation d'air filtré à l'entrée.

Une contamination se produit également par les parois des récipients de verre. Elle est très faible si le contact n'est pas prolongé, mais comme nous l'avons signalé par ailleurs (p. 323), toutes les solutions stockées doivent être conservées dans des récipients de polyéthylène que l'on referme immédiatement après usage. Il faut naturellement n'y plonger que des pipettes extrêmement propres, tant intérieurement qu'*extérieurement*.

Les contaminations que nous avons observées lors de nos essais ont été en moyenne les suivantes:

Acides utilisés pour la minéralisation	0.3 μg;
Support KCl 0.1 et 0.01 N, effets du contact avec les parois	0.03 μg;
Contaminations diverses (évaporations, neutralisations par NaOH, etc.)	0.07 μg;
Total moyen	0.4 μg.

Ne disposant pas d'une enceinte formée, les évaporations sont faites à l'air libre.

Lorsque les dosages sont faits dans les mêmes conditions, on n'observa-pas de variations importantes dans la contamination.

TABLEAU II

DOSAGE POLAROGRAPHIQUE DU Zn: COURBE D'ÉTALONNAGE EN MILIEU KCl 0.01 N

(Prises de 1 ml)

Prises (μg/ml)	*Sensibilité de l'appareil*	*Hauteur du saut (μA)**	*Rapport (μg/μA)*
4.340	0.40	1.993	2.178
3.255	0.40	1.513	2.151
2.170	0.40	0.995	2.181
1.085	0.40	0.507	2.140
0.953	0.10	0.438	2.176
0.715	0.10	0.328	2.180
0.477	0.10	0.213	2.240
0.238	0.10	0.112	2.125
0.0953	0.015	0.0453	2.104
0.0715	0.015	0.0313	2.284
0.0477	0.015	0.0195	2.446
0.0238	0.015	0.0100	2.380

Valeur moyenne du rapport μg/μA (calculé sur les 9 premières mesures) 2.164

Erreur relative ±3.51%

* Valeur du blanc (soln. de KCl 0.01 N) déduite.

RÉSULTATS

Courbe d'étalonnage sur solutions de Zn pur

Une courbe d'étalonnage a été établie à l'aide de diverses concentrations de Zn en milieu KCl 0.01 *N* comme solution de base.

La courbe d'étalonnage a été établie dans les limites de 0.02 à 5 μg de Zn par ml en trois séries utilisant les facteurs d'échelle 0.40, 0.10 et 0.015 de l'appareil de mesure (voir dosage polarographique, page 324). Les valeurs données dans le Tableau II ont été obtenues.

Le report de ces valeurs permet d'établir le graphique ci-contre (Fig. 1).

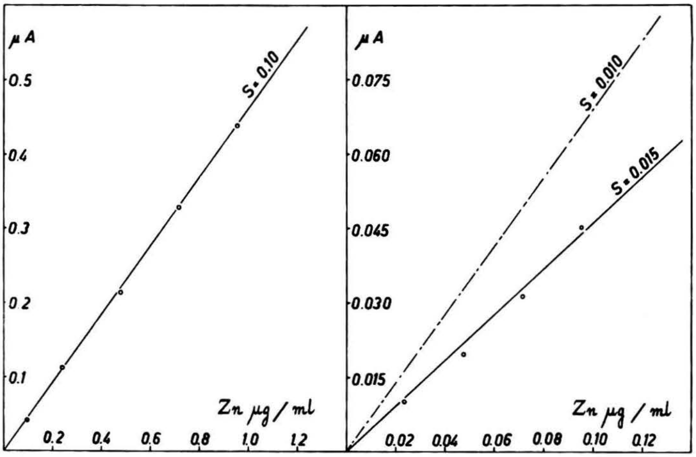

Fig. 1.

TABLEAU III

DOSAGE DU Zn DANS LE SANG

Sang	*Prises (ml)*	*Traceur*[a] *^{65}Zn (cpm)*	*Etalon interne (μg)*	*Activité finale (cpm)*[b]	*Pertes (%)*	*Hauteur du saut (μA)*		*Teneur en Zn (μg/ml)*
						(a)	*(b)*	
	0.2	17240	—	13960	19	1.229	0.996	10.9
A	0.2	17240	—	13275	23	1.119	0.905	9.9
	0.2	17240	2.38	14480	16	2.119	2.020	10.1
	blanc	17240	—	—	—	0.422	—	—
	0.2	17240	—	14315	17	1.114	0.862	9.4
B	0.2	17240	—	13450	22	1.046	0.829	9.0
	0.2	17240	2.38	13615	21	1.908	1.910	8.9
	blanc	17240	—	—	—	0.399	—	—
C	0.5	17240	—	9345[c]	45.8	1.573	2.107	9.2
	blanc	17240	—	—	—	0.431	—	—
D	0.2	17240	—	14310	17	1.036	0.795	8.7
	blanc	17240	—	—	—	0.376	—	—
E	0.2	17240	—	13785	20	1.073	0.831	9.1
	blanc	17240	—	—	—	0.408	—	—

[a] Activité de la solution de traceur (1 ml) en cpm (moyenne de 5 mesures de 1 min).

[b] Moyenne de 5 mesures de 1 min, faites dans les mêmes conditions que pour [a].

[c] Ce chiffre anormalement bas est dû à des pertes accidentelles.

(a) Hauteur des sauts non corrigés.

(b) Hauteur des sauts après déduction du blanc et compte tenu des pertes.

Analyses de différentes échantillons de sang

Des analyses ont été effectuées sur différents échantillons de sang selon le mode opératoire décrit sur p. 323 et les valeurs données dans le Tableau III ont été trouvées.

Les dosages se font dans d'excellentes conditions car on se trouve bien au dessus des possibilités limites de la méthode. Le saut polarographique du zinc séparé du sang est comparable à celui que donne une solution pure, il ne se produit aucune influence gênante et la mesure de sa hauteur peut se faire avec précision.

Durée de l'analyse

La méthode que nous proposons permet d'effectuer une série d'analyses (par exemple sur 4 prises de sang différentes) en 5 h environ, pour autant que tout le matériel et les solutions nécessaires soient prêts à l'emploi.

CONCLUSION

La méthode décrite permet, du fait de son extrême sensibilité et moyennant certaines précautions, d'effectuer rapidement le dosage du zinc en partant de très petites quantités de sang. Elle peut naturellement s'appliquer à d'autres matières biologiques avec, éventuellement, des modifications en ce qui concerne le processus de minéralisation.

Les déterminations polarographiques peuvent être faites sur n'importe quel appareil courant, avec une sensibilité moindre il est vrai, mais encore suffisante. On peut, si besoin est, faire la détermination polarographique en utilisant, non pas une semi-micro, mais une microcuve[8] permettant de travailler sur un volume de 0.1 ml au lieu de 0.5 ou 1 ml.

POHL[9], traitant du dosage des impuretés dans les semi-conducteurs, donne un certain nombre de règles générales devant présider à ces analyses. Parmis ces règles, nous rappelerons les suivantes qui, selon nous, doivent être prises en considération lors du dosage dont il a été question dans cet exposé:

„Limiter au maximum les changements de récipients" (il y a toujours des pertes ou des contaminations lors des transvasements);

„Eviter les interruptions dans la marche des analyses; les durées de contact avec les parois des récipients varient alors et les adsorptions ou contaminations ne sont plus reproductibles";

„Tenir extrêmement propre toute la verrerie et la place de travail. La verrerie doit être nettoyée par les personnes mêmes qui effectuent les analyses".

REMERCIEMENTS

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RÉSUMÉ

Une méthode de dosage polarographique du zinc dans le sang a été mise au point. 0.2–0.5 ml d'échantillon sont désagrégés au moyen des acides nitrique et perchlorique; le zinc est extrait par la dithizone puis réextrait par une solution d'acide nitrique dilué. La précision du dosage est de ± 5%. Une étude systématique des pertes effectuées au cours des diverses opérations a été réalisée grâce à l'emploi de ^{65}Zn. Les diverses causes de contamination ont été soigneusement examinées.

SUMMARY

A polarographic method of assay of zinc in blood is described. 0.2–0.5 ml of the sample are decomposed with nitric and perchloric acids; zinc is extracted by dithizone, then re-extracted by a diluted nitric acid solution. The accuracy of the method is ± 5%. A systematic study of the different losses which occurred during the procedure was made with ^{65}Zn, and all sources of contamination were thoroughly examined.

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STRUCTURE OF THE COPPER–MANNITE COMPLEX DETERMINED IN SOLUTION BY A.C. POLAROGRAPHY

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INTRODUCTION

Co-precipitation of mannite with cupric hydroxide, formed by the reaction between copper sulfate and alkali hydroxide, from an extract from seaweed containing mannite, was found to occur by T. TAKAHASHI[1]. According to him, the percentage precipitation of mannite depends upon the kind and amount of alkali hydroxide, because the precipitated mannite dissolves in a large excess of caustic alkali or ammonia.

The structure of the dissolved mannite–copper complex has been entirely obscure. The present paper studies the complex using a.c. polarography.

APPARATUS

The a.c. polarograph was an a.c. bridge type, details of which have already been reported[2,3]. The a.c. voltage of 10 mV was superimposed on the applied d.c. voltage and the standard capacity (C_s) was 0.2 μF. A 1 N calomel electrode was employed as the reference electrode, which was connected to the polarographic cell by an agar-agar bridge.

Properties of the dropping mercury electrode were; $m = 2.77$ mg/sec, $t = 3.75$ sec (—0.6 V *vs.* N.C.E. in 1 N potassium hydroxide solution), and the apparatus was contained in liquid paraffin at 25°. Hydrogen was used to remove oxygen.

RESULTS

The titration curve of copper ion with potassium hydroxide in the presence of mannite

The titration curves of 0.5 mM copper sulfate solutions (60 ml) containing mannite of various concentrations, with 0.1 N potassium hydroxide, are shown in Fig. 1. Curve (1) is the titration curve obtained in the absence of mannite, and the alkali titre is much smaller than the equivalent titre calculated from the amount of copper.

In the presence of mannite, the alkali titre increases, according to the curves (2), (3), (4) and (5), in accordance with the mannite concentration, until it equals the equivalent titre at over 2.5 mM mannite, showing the precipitation of copper with mannite as a mannite–2[$Cu(OH)_2$] complex[1].

The solubility of copper in alkali hydroxide solution containing mannite

The solubility of copper is $2.18 \cdot 10^{-3}$ in 1 N potassium hydroxide and less than that in 0.1 N potassium hydroxide[4]. The solubility of copper increases with the increase of mannite concentration, as is shown in Fig. 2. The determination of the solubility was carried out according to the following procedure.

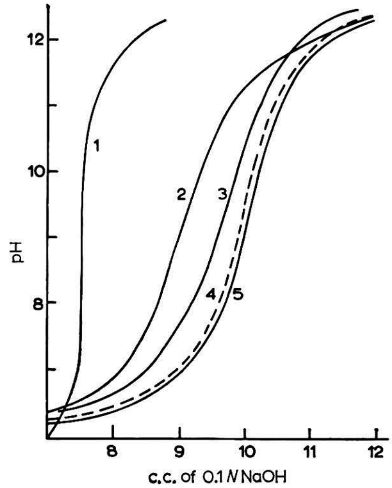

Fig. 1. Titration curves of copper ion by sodium hydroxide in the presence of mannite: (1), no mannite; (2), 0.01 M mannite; (3), 0.02 M mannite; (4), 0.05 M mannite; (5) 0.1 M mannite.

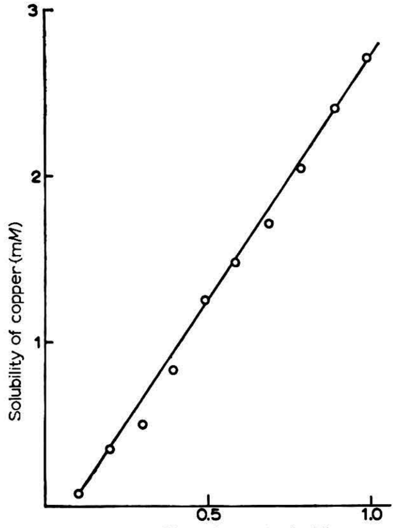

Fig. 2. Relationship between copper solubility and mannite concentration.

0.5 mM copper sulfate, 5 mM potassium hydroxide and mannite at the particular concentration were mixed in a 50 ml flask for three hours at 18°, and then the aliquot solution was polarographed in 0.5 M potassium bicarbonate. The a.c. polarogram of copper in 0.5 M potassium bicarbonate shows one wave of a definite shape, whose height is proportional to the copper concentration. But at less than 0.05 mM mannite, a polarographic method cannot be used, because the precipitate of mannite–copper complex changes to the colloidal state, capable of passing through filter paper. A photoelectric photometer was used to determine the critical concentration of mannite at which the colloidal complex of mannite and copper dissolved completely. Figure 3 shows that the presence of 2.2 mM or 5 mM mannite is necessary for complete dissolution of 10 mM copper sulfate in 0.1 N or 0.05 N potassium hydroxide; *i.e.* it was discovered that more mannite was necessary as the concentration of alkali hydroxide decreased. The ordinate of Fig. 3 is a scale expressed as the difference between the transparency of the sample solution and the transparency of a standard turbidity tube.

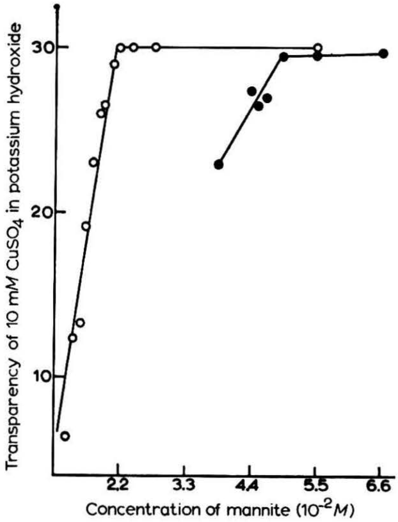

Fig. 3. Determination of copper solubility by turbidimetry: ●, in 0.05 N KOH; ○, in 0.1 N KOH.

Polarograms of copper in the presence of mannite

H. SHIRAI[5] discovered that the a.c. polarogram of 1 mM copper sulfate shows two waves in 0.1–0.5 N sodium hydroxide. But, in the presence of mannite, both d.c. and a.c. polarograms show one wave as shown in Fig. 4. Table 1 shows that the gradient on the d.c. polarogram, *i.e.*, $\log[i/(i_d - i)]$ *vs.* E, depends upon the concentrations of mannite and copper ions.

TABLE 1

THE VALUES OF $\log[i/(i_d - i)]$ *vs.* E OF A COPPER POLAROGRAM IN 0.2 N SODIUM HYDROXIDE CONTAINING MANNITE AT VARIOUS CONCENTRATIONS

Conc. of mannite (M)	*0.2 mM $CuSO_4$*	*1 mM $CuSO_4$*
0.027	52 mV	56 mM
0.054	32 mV	49 mM
0.081	—	45 mM

At a definite concentration of mannite, the gradient increases with increase of copper ion, while it decreases with increase of mannite concentration at a definite concentration of copper ion.

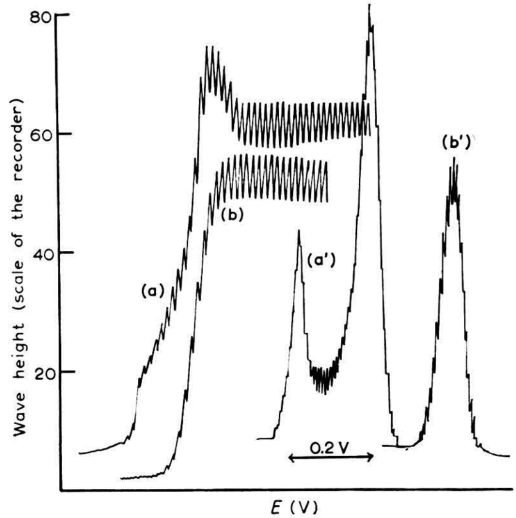

Fig. 4. A.c. and d.c. polarograms of 1 mM copper ion in the presence of mannite in sodium hydroxide: (a), d.c. polarogram in 1 N NaOH (1.5 μA per 10 scales); (a'), a.c. polarogram in 1 N NaOH (0.2 mmho per 10 scales); (b), d.c. polarogram in 0.5 N NaOH (1.2 μA per 10 scales); (b') a.c. polarogram in 0.5 N NaOH (0.33 mmho per 10 scales).

The influence of the concentration of sodium hydroxide on the peak potential of the a.c. polarograms

Figure 5 shows that the peak potentials of 1 mM copper sulfate in the presence of 0.0054 or 0.027 M mannite shift 60 mV *vs.* the change (ΔE) in unit concentration of alkali hydroxide.

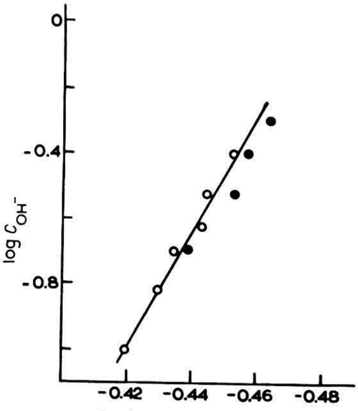

Fig. 5. Peak potential shift *vs.* unit concentration of alkali hydroxide (1 mM $CuSO_4$): ○, 0.5% mannite; ●, 0.1% mannite; R_s = 0.5 kΩ.

The number (p) of OH groups liberated in the electrode reaction was calculated from the values of the gradient (given in Table I) by using the following equation[6]:

$$\Delta E = -p \frac{0.060}{2\alpha} \Delta \log C$$

where α is a value depending on the electrode reaction rate ($0 < \alpha > 1$, almost 0.5–0.6). The result of the calculation showed the value of p is approximately one.

Polarographic determination of copper

The a.c. polarogram of copper in alkali hydroxide containing mannite is one wave,

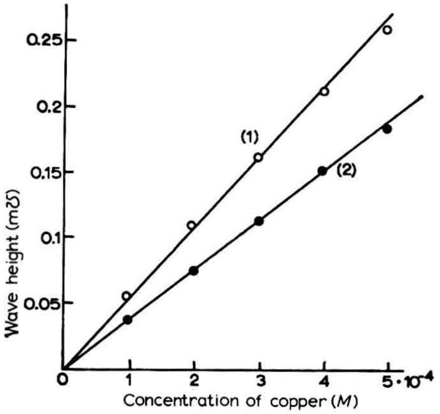

Fig. 6. Calibration curve of copper ion in the presence of mannite in alkali hydroxide:(1), in the presence of 0.05 M mannite in 0.5 M NaOH; (2), in the absence of mannite, in 0.5 M NH_4Cl–NH_4OH.

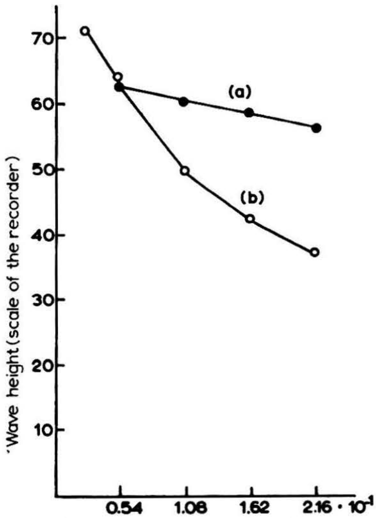

Fig. 7. Influence of mannite concentration on the wave or peak height of d.c. or a.c. polarograms of 1 mM copper sulfate: (a), d.c. polarogram, (b), a.c. polarogram.

as shown in Fig. 4, and there is a proportional relationship between the peak height and copper concentration (Fig. 6). But the wave height of the d.c. polarogram, as well as the peak height of the a.c. polarogram, decreases in the presence of a large excess concentration of mannite; in particular, the peak height decreases more markedly.

The polarographic analysis of copper ion in the presence of mannite is more sensitive than the conventional polarographic analysis in ammonium chloride–ammonia supporting electrolyte, provided that the concentration of mannite is insufficient to make the wave height lower (Fig. 7). The authors believe that a polarographic method is suitable for the determination of copper ion in alkali hydroxide containing mannite.

DISCUSSION

Mannite–2[$Cu(OH)_2$] complex dissolves in an excess of alkali hydroxide and colours it blue, but the state in which such a dissolved complex exists is not known.

According to the present results, and for liberation of one OH group during the electrode reaction, it is considered that mannite–2[$Cu(OH)_2$] changes to a complex, mannite–2$[Cu(OH)_3]^-$, which dissolves in excess alkali hydroxide solution, giving one wave in both d.c. and a.c. polarographs. Of the two waves of copper which occur in the absence of mannite, the first wave is due to the reduction of $Cu(OH)_2$, and the second wave is due to the reduction of $[Cu(OH)_4]^{2-}$.

SUMMARY

It was found that mannite–copper hydroxide complex dissolves in excess alkali hydroxide as a complex such as mannite–2$[Cu(OH)_3]^-$. The polarographic analysis of copper ion is more accurate in the presence of mannite than the more conventional determination in the absence of mannite.

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INTERPRETATION OF THE RESULTS OBTAINED WITH THE CAMBRIDGE UNIVECTOR A.C. POLAROGRAPH UNIT

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INTRODUCTION

Alternating current polarography has been extensively studied by BREYER and co-workers both as an analytical tool and for the elucidation of the mechanisms of electrode processes[1]. The instrument used by these workers (hereafter called a conventional a.c. polarograph) measures, as a scalar quantity, the alternating current which flows through the polarographic cell as a result of the superposition of a low amplitude, audio-frequency sinusoidal voltage onto the normal direct polarising voltage. The Cambridge Univector A.C. Polarograph Unit, when connected to a d.c. polarograph, measures only the component of the above alternating current which is in phase with the applied alternating voltage[2]. Both instruments produce peak-shaped polarographic waves, but in the case of the Univector Unit the base current (that alternating current which flows due to the Helmholtz–Gouy capacity of the electrical double layer) is eliminated. The purpose of this paper is to compare the Univector Unit with the conventional a.c. polarograph from a somewhat fundamental viewpoint and to indicate some of the pitfalls which may be encountered in the operation of the Univector Unit.

FERRETT *et al.*[3] have compared the Univector Unit, the Mervyn–Harwell Square Wave Polarograph and the Southern Cathode-Ray Polarograph. Their study is mainly from an analytical point of view and compares such things as sensitivity, reproducibility, accuracy etc.

PRINCIPLES OF THE INSTRUMENT

Since the only full description of the mode of operation of the Univector Unit is to be found in the original Patent Specifications[2,4], and since an understanding of the mode of operation of the instrument is essential to the interpretation of the results obtained in this investigation, it is necessary to give a brief description of the principles of the Univector Unit. Fig. 1 shows a block diagram of the circuit of the instrument.

The equivalent circuit of the polarographic cell under the conditions of a.c. polaro-

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graphy may be represented as in Fig. 2(a)*. It is sometimes more convenient to use the reciprocal of Z_f, *i.e.* the faradaic admittance[6,7].Fig. 2(b) shows a vectorial representation of the phase relationships of the equivalent circuit (according to Randles[5] and Bauer and Elving[7]). It can be seen that the current I may be resolved into two components: one, $V_Z\omega C_H$ (where ω is the angular frequency) represents the current passing through C_H and the other, I_f, the faradaic current through Z_f. $V_Z\omega C_H$ is represented at right angles to V_Z since it is 90° out of phase with it. The voltage drop across R_x is in phase with the current I and so is drawn parallel to it.

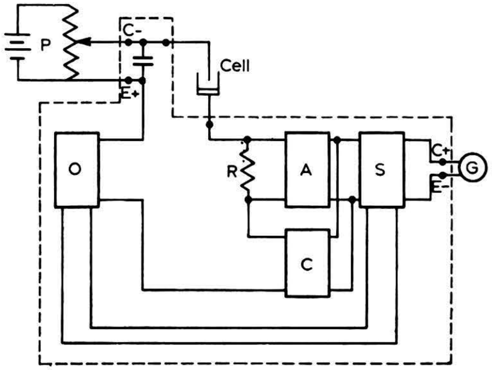

Fig. 1. Block diagram of circuit of Univector Unit. Components outside dashed line are external to the instrument. *P*, potentiometer; *A*, amplifier; *S*, phase sensitive rectifier; *C*, compensator amplifier; *O*, oscillator; *G*, galvanometer; C_+, C_-, E_+, E_-, CELL, terminals.

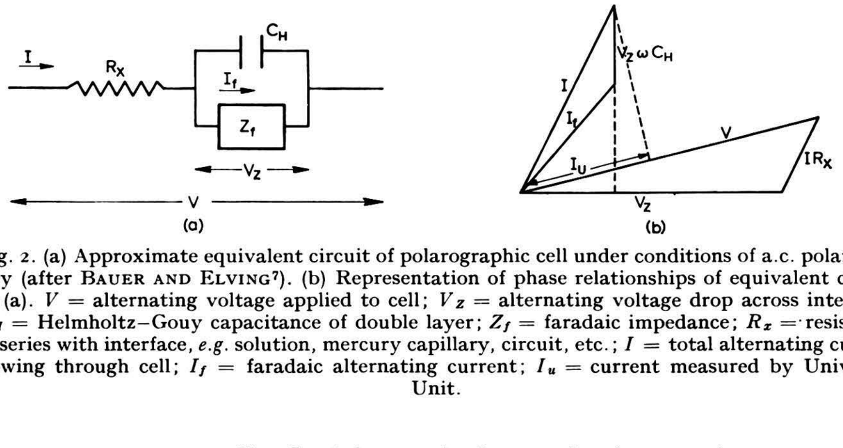

Fig. 2. (a) Approximate equivalent circuit of polarographic cell under conditions of a.c. polarography (after Bauer and Elving[7]). (b) Representation of phase relationships of equivalent circuit of (a). V = alternating voltage applied to cell; V_Z = alternating voltage drop across interface; C_H = Helmholtz–Gouy capacitance of double layer; Z_f = faradaic impedance; R_x = resistance in series with interface, *e.g.* solution, mercury capillary, circuit, etc.; I = total alternating current flowing through cell; I_f = faradaic alternating current; I_u = current measured by Univector Unit.

The Univector Unit comprises a circuit which will measure only the component

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* It is stated in the Patent Specifications[2,4] that the alternating current flowing through the polarographic cell is composed of a current in phase with and a current 90° out of phase with the voltage drop across the cell (V, Fig. 2). This could be misunderstood to imply that the equivalent circuit of the electrode–solution interface is simply a resistor and a capacitor in parallel and this would be an oversimplification of the true representation.[5,6] Using the circuit of Fig. 2 the sum of the faradaic and capacitative currents may however be resolved into components 90° out of phase with each other.

of the current (I_u in Fig. 2(b)) which is in phase with the voltage V. When no faradaic current is flowing (*i.e.* Z_f is infinite) $I = V_Z \omega C_H$ and represents the base current which is 90° out of phase with V_Z and has only a small component on V. Hence, when the current is measured with the Univector Unit, a smaller value is obtained than if it were measured with a scalar instrument. If R_x is small, then I_u is very small. When a faradaic current (I_f) flows, it has a larger relative component along V than $V_Z \omega C_H$ since its phase angle is generally close to 45° with V (RANDLES[5]). This results in increased sensitivity of measurement of the faradaic current since the base current is virtually eliminated. The reduction in magnitude of the faradaic current is insignificant compared with the advantage of eliminating the base current.

The phase discrimination of the Univector Unit is accomplished by means of a phase sensitive rectifier. In Fig. 1 an alternating voltage from the oscillator O is superimposed onto the direct polarising voltage from the potentiometer P. The alternating current flowing through the polarising circuit causes a voltage drop across the resistor R which is amplified by A and passed to the phase sensitive rectifier S. This is actuated by alternating voltage from O in such a way that the direction of the current is reversed in alternate half cycles of the applied voltage. Currents in phase with the alternating voltage from the oscillator are rectified as shown in Fig. 3(a) and a resultant current flows through the galvanometer G. Currents 90° out of phase with the voltage from the oscillator are rectified as shown in Fig. 3(b). In the latter case the current in the first quarter cycle cancels that in the second, etc., and no resultant current ensues.

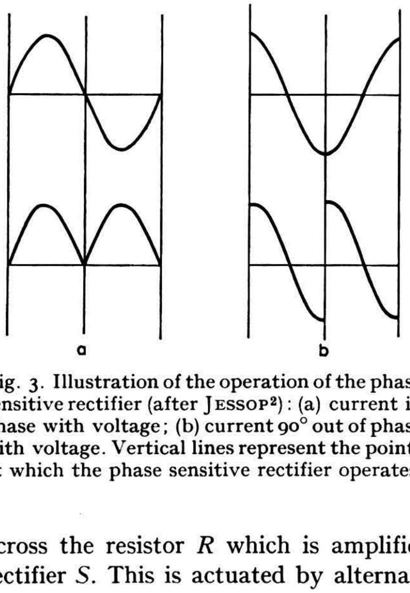

Fig. 3. Illustration of the operation of the phase sensitive rectifier (after JESSOP[2]): (a) current in phase with voltage; (b) current 90° out of phase with voltage. Vertical lines represent the points at which the phase sensitive rectifier operates.

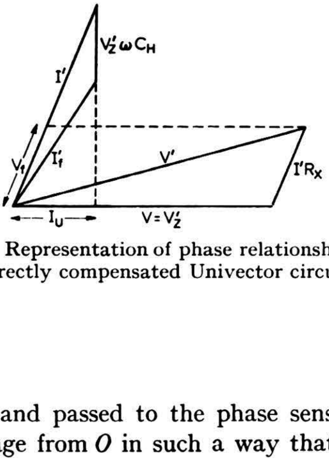

Fig. 4. Representation of phase relationships of correctly compensated Univector circuit.

The compensator amplifier provides a voltage which is proportional in magnitude to and in phase with the current I, and which is fed back into the polarising circuit and cancels the voltage drop across the series resistance R_x. In Fig. 4, the feedback voltage, V_f is added vectorially to the voltage V from the oscillator to give a new total applied alternating voltage V'. This causes a new current I' to flow through the circuit. If $V_f = I'R_x$ (the new voltage drop across the series resistance) then the new voltage drop across the interface V_Z' is equal to the old alternating voltage (V) across the cell. Since the phase sensitive rectifier cancels currents 90° out of phase with V, it can be seen from Fig. 4 that the base current $V_Z'\omega C_H$ will be entirely eliminated when the compensator is correctly adjusted (*i.e.* when $V_f = I'R_x$), and only the component of the faradaic current on V will be measured.

EXPERIMENTAL ARRANGEMENT

Instructions are supplied by the manufacturers for the connection of the Univector Unit to Cambridge Polarographs *via* terminals marked similarly on both instruments[8]. The method of connecting the Univector to a home-made or commercial polarograph other than that manufactured by the Cambridge Instrument Company may not, however, be evident from these instructions. Fig. 1 shows the terminals on the Univector Unit to which the potentiometer (C_- and E_+), galvanometer with Ayrton shunt, or other current measuring device (C_+ and E_-) and polarographic cell (CELL) should be connected for Univector operation.* When E_+ and E_- are short-circuited and C_+ and C_- are connected to the CELL terminals (*i.e.* the selector switch is set on "D C"), the instrument may be used to take a d.c. polarogram.

The results reported in this paper were obtained with the Univector Unit connected, in this manner, to a home-made d.c. polarograph. A critically damped Cambridge galvanometer of short period and maximum sensitivity $4.25 \cdot 10^{-10}$ A/mm was used to measure the current.

The conventional a.c. polarograph has been previously described by BREYER, GUTMANN AND HACOBIAN[9,10]. A Philips GM 4574 preamplifier and GM 6015 vacuum tube voltmeter were used instead of those originally specified. The usual precautions regarding single point earthing and shielding of leads were taken when using both instruments.

CHARACTERISTICS OF THE INSTRUMENT

The frequency of operation of the Univector Unit** was measured by the conventional Lissajous figure technique with the aid of a Tektronix Model 502 Oscilloscope and a Philips GM 2308 audio-frequency oscillator and found to be 33 ± 2 cycles/sec. The amplitude of the alternating voltage was found to be 26–28 mV (depending upon the warm-up time allowed) measured across the cell terminals with a Philips GM 6015 vacuum tube voltmeter. When the output from the instrument (terminals C_+ and E_-) was applied to the input of the vertical amplifier of the oscilloscope in parallel with a 3000 ohm resistor, there was evidence of about 1% ripple on the direct voltage. The overall gain of the instrument was found to be approximately 1; *i.e.* 1 μA a.c. at the input produces 1 μA d.c. at the output. The gain is variable over a small range by means of the sensitivity control.

In order to check the theory upon which the instrument operates and to determine the characteristics of the amplifier, the equivalent circuit of Fig. 2(a) was constructed from two decade resistance boxes and a decade capacitance box (Z_f was represented as a resistance) and connected to the Univector Unit in place of the cell.

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* Correct polarities must be observed.

** The measurements reported in this paper were obtained with the Univector Unit Serial No. C651398.

It was found that provided R_x was zero and Z_f was infinite (and the small series resistance inside the instrument was compensated) the current remained zero no matter what the value of C_H. When R_x was kept zero and Z_f varied from 2000 Ω to 100 Ω, with C_H equal to 1 μF, the plot of output current *vs.* $1/Z_f$ (representing the faradaic admittance) was linear above a value of Z_f of 600 Ω. At lower values of Z_f, the current reached a limiting value presumably due to overloading of the amplifier (see Fig. 5). No change in current could be detected when C_H was varied provided that R_x was zero.

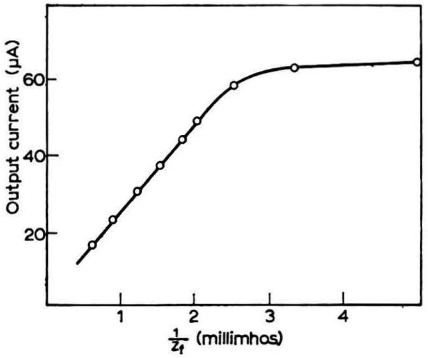

Fig. 5. Characteristics of Univector Amplifier.

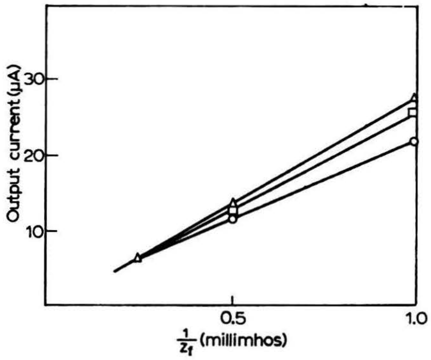

Fig. 6. Effect of compensation on output current: △, $R_x = 0$; □, $R_x = 100\ \Omega$, Univector correctly compensated; ○, $R_x = 100\ \Omega$, Univector uncompensated.

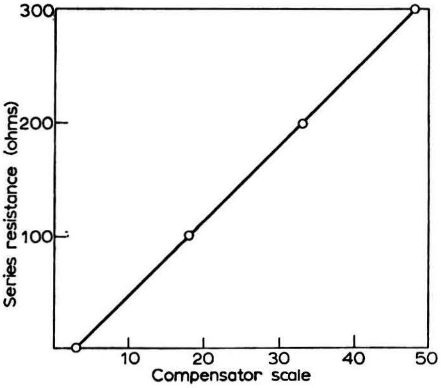

Fig. 7. Calibration of compensator scale.

Fig. 6 shows the effect of compensation on the output current for an external series resistance of 100 Ω and indicates the value of the compensator for polarographic measurements when the faradaic impedance is below 4000 Ω. It was found that the maximum value of R_x which could be successfully compensated was 300 Ω. Fig. 7 shows compensator scale readings plotted against series resistance.

The above results substantiate the theory upon which the design of the Univector Unit is based. They indicate that the instrument should not be used to measure currents higher than about 40 μA.* This is approximately equal to the in-phase component of the faradaic current given by a millimolar cadmium solution. It should normally be possible to keep the series resistance well below 300 Ω by the use of a high concentration of supporting electrolyte (0.5–1 M) and a "pool-condenser" reference electrode[11]. The use of the latter in conjunction with the Univector Unit was found not to alter the height or shape of waves, compared with those obtained using a mercury pool anode.

APPLICATION TO FARADAIC PROCESSES

The phase angle for the Cd(II) reduction has been measured by BAUER AND ELVING[7] and found to be close to 45° at low frequencies. Currents measured with the Univector Unit should then be roughly $1/\sqrt{2}$ times the scalar current. Fig. 8 shows a comparison between the waves obtained with a conventional a.c. polarograph and a Univector Unit for 10^{-4} and 10^{-5} M cadmium solutions. It can be seen that the Univector Unit gives an increase in sensitivity even though the current measured is smaller than in the case of the conventional a.c. polarograph.

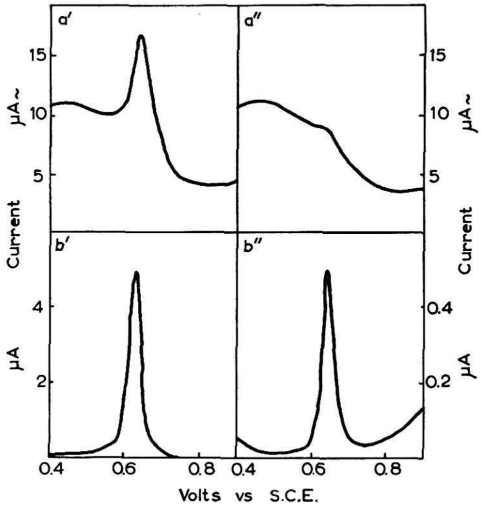

Fig. 8. Comparison of conventional a.c. polarogram with Univector a.c. polarogram. Cadmium in 1 M potassium chloride + 0.01 M hydrochloric acid: (i) 10^{-4} M Cd; (ii) 10^{-5} M Cd; (a) polarogram obtained with conventional a.c. polarograph (27 mV, 33 cycles/sec); (b) polarogram obtained with Univector Unit.

At a concentration of 10^{-6} M Cd in 1 M supporting electrolyte, a well defined wave can still be obtained with the Univector Unit, but at the high galvanometer sensitivity necessary for this measurement, current readings at drop fall vary from drop to drop and impurities in the supporting electrolyte (*e.g.* Pb and Cu)** produce

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* The manufacturers do not advise the use of the instrument for current measurement above about 20 μA.[8]

** Analytical Reagent grade chemicals were used without further purification.

quite high waves. FERRETT *et al.*[3] have explained the first phenomenon in terms of slight variations in the capillary characteristics, whilst JESSOP[12] suggests that this may be due to a "random direct current component from the phase sensitive rectifier due to the drop falling and thus stopping the a.c. at different portions of the a.c. cycle". The latter difficulty can be partially overcome by the use of a 0.1 *M* supporting electrolyte provided that the total series resistance does not exceed 300 Ω. At this high galvanometer sensitivity the base current is not independent of the polarising potential and its actual value depends upon the potential at which the compensator is adjusted to give zero current.

No difference in summit potential was observed for the two instruments but the waves appear to be narrower in the case of the Univector Unit when the conventional a.c. polarograph is operated at the same alternating voltage.

Irreversible processes do not give waves on either instrument[1,3].

Assuming that other reversibly reduced metal ions behave similarly to cadmium, the above results indicate that metal ions may be determined with accuracy, using the Univector Unit, at a concentration between 10^{-5} and 10^{-6} *M*, an increase in sensitivity of 10 to 100 times compared with a conventional a.c. polarograph.

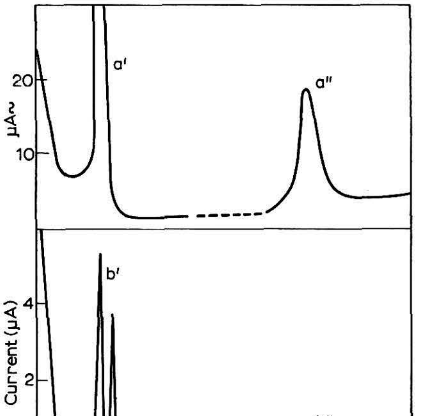

Fig. 9. Tensammetric waves of half-saturated *cyclo*hexanol solutions: (i) positive tensammetric wave; (ii) negative tensammetric wave; (a) graph obtained with conventional a.c. polarograph (27 mV, 33 cycles/sec) using 1 *M* sodium sulphate as supporting electrolyte; (b) corresponding graph obtained with Univector Unit; (c) graph obtained with Univector Unit using 0.1 *M* sodium sulphate as supporting electrolyte.

APPLICATION TO TENSAMMETRIC PROCESSES

Compounds which are reversibly adsorbed and desorbed on a mercury surface generally give rise to the so-called tensammetric waves which result from an increase in the differential capacitances of the dropping mercury electrode during an adsorption–desorption equilibrium[13].

The equivalent circuit for a tensammetric process is not the same as that for a faradaic process, but no agreement has been reached regarding its actual nature. However, although the impedance of the double layer at the electrode surface cannot be regarded as wholly due to a capacitance, the greatest proportion of it is representable in this manner[13,14]. Consequently, the phase angle of a tensammetric current will be close to 90° with the applied voltage and the corresponding current measured by the Univector Unit will, in general, be very small.

Many tensammetric currents have highly distorted waveforms owing to the presence of a large proportion of harmonics[15]. The positive *cyclo*hexanol wave has such a distorted waveform and, instead of the normal single wave obtained with a conventional a.c. polarograph, a double wave with a trough* is obtained when the current is measured with a Univector Unit, provided that the series resistance is below 150 Ω (see Fig. 9(a) and (b)).

By the following technique, the wave forms of the total current flowing through the polarographic cell and the voltage drop across the cell were obtained at salient points on the positive *cyclo*hexanol wave.

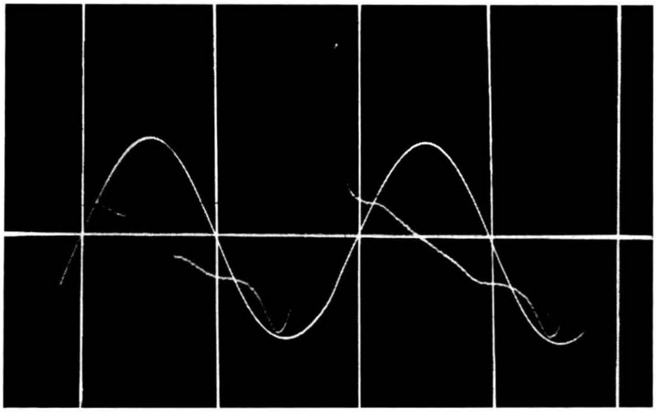

Fig. 10. Waveform of voltage across cell (sinusoidal) and current passing through cell (distorted) for *cyclo*hexanol (27 mV, 33 cycles/sec) at potential corresponding to positive peak of positive tensammetric wave in 1 *M* sodium sulphate. Vertical lines indicate the points at which the Univector phase sensitive rectifier would operate.

The voltage drop across the cell was displayed on one beam of a Tektronix Model 502 Dual Beam Oscilloscope and the current passing through the cell, after amplification with a Philips GM 4574 preamplifier, was displayed on the other beam. Since both beams are operated from the one sweep source they are triggered in

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* This trough extends below the zero line under certain conditions.

phase. This enables the points on the current waveform at which the phase sensitive rectifier in the Univector Unit would operate, to be determined (see Fig. 3). The vertical lines in the plates indicate these points.

Figs. 10–12 show the wave forms obtained for a half-saturated *cyclo*hexanol solution in 1 *M* sodium sulphate at potentials corresponding to those of the two peaks and the trough of the double wave obtained with the Univector Unit.

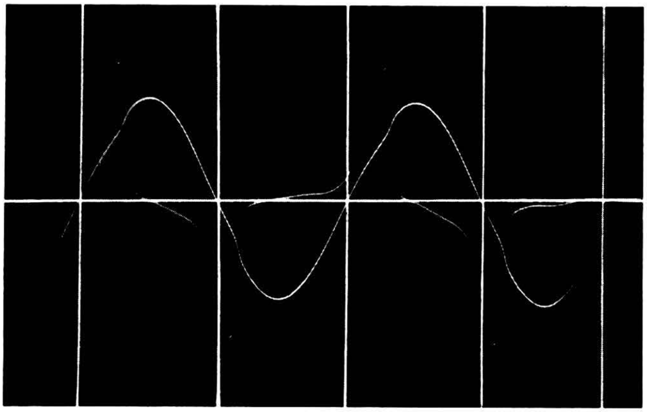

Fig. 11. As Fig. 10 for potential corresponding to trough of positive tensammetric wave in 1 *M* sodium sulphate.

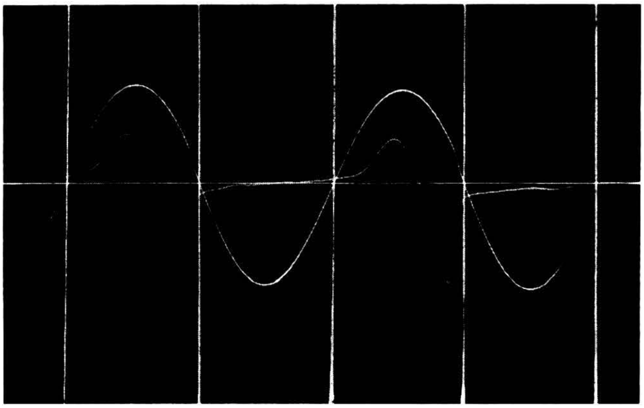

Fig. 12. As Fig 10 for potential corresponding to negative peak of positive tensammetric wave in 1 *M* sodium sulphate.

When these waveforms are rectified as in Fig. 3, it becomes obvious that the average current during one cycle changes sign during the potential range of the wave. At the potentials corresponding to the peaks, the average current has the opposite sign to that at the potential corresponding to the trough. These results explain the double wave obtained with the Univector Unit.

If a high series resistance is introduced into the polarising circuit (*e.g.* a low concentration of supporting electrolyte is employed), the phase angle of the current becomes smaller. Figs. 13 and 14 show the current waveform obtained with half-saturated *cyclo*hexanol in 0.1 M sodium sulphate, indicating that the current and voltage are almost in phase*. Fig. 9(c) shows the corresponding Univector polarogram. The same result can be obtained by placing a 300 Ω resistor in series with the cell and using 1 M supporting electrolyte.

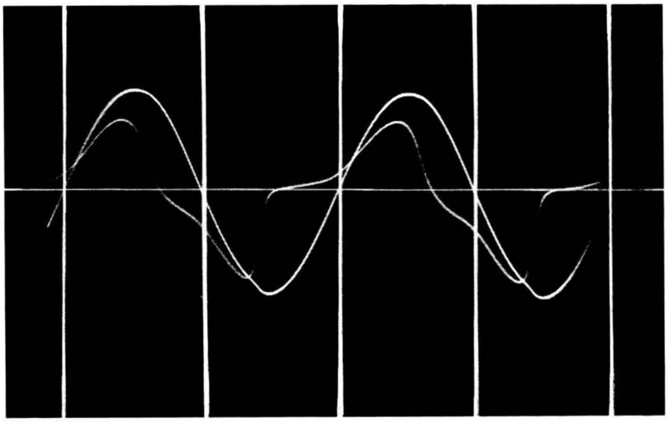

Fig. 13. As Fig. 10 for potential corresponding to summit potential of positive tensammetric wave in 0.1 M sodium sulphate.

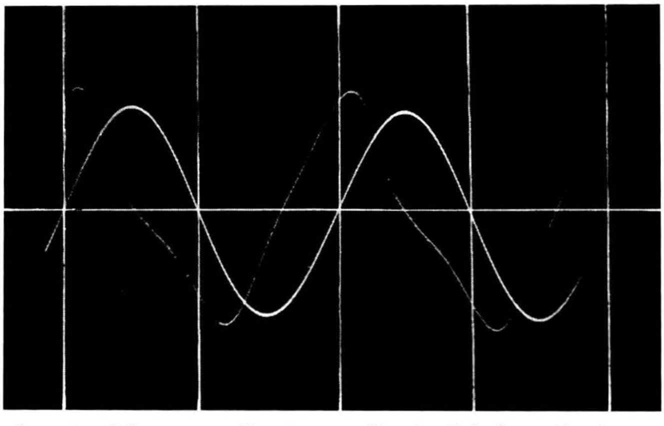

Fig. 14. Fig. 10 for potential corresponding to summit potential of negative tensammetric wave in 0.1 M sodium sulphate.

This phenomenon can be explained if the tensammetric process is considered to

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* Strictly speaking it is not possible to compare the phase angle of a distorted wave form with a purely sinusoidal one. From the mode of operation of the Univector Unit and for the purposes of this paper, it is justifiable to take the phase angle as the angular distance between the maximum and minimum values of current and voltage in each cycle.

be represented by a capacitance. The circuit parameters can then be represented vectorially by the equation:

$$Z = R_x - j/\omega C_T$$

where Z is the total impedance, R_x is the series resistance, ω is the angular frequency, C_T is the tensammetric capacitance and j is $\sqrt{-1}$. When $R_x \gg -j/\omega C_T$, the phase angle of the current will be mainly determined by R_x, *i.e.* it will be zero. If $-j/\omega C_T \gg R_x$, the phase angle will be that due to the capacitance, *i.e.* it will be 90°. Between these two extremes it will have intermediate values. Thus, as R_x is increased the phase angle of the current at the summit potential will be decreased and this will naturally result in an increase in the current reading of the Univector Unit. This is demonstrated in Figs. 9(b) and (c) where the negative *cyclo*hexanol wave (which does not have a highly distorted waveform, *cf.* Fig. 14) is seen to increase in height when the supporting electrolyte concentration is changed from 1 M to 0.1 M. There is no such change when the wave is measured with a conventional a.c. polarograph[16].

Similar results have been obtained for *n*-octyl alcohol in which case both waves are distorted[15] and 8-hydroxyquinoline where the one tensammetric wave obtained[17] is not appreciably distorted. In the case of pyridine, the addition of a high series resistance has the same effect as above but although the current waveform is highly distorted, no double wave appears when the series resistance is low. A careful examination of this waveform in the manner described above, however, predicts only one wave.

It was found that for a solution of saturated *n*-octyl alcohol in 1 M sodium sulphate, the minimum external series resistance required to produce a single wave was 150 Ω. Above 1200 Ω the wave heights decreased due to the effect of decreasing voltage drop across the interface.

Satisfactory compensation of the Univector Unit at potentials at which there was an adsorbed film was not obtained. A point was reached beyond which further compensation did not result in a decrease in current. This would indicate the presence of an equivalent parallel resistance in the interface in the presence of an adsorbed film. Compensation could be obtained as usual at potentials where the surfactant was desorbed.

The above results, in which wave splitting was observed, were obtained with the compensator set at full scale since this was found to enhance the effect.

Summit potentials of waves obtained with both instruments were found to be identical.

From the above results it can be seen that the conventional a.c. polarograph is a more suitable instrument for the examination of tensammetric waves than the Univector Unit. Although the Univector Unit can be made to give quite good tensammetric waves in the presence of a high series resistance without compensation, this arrangement is unsuitable for precise work since the wave height and shape are very sensitive to the small and unavoidable day-to-day changes in series resistance. The sensitivity of the Univector Unit for tensammetric waves is at the best no better than that of the conventional a.c. polarograph. This has been quantitatively demonstrated in the case of 8-hydroxyquinoline where the lowest concentration at which waves are obtained with either instrument is $2 \cdot 10^{-6}$ M in 0.1 M ammonium acetate supporting electrolyte.

CONCLUSION

The Cambridge Univector Polarograph Unit has been shown to be 10 to 100 times more sensitive than the conventional a.c. polarograph for metal ion determinations. In these cases the phase angle of the current with respect to the alternating voltage is approximately 45°. Tensammetric processes, the currents from which generally have a phase angle close to 90° and often have a highly distorted wave form, do not produce good waves when the current is measured with a Univector Unit except in the presence of a large series resistance. Faradaic processes whose phase angle is near 90° would be expected to behave similarly but no cases of this have as yet been studied. Electrode reactions involving a rearrangement current, *i.e.* a simultaneous faradaic and tensammetric process[18], could give rise to anomalous waves when examined with the Univector Unit.

Before the results of a fundamental investigation with the Univector Unit could be fully interpreted, at least an approximate value of the phase angle for the reaction current and its wave form would have to be determined.

ACKNOWLEDGEMENTS

The authors wish to thank Prof. B. Breyer for his encouragement during this work and Mr. T. Biegler for helpful discussions. One of us (J.W.H.) also wishes to thank the University of Sydney for a Commonwealth Post-Graduate Studentship which made this work possible.

SUMMARY

The Cambridge Univector Polarograph Unit is compared with an a.c. polarograph of the type used by Breyer and co-workers. A description of the mode of operation of the Univector Unit is followed by a discussion of some of its electrical characteristics. Details for the connection of the Univector Unit to a homemade d.c. polarograph are also given. The waves obtained for polarographic and tensammetric processes are discussed with reference to the mode of operation of the instrument and the occurrence of some anomalous tensammetric waves is explained.

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Short Communications

Direct potentiometric determination of pyruvic acid with vanadium(V)

Methods have been used for the oxidative determination of a large number of organic compounds with various oxidants[1]. Since such processes involve reaction between neutral molecules and the oxidant, they are not fast enough to be followed by direct titration and generally an excess of the oxidant is used, the excess being determined by back-titration with some inorganic reductant.

Oxidation of oxalic acid with permanganate[2] and ascorbic acid with iodate[3] are among the few examples of direct titrimetric determination of organic compounds by oxidimetric methods. During studies on the oxidimetric determination of organic compounds by cerium(IV)[4,5,6] and vanadium(V)[7,8,9] in these laboratories, it was observed that certain easily oxidisable groups (α-keto or α-hydroxy acids), when attached to a group more stable towards oxidant, undergo oxidation fast enough to be followed by direct titration, *e.g.*, it was observed that oxidation of mandelic acid in cold and diffused light proceeds to benzoic acid almost instantaneously, and it was possible to titrate mandelic acid[6,7] with these oxidants even in the presence of other oxidisable compounds, which are otherwise slowly oxidised at elevated temperatures and higher acidity. It was observed that aliphatic α-keto acids, such as pyruvic acid, exhibit similar behaviour towards the oxidant, and it was possible to determine pyruvic acid by direct titration with vanadium(V). Since vanadium(V) is a mild oxidant, it has been preferred for the direct determination of pyruvic acid when present alone, or in the presence of organic compounds more resistant towards oxidation.

Although a visual indicator, such as N-phenyl anthranilic acid or barium diphenylamine sulfonate, can be used in vanadate titrations, these have limitations of being applicable only in a limited range of acid concentration, and hence it was preferred to use potentiometric end-point determination. Limitations of visual indicators in vanadimetry have been discussed by various workers, and it has been reported that even the data of standardisation of vanadate solution with iron(II) do not strictly agree with potentiometric results, unless strict conditions of acidity are maintained. A potentiometric method, on the other hand, gives correct and reproducible results in a wider range of acid concentrations, and has been described as most satisfactory for determining the end-point in vanadate titrations.

EXPERIMENTAL

Preparation and standardisation of vanadium(V) solution[8] from vanadium pentoxide have been described elsewhere.

An approximately 0.02 *M* aqueous solution of pyruvic acid was prepared, and its strength was determined both by acidimetric titration and oxidimetric determination with permanganate.

Since pyruvic acid may undergo decarboxylation at high acid concentration and high temperature due to addition of sulphuric acid, it was preferred to add aqueous pyruvic acid, from a burette, to vanadate solution having an initial sulphuric acid concentration of about 9 *F* in the titration vessel. The electrode system consisted of a bright platinum indicator electrode and a S.C.E. reference electrode. A Cambridge pH meter (battery operated) was used for e.m.f. measurements, and the solution was stirred magnetically. Table I gives the results of some of the determinations.

TABLE I

Mmoles of pyruvic acid		*Acid Concn.*	*Approx. time in min*	*(dE/dv) max*
Taken	*Found*			
0.20	0.196	9 *F*	2 min	430
0.25	0.250	8 *F*	2 min	410
0.30	0.305	6 *F*	4 min	390
0.25	0.254	5 *F*	5 min	380

The reaction can be carried out at lower acid concentrations also, but in these cases, more time should be allowed after addition of each portion of the titrant.

DISCUSSION

It has been observed that determination of pyruvic acid by direct potentiometric titration with vanadium(V) is a useful method for its estimation in complex mixtures of amino acids and their deamination products, *i.e.*, in such mixtures where pyruvic acid is actually found in biochemically important mixtures.

The present method is an addition to the few direct titrimetric methods used in organic analysis and it is expected that it will find application in biochemical analysis.

SUMMARY

A method for the direct potentiometric oxidimetric determination of pyruvic acid with vanadium(V) has been described.

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A device for the application of samples in cellulose acetate electrophoresis

An important technique in the armament of scientists is zone electrophoresis. In cellulose acetate electrophoresis, the device described has achieved notable success in:

(1) the application of samples in a straight line, and exactly parallel to the path of migration.

(2) making reproducibility far easier, and

(3) allowing sharper, faster, applications.

DESCRIPTION

To apply the samples in a straight line, a movable Perspex bridge is incorporated in the electrophoretic apparatus. The bridge is approximately 3 cm wide and 2.5 cm deep and a few thousandths of a mm shorter in length than the internal walls of the electrophoretic apparatus.

The bridge rests on Perspex shelves, one cm above the surface of the suspended strips. The applicator is a stainless steel wishbone 1.5 cm long, the arms of which are separated by a distance equal to the width of the strips, minus 1 cm (*e.g.*, 1.5 cm for the standard 2.5 cm strips). Suspended between the ends of the arms are two parallel stainless steel wires, 0.005 of an inch thick (.0127 cm) and separated by 0.030 of an inch (.0762 cm). The shaft of the wishbone is embedded in a square shaft of Perspex 15 cm long, so that the planes of the two wires are parallel to the sides of the shaft. (See Fig. 1).

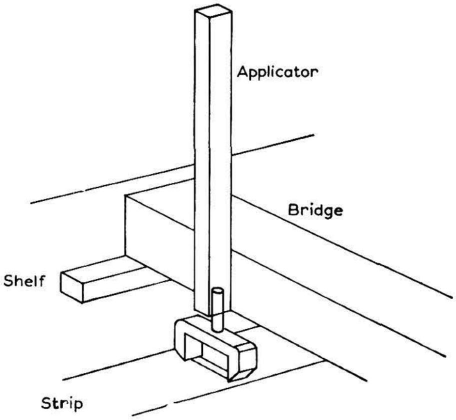

Fig. 1

METHOD

The cellulose acetate strips are placed in position after being wetted by buffer, and their anode ends are marked with a pencil at the junction of the strip holder and filter paper with the strip. The bridge is then positioned to coincide with a reference mark on the Perspex shelf or with a mark on the control strip, and the current is turned on.

The applicators charged with the samples are then placed flat against the bridge and contact is made with the strips. The bridge is then removed and the apparatus closed. With standard applicators, the origins of the samples are in a straight line, of standard width, parallel to the flow of current, and if calibrated pipettes were used to apply the samples to the wires of the applicators, are of similar amounts.

ACKNOWLEDGEMENT

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Protein Foundation, Inc.,
Boston, Mass. (U.S.A.)

CALVIN A. SARAVIS

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J. Electroanal. Chem., 3 (1962) 350–351

Book Reviews

Contributi Teorici e Sperimentali di Polarografia, Vol. 5, Supplement to *Ricerca Scientifica*, 1960, 315 pages, lire 2,500.

The series of "Contributi Teorici e Sperimentali di Polarografia" continues with this fifth volume. Only the second half, of the book can really be considered to concern the title of the series. In fact, the first half, with its twelve chapters, reports lectures given during a meeting organized by the Polarographic Centre of the Italian National Research Council, and by the Institute of Physical Chemistry of the University of Padua, which develop the very broad theme: "Relationships between Constitution and Physico-chemical Behaviour". The second half, as is customary, reports more strictly polarographic papers presented during the summer courses of the Polarographic Centre. No discussion is given after each of the published papers.

J. Electroanal. Chem., 3 (1962) 351

Systematic Qualitative Analysis, by G. A. MORRISON, Butterworths and Co., Ltd., London, 1961, ix + 198 pages, £1. 5s.

This short book of nearly 200 pages, including the appendix and an index, is intended for first year University students, for whom preparatory texts are sometimes too poor, and for whom textbooks are too advanced. In fact, the scheme adopted is the classical one, with sub-divisions into chloride, sulphide, hydroxide, carbonate and alkali groups, and with the practical operations conducted on the semi-micro scale. Some less common cations and anions are introduced. Systematic presentation of the analysis is preceeded by a whole chapter dealing with the most important theoretical concepts encountered in this type of analysis: *i.e.* dissociation constants, buffered solutions and solubility constants. A second short chapter describes semi-micro apparatus and techniques.

The best choice of didactic material and methods is an endless matter for discussion, so that it is very difficult to give a critical judgment of a book of this kind. It must be stressed that such a book nearly always fulfils the purpose for which it has been written, and this is also the case with this book, although some criticism could be made *e.g.* of the lack of equations, and some insufficiently clear descriptions.

The print is very clear and good, so that the book is easy to read.

Paper Electrophoresis, by L. P. Ribeiro, E. Mitidieri and O. R. Affonso, Elsevier, Amsterdam, 1961, vii + 442 pages, Dfl. 37.50.

This book deals with various aspects of paper chromatography. Chapter 1 describes the historical side of electrophoresis and the terminology in use. In chapter 2 some theorical considerations are reviewed and experimental work is considered in chapter 3; various methods and the apparatus in use are discussed.

The 4th chapter deals with quantitative analytical determination of proteins, whose qualitative aspects are so often important for diagnostic purposes. Chapter 5 concerns the proteins of human serum; the 6th, proteins of animal serum; the 8th, proteins in biological fluids and in cells; the 9th, haemoglobins; the 10th, lipoproteins, and the 11th, glycoproteins and mucoproteins.

The use of paper electrophoresis allows the investigation of various aspects of chemistry and protein biochemistry, as is explained in the 7th chapter. Chapters 12 and 18 discuss applications of such methods to enzymes, hormones, vitamins, carbohydrates, nucleic acids, amino-acids, and inorganic substances.

Immunochemistry is studied by using e.f.c., and is summarized in chapter 19; the book ends with a chapter of other applications not included in the classification made by the Authors. Because of its nature, the book is recommended to all those who use electrophoresis as a fractionating or analytical technique, and to all those who must rapidly bring themselves up-to-date with the various subjects treated. A comprehensive bibliography is very helpful to those who wish to carry their study of the subject further.

C. Casinovi, Istituto Superiore di Sanità, Rome

J. Electroanal. Chem., 3 (1962) 352

Treatise on Analytical Chemistry, by J. M. Kolthoff and P. J. Elving, with the assistance of E. B. Sandell, Part 1, Vol. 3, Interscience, N. Y. and London, 1961, xvii + pages 1309–1750, $16.75.

The review of Vols. 1 and 2 of this Part I of the "Treatise on Analytical Chemistry" have been published already in this journal (2 (1961) 92 and 3 (1962) 154) so that general comments on it will be omitted here. This volume concludes Section C of Part I, devoted to principles and techniques of separations, and concerns three main subjects: liquid-liquid extraction (chapter 31), precipitation and crystallization (chapter 32) and chromatography (chapters 33–37). Generally speaking, chromatography is too wide a word to-day, because it is employed for very different techniques, such as column liquid-solid adsorption, (classical chromatography), many ion-exchange processes, paper chromatography and gas chromatography. In the opinion of the reviewer, even if some principles are common to these four different chromatographic techniques, it would be advisable to differentiate them better, also by name, because techniques and fields of application are too different. In fact, the five chapters relating to "chromatography", have been written by different authors because it is almost impossible to be an expert in all the different types of chromatography quoted above.

The standard of this Volume is at the same high level as the preceeding Volumes of this Part, and the general distribution of the material follows a scheme similar to that adopted previously. Perhaps, in this third Volume, the description and discussion of experimental work and techniques have been developed a little more.

Very modern techniques have been taken into consideration too, *e.g.* the very new purification method using zone melting, which is not yet widely employed as an analytical laboratory technique.

G. Milazzo, Istituto Superiore di Sanità, Rome

J. Electroanal. Chem., 3 (1962) 352

Reagent Chemicals, written on behalf of the American Chemical Society, American Chemical Society, Washington, D.C., 1961, xv + 564 pages, $10.

The third edition of this publication by the American Chemical Society deals with the problem of the purity of reagents, and contains numerical data and detailed procedures of analysis for over 250 reagents. For each reagent, the minimum assay, some physico-chemical quantities, maximum tolerated impurities, and methods of testing are given.

The general methods of testing are often classical (and old) ones, although for many impurities, more sensitive or more specific reagents have been successfully used for several years.

This book can be very useful for continuous production control and for simple rapid testing in the laboratory because it describes the most common impurities to be expected in any reagent, and the average purity attained by the so called "analytical grade" reagents.

J. Electroanal. Chem., 3 (1962) 352

1. Fundamental electrochemistry

1265 – New electrochemical basis for the concept of pH. G. Valensi (Chemical Institute, University of Poitiers, France). *Corrosion et anti-corrosion*, 7(1959) 185–194.
In order to obviate ambiguities arising from the current definition of pH, particularly in the field of analytical and biological chemistry, the following new definition is proposed:

$$\mathrm{pH} = -\frac{\log m_A \gamma^2{}_{\pm(\mathrm{HCl})}}{\gamma_{\pm(\mathrm{KCl})}}$$

where γ is the mean activity coefficient (that can be experimentally determined). The method described for pH-measurement is more accurate and reliable than the classical one. [Ca.Cas.]

1266 – Ambiguïté de la notion de pH. Étude de l'activité des ions H^+ au moyen de piles sans jonction liquide. M. Laloi (Centre d'Etudes et de Recherches de Chimie Organique Appliquée, C.N.R.S. Bellevue, S & O, France). *Bull. soc. chim. France*, (1961) 1663–1670.
L'auteur présente ici une revue sur les piles sans jonction employées pour mesurer le pH.
Après un bref exposé théorique–qui rappelle l'ambiguité de la notion de pH–on décrit la préparation de différentes électrodes (électrode normale à hydrogène, électrode à sels d'argent, électrode à sels de mercure, électrodes à amalgames). En outre, l'auteur indique les performances qu'il est possible d'espérer de ces électrodes en insistant sur les précautions qui sont nécessaires pour obtenir des mesures stables et reproductibles.
Une bibliographie importante (72 références) permet de se rendre compte des applications des méthodes précédentes. [J.Des.]

1267 – Report on the standardization of pH and related terminology. R. G. Bates and E. A. Guggenheim. (Dr. Bates: National Bureau of Standards, Washington, 25, D.C., U.S.A.; Prof. Guggenheim: Department of Chemistry, Reading University, Great Britain). *Pure and Appl. Chem.*, 1 (1960) 163–168.
The degree of standardization of pH achieved in Great Britain, United States and Japan is summarized. There is international agreement for the symbol: pH. In the three existing standards this definition of pH is used. Details are given about the primary standards specified in the American and in the U.K. and Japanese definitions. Ionic activity coefficients for solutions containing only 1:1 electrolytes are treated as an introduction to the discussion of the interpretation of pH. [Su.Mo.Ce.]

1268 – An operationally defined pH scale from 25° to 275°. Richard S. Greeley (Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 32 (1960) 1717–1718.
Values for the electric tensions and the standard electric tension of the AgCl/Ag electrode are derived from measurements of the electric tensions of the cell $\mathrm{AgCl{-}Ag/HCl}(M)/\mathrm{Pt{-}H_2}(p)$ from 25° to 275°, using concentrations from 0.005–0.5 *M*, and to 1.0 *M* in some cases, at hydrogen pressures of about 1 atm. The mean ionic activity coefficients for the corresponding HCl solutions have been calculated.
The author suggests the use of these measurements to extend the operationally defined pH scale to temperatures above 95°. A table is given with values of the pH of HCl solutions from 0.001–1.0 *M* and for temperatures from 25°–275°; the author suggests that the values for 0.1 *M* HCl shall be taken as an extension of Bates scale of pH for 0.1 *M* HCl, which includes values from 0°–95° (Bates "Electrometric pH Determinations" Wiley, p. 87). In the range 225–275° the variation in the readings is ± 0.1 pH unit [Su.Mo.Ce.]

1269 – A unified pH scale (in Russian). N. A. Ismailov (Gorky University, Karkov, U.S.S.R.). *Doklady Akad. Nauk, S.S.S.R.*, 127 (1959) 104–107.
In a given non-aqueous medium M, the pH is given by definition as $\mathrm{p_{HL}} = \log a^*{}_{\mathrm{MH}^+} = -\log m_{\mathrm{MH}^+}\gamma^*{}_{\mathrm{MH}^+}$ where $a^*{}_{\mathrm{MH}}$ is the activity of H^+ ions in the given medium and γ^* is the activity coefficient. By comparison with an infinitely dilute aqueous solution, we have $\mathrm{p_A} = \log a_{\mathrm{H}^+} = -\log a^*{}_{\mathrm{MH}^+} - \log \gamma_{\mathrm{OH}^+} = \mathrm{p_{HL}} - \log \gamma_{\mathrm{OH}^+}$ where $\log \gamma_{\mathrm{OH}^+}$ can be calculated from the chemical solvation energies $A_{x\mathrm{H}^+}$ of protons in water, and in the solvent M: $\log \gamma_{\mathrm{OH}^+} = (A_{x\mathrm{H+H_2O}} - A_{x\mathrm{H+M}})\ 2.3\ RT = \Delta A_{x\mathrm{MH}^+}/2.3\ RT$. In ammonia, water, methanol, propanol, *n*-butanol, *iso*-butanol, *iso*-amyl alcohol,

benzyl alcohol and formic acid, log γ_{OH^+} has the value —16.6; 0.0; 3.3; 4.2; 4.2; 4.7; 4.5; 4.45; 3.1 and 8.6 respectively. A comparison of the pH values in aqueous solution on this unified scale for different solvents is given. The cases of acetic and hydrochloric acids are dealt with in detail.
[Ca.Cas.]

1270 – Calculation of hydrogen ion concentration in electrolyte solutions. III. Limits of applicability of the formulae for ideal solutions of dibasic acids. I. Zsakò (Physical Chemistry Institute, Bubes-Bolyai University, Cluj, Rumania). *Studi Cercetari Chim.* (*Cluj*), 10 (1959) 97–111.
Simplification of the general equation gives 38 approximate equations, which were applied in calculating the hydrogen ion concentration of various dibasic acid solutions. (See abstract no. 1272.)
[Ca.Cas.]

1271 – Measuring units of acidity (in German). K. Schwabe (Institut für Elektrochemie und physikalische Chemie, Technische Hochschule, Dresden, Deutschl.). *Abhandl. sachs. Akad. Wiss. Leipzig Math.-naturw. Kl.*, 46 (1959) 1–24.
It is shown that units for measuring acidity are possible only on the basis of the Arrhenius or Brönsted definitions. A comparison is made between potentiometric, colorimetric and catalytic measurements of acidity and is extended to non-aqueous solvents, but the results of such a comparison are very poor. Also, the Hammett function has been utilized for comparing acidity in different solvents.
[Red.]

1272 – Calculation of hydrogen ion concentration in electrolyte solutions. II. Limits of applicability of the formula in ideal monobasic acids solution (in German). I. Zsakò (Physical Chemistry Institute, Bubes-Bolyai University, Cluj, Rumania). *Studi Cercetari Chim.* (*Cluj*), 10 (1959) 79–96.
From the general formula (I. Zsakò, *ibid.*, 9 (1958) 67) some simplified equations(II) are derived from which the hydrogen ion concentration can be calculated in solutions of acids (10^{-10}–1 *M*), whose dissociation constants lie in the range 10^{2}–10^{16}. The accuracy of the results is given in graphic form.
[Ca.Cas.]

1273 – Fundamental principles of electrochemical kinetics (in German). E. Lange (Institut für physikalische Chemie, Universität Erlangen-Nürnberg, Deutschland). *Z. physik. Chem.* (*Leipzig*), 217 (1961) 42–70.
A survey of fundamental concepts and parameters of electrochemical kinetics is given. Uniform symbols and expressions for the different parameters and effects based on the program of C.I.T.C.E. are proposed.
[H.W.Nür.]

1274 – Reaction steps of electrochemical phase-boundary reactions (in German). W. Lorenz and G. Salié (Institut für physikalische Chemie, Universität Leipzig, Deutschland). *Z. physik. Chem.* (*Frankfurt*), 29 (1961) 390–396.
On the basis of the concept that the initial and final states of a particle taking part in an electrochemical reaction have configurative differences (degree of solvation etc.), the principles for a refined mathematical treatment of electrode reactions are outlined. When the configurative differences are intensive enough, the electrode reaction covers several discrete intermediate configurations which correspond to certain states of adsorption.
[H.W.Nür.]

1275 – Kinetics of phase formation. III. On critical supersaturation of aqueous electrolytes (in German). M. Kahlweit (Max-Planck-Institut für physikalische Chemie, Göttingen, Deutschland). *Z. physik. Chem.* (*Frankfurt*), 28 (1961) 245–249.
Auf Grund des "Theorems der übereinstimmenden Zustände" lasst sich folgende Regel für die Übersättigbarkeit Γ einer wässrigen, ungerührten Elektrolytlösung formulieren:

$$\ln \Gamma_{\mathrm{m}} \approx \left(\frac{8.6 \cdot 10^{-26}}{40 + \ln c_s}\right)^{1/2} \cdot \left(\frac{H_L{}^1}{T}\right)^{1/2}.$$

Die Grösse $H_L{}^1$ (in erg. Mol^{-1}) ist die ,,letzte Lösungswärme" des Salzes. $C_s \equiv$ Sättigungskonzentration in Mol cm^{-3}.

$$H_L{}^1 = H_L{}^s + c_s\left(\frac{\delta H_L}{\delta C}\right)_{C_s}$$

mit $H_L{}^s$ = Ganze molare Lösungswärme; H_L = integrale Lösungswärme; C = Konzentration. Die Temperatur ist in °Kelvin einzusetzen.
[H.W.Nür.]

1276 – On the theory of simultaneous deposition of different metal ions(in German). A. T. Vagranýan and T. A. Fatueva (Institut für Elektrochemie, Akademie der Wissenschaften, Moskau, U.S.S.R.). *Z. physik. Chem.*, *(Leipzig)*, 216 (1961) 163–175.
The velocity of discharge for metal ions deposited simultaneously at the same electric tension is frequently not equal to the sum of the single discharge velocities for seperate deposition. This is caused by variations in electrode conditions, alterations of concentrations of both sorts of metal ions in the electric double layer and variations in solvation of the ions compared with the case of separate deposition. For the simultaneous deposition of Co and Ni a strong diminution of discharge velocity is observed for both ions, while for Ni and Fe only discharge of Ni is reduced, the discharge of Fe being accelerated. [H.W.Nür.]

1277 – Theory of electrolysis on a plate electrode during combined concentration and chemical polarisation under conditions of natural convection (in Russian). L. P. Kholpanov (Institute of Chemical Technology, Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 2223–2227.
Based on a previously proposed theoretical method (L. P. Kholpanov, *Zhur. Fiz. Khim.*, 35 (1961) 1567) for calculating the rate of an electrochemical reaction during combined concentration and chemical polarisation, the equation:

$$\ln i = n \ln (1 - i/i_{\text{lim}}) + \ln kzFa_0^n - A_{\text{eff}}/RT$$

has been deduced for the current density at the surface of a plate electrode under conditions of natural convection. Using this formula:

$$i = \cfrac{zFc_0}{\cfrac{U_t x^{1/4}}{0.7\, DPr^{1/4}[g\alpha/4\nu^2]^{1/4}} + \cfrac{1}{kf \exp(-A_{\text{eff}}/RT)}}$$

is proposed for the activation energy of the electrode process under conditions of natural convection. [Ot.So.]

1278 – Theory of electrical transport. II. Multicomponent metallic systems (in Russian). D. K. Belaschenko and B. S. Bokhstein (Institute for Steel Research, Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 2228–2233.
An equation has been derived to describe the steady state at the passage of direct current through a multicomponent solution of metals using methods of irreversible process thermodynamics. [Ot.So.]

1279 – The movement of molecules in non-uniform electric fields. D. A. J. Swinkels and E. P. A. Sullivan (Newcastle University College, N.S.W.; present address, Department of Chemistry, The University of Sydney, Australia). *Australian J. Chem.*, 14 (1961) 487–492.
In a non-uniform electrical field translational movement of polar molecules occurs (cf. Karagouris, *Nature*, 161 (1948) 855), a phenomenon termed "dielectrophoresis" (Pohl, *J. Appl. Phys.*, 29 (1958) 1182). Theoretical discussion of this effect is given and experiments reported which show concentration separations effected in polar solute/non-polar solvent solutions. Separations obtained experimentally exceeded the predictions of the simple theory used. Extension of the work is envisaged to study the electrical analogue of the Gouy magnetic balance, and the possibility of an electric moment chromatograph. [H.H.Ba.]

1280 – Thermodynamics of ion association in aqueous solutions. G. H. Nancollas (University of Glasgow, Scotland). *Quart. Rev. (London)*, 14 (1960) 402–406.
A review on ion association determined, among other experimental methods, by conductivity and potentiometry. [Red.]

1281 – Faradaic rectification and electrode processes. Paul Delahay, Mitsugi Senda and Carl H. Weis (Coates Chemical Laboratory, Louisiana State University, Baton Rouge, La., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 312–322.
The authors give a general theory of faradaic rectification (which arises from asymmetry of the current–electric tension curve with respect to the equilibrium electric tension), and previous theories are extended and clarified. Control of electrochemical variables must be considered in two respects: control of current, or of electric tension as a harmonic-free sinusoidal function of time, and control of the mean values of current or electric tension. In practice, the mean values are controlled at electric tensions equal to the equilibrium electric tension, or at zero current. In either

case, the rectification current and the rectification voltage, respectively, are the same regardless of whether alternating current or electric tension is applied. A general relation is given for the rectification voltage (for the case of zero mean current) with no assumptions concerning the form of the current-electric tension characteristic. Relations are also described which include consideration of double layer charging, with and without rectification from the double layer itself, which show the time dependence of the rectification voltage. The influences of the amplitude and frequency of the applied voltage on the mean rectification voltage–time curves are discussed and experimentally verified, using data from studies of Ti(IV)–Ti(III) in tartaric acid solutions and mercury(I) in perchloric acid solutions, with a mercury electrode. Particular forms of the rectification voltage equation are derived in terms of the resistive and capacitive components of the series equivalent circuit for the faradaic impedance for a simple electron transfer process (experimental data given), and for an electron transfer process with a preceding chemical reaction. Procedures for calculation of the exchange current density and the transfer coefficient, with and without corrections for the double layer structure, are discussed. Effects of the circuit resistance on the theory presented are also discussed. The general relations show that when the electric tension is controlled at the equilibrium value, the rectification current is the same as that obtained in the electric tension–step potentiostatic method. It is pointed out, that kinetic studies of very fast reactions should be feasible using the measurement of rectification effects. Apparatus for measurement of rectification voltages by application of a single msec pulse of 2 Mc frequency alternating voltage is described. [R.Mur.]

1282 – Dissociation of water between 100 and 300° (in German). K. Schwabe (Institute for Electrochemistry and Physical Chemistry, Dresden, Germany). *Chem. Tech.*, 11 (1959) 554–555.
Values for the dissociation constant of water are calculated in the temperature range 100–300° using earlier data; a maximum of K_w is found at 240–250°, the corresponding pH being 5.6–5.7. [Ca.Cas.]

1283 – The effect of sinusoidal current on electrode processes. I. The effect of the sinusoidal current on the overvoltage of hydrogen on the mercury electrode (in Hungarian). T. Erdey-Gruz, J. Dévay, I. Vajasdy and Gy. Horányi (Institute of Physical Chemistry and Radiology, Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 244–253.
Es wurde die Wirkung von Sinusstrom auf die Wasserstoffüberspannung an Quecksilberelektrode in einem selbst konstruierten Apparat durch Spannungsmessungen untersucht, wobei gefunden wurde, dass die Wasserstoffüberspannung durch den auf den polarisierenden Gleichstrom superponierten Welchselstrom herabgesetzt wird. Die Abnahme der Überspannung ist desto grösser, je grösser die Stromdichte und je kleiner die Frequenz des Sinusstromes ist. Die Wirkung ist beinahe der Grösse, der durch den Wechselstrom verursachten periodischen Spannungsschwankungen proportional. Die Erscheinung lässt sich durch eine Modellschaltung erklären in welcher ein Kondensator und ein Widerstand parallel geschaltet sind. Die Kapazität des Kondensators entspricht der Kapazität der elektrochemischen Doppelschicht und die Charakteristik des Widerstandes ist durch die Tafel'sche Gleichung gegeben. Die annähernden Berechnungen unterstützen die Gültigkeit des Modells. (144 Zitaten). [J.Inc.]

1284 – The effect of sinusoidal current on electrode processes. II. The mathematical investigation of the effect of sinusoidal current on hydrogen overvoltage on a mercury cathode (in Hungarian). T. Erdey-Gruz, J. Dévay, Gy. Horányi, I. Vajasdy and L. Mészáros (Institute of Physical Chemistry and Radiology, Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 378–384.
Es wurde eine Formel für die Wasserstoffüberspannung an einer Quecksilberkathode bei der Elektrolyse mit asymmetrischem Wechselstrom für den Fall abgeleitet, wenn die Amplitude der periodischen Schwankungen der Überspannung ziemlich gross ist. Die Ableitung wurde nach dem Modell gemacht, in welchem die Elektrode durch parallel geschalteten Kondensator und Widerstand ersetzt wurde. Die Kapazität des Kondensators entspricht der Kapazität der elektrolytischen Doppelschicht und die Charakteristik des Widerstandes ist durch die Tafel'sche Gleichung gegeben. Die gemessenen und die mit Hilfe von der Formel berechneten Überspannungswerte stimmen gut überein. (See preceding abstract). [J.Inc.]

1285 – The effect of sinusoidal current on electrode processes. III. The effect of sinusoidal current on the distribution of the direct current on a mercury cathode (in Hungarian). T. Erdey-Gruz, J. Dévay and R. Szegedi (Institute of Physical Chemistry and Radiology, Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 384–387.
Gemäss den Messergebnissen wird die Stromstreuung an Quecksilberkathoden in 1 *N* Schwefelsäure-Lösung durch ungleichmässig verteilten, asymmetrisch superponierten Wechselstrom

beeinflusst, weil die Überspannung an den Elektroden durch Wechselstrom herabgesetzt wird. Wenn diese Erscheinung an anderen Elektroden auch zustande kommt, kann sie den kathodischen Schutz von Metallen oder die lokale Dichte von galvanischen Niederschlägen beeinflussen. (62 Zitaten). (See preceding 2 abstracts). [J.Inc.]

1286 – Measurement of the impedance of a copper electrode in an acid electrolyte (in Russian). N. P. Gnusin (Railway Research Institute, Gomel, White Russian S.S.R., U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 2217–2222.
The use of alternating current for the investigation of various effects accompanying electrode processes is gaining more and more importance. The theory of the passage of alternating current through the metal–solution interface (so-called theory of Faraday impedance) is now sufficiently well developed. For many branches of electrochemistry, knowledge of the resistance of an electrode immersed in an ionic solution is of considerable importance. The applicability of the classical theory of Faraday impedance to solid electrodes established in the abstracted paper promises to be of use in the study of electrode processes underlying the majority of electroanalytical methods. [Ot.So.]

1287 – Transference numbers of ZnI_2 in dilute aqueous solutions (in English). J. H. Sahay (Department of Chemistry, Ranchi College, Ranchi, India). *Current Sci.*, 28 (1959) 15–16.
Transference numbers for ZnI_2, measured by the moving boundary method, have been found to lie in the range from 0.39972 (for a 0.01013 *N* solution) to 0.34110 (for a 0.2990 *N* solution); only at very high dilutions does the slope of the diagram transference number *vs.* square root of the concentration agree with the limiting value given by the Onsager equation. There is no agreement between the known values for the transference number with the experimental data found in dilute solutions by means of the Hittorf equation or by means of the E.M.K. method. In aqueous solutions, ZnI_2 cannot be considered as an electrolyte. [Ca.Cas.]

1288 – Charge-transfer coefficients and electric tension dependence of the Tl/Tl^+ electrode reaction (in German). G. Salié and W. Lorenz (Institut für physikalische Chemie, Universität Leipzig, Deutschland). *Z. physik. Chem. (Frankfurt)*, 29 (1961) 408–412.
Intermediate reaction states in the phase boundary may be determined only when there is accentuated adsorption, as for example with the system Tl/Tl^+ on mercury electrodes. In 1 *M* $NaClO_4$ the frequency dependence of the impedance was recorded (impedance spectra). According to a theory developed by the authors, parameters are calculated from measured reaction impedance, which permits a mathematical treatment of the several reaction states, and the mechanism of charge-transfer during the electrochemical phase boundary reaction (electrode reaction). [H.W.Nür.]

1289 – Hydrogen overvoltage on lead and some of its alloys (in Russian). I. A. Aguf and M. A. Dasoyan. *Zhur. Priklad. Khim.*, 32 (1959) 2022–2031.
Hydrogen overvoltage has been measured on lead, lead–antimony and lead–antimony–silver alloys. It has been shown that Ag content up to about 5% decreases overvoltage on the last named alloy. A formula is proposed for the dependence of overvoltage on the logarithm of current density, taking into account possible adsorption of sulphate ions on the lead and depolarisation processes. A method is further demonstrated for the calculation of overvoltage on alloys. [Ot.So.]

1290 – Influence of organic complexing agents on the redox potential of the system V^{4+}/V^{3+} (in Russian). I. A. Zserkovnitskaya, E. D. Prudnikov and N. A. Kustova. *Vestnik Leningrad Univ., Ser. Fiz. i Khim.*, [10] 16 (1961) 133–136.
Changes of the electric tension of the system V^{4+}/V^{3+} in the presence of complex forming agents; citric, malonic, sulphosalicylic and *o*-amino-phenyl-arsenic acids, and its dependence on the pH value, have been investigated. A platinum and a sulphate–oxide electrode have been used. The atomsphere was carbon dioxide, temperature 25 ± 0.5°. 50 ml of 0.01 *N* solutions of both vanadium valency states were used (V^{3+} having been obtained by reduction of ammonium vanadate on a platinum electrode). On addition of the complexing agent, values of the electric tension were plotted against its concentration. In the pH region 5.5–8, redox electric tensions decrease with pH in all cases, the decrease being practically linear. [Ot.So.]

1291 – Electrochemical behaviour of cobalt in sulphuric acid (in Russian). V. I. Kravtsov and N. Kh. Pikov. *Vestnik Leningrad Univ., Ser. Fiz. i Khim.*, [4] 16 (1961) 70–74.
Anodic and cathodic ϕ — log i as well as c — ϕ curves on active cobalt in 1 *N* H_2SO_4 have been investigated galvanostatically. The increase in anodic current density on the preliminary cobalt electrode polarisation was shown to result in the shifting of the anodic ϕ — log i curves toward negative values of the electric tension, and c — ϕ curves towards the greater capacity. The above

mentioned shift of the anodic ϕ — log i curves is determined both by the extension of a real electrode surface and by the increase of its surface activity. [Ot.So.]

1292 – Comparison between radiochemical and electrochemical studies of the adsorption of ions on platinum (in German). J. Richter and W. Lorenz (Institut für physikalische Chemie, Universität Leipzig, Deutschland). *Z. physik. Chem. (Leipzig)*, 217 (1961) 136–137.
Adsorption values of iodine and iodide ions on Pt, determined by electrochemical methods, are quite different. By electrochemical methods a real surface effect is measured, but the interpretation of the radiochemically determined irreversible sorption of molecules and ions seems still to be an open question. [H.W.Nür.]

1293 – Electrode processes in acetonitrile (in Russian). E. A. Aykazyan and R. A. Arakelyan (Institute of Organic Chemistry, Academy of Sciences of the Armyan S.S.R.). *Izvest. Akad. Nauk, Armyan. Otdel. Khim. Nauk*, 113 (1960) 225–233.
The process of anodic chlorine evolution from acetonitrile solutions of hydrogen chloride on the platinum electrode was investigated. A rotating Pt disc electrode and a saturated calomel electrode were used. The following mechanism is proposed: (1) $HCl + CH_3CN = CH_3CNH^+Cl^-$ (2) $CH_3CNH^+Cl^- = CH_3CNH^+ + Cl^-$. The equilibrium in equation (2) is displaced strongly to the left. Chlorine evolution takes place mainly according to the equation: $2(CH_3CNH^+Cl^-) \rightarrow 2CH_3CNH^+ + Cl_2 + 2e$. In the electric tension range 1.8–2.3 V, strong passivation of the Pt electrode to the anodic process described is observed. [Ot.So.]

See also abstracts nos. 1309, 1328.

2. Apparatus and accessories

1294 – Measuring methods and applications of dielectric constant meters for chemical and structural analyses. I. General principles and commercial d.c. meters (in German). Karl Slevogt (Institut z. Entwicklung chem.-phys. Analysenmethoden, Weilheim/Obb., Deutschland). *Z. Instrumentenk.*, 69 (1961) 160.
Nach einem kurzen Überblick über die für verschiedene Frequenzgebiete ganz unterschiedlichen Verfahren zur Bestimmung der Dielektrizitätskonstanten und des dielektrischen Verlustfaktors werden einige charakteristischen kommerziellen Gerätetypen näher besprochen. Für niedere Frequenzen (25Hz–100 kHz) handelt es sich um eine modifizierte Scheringbrücke, deren Nullabgleich nach der Gestalt einer "Phasenellipse" auf den Leuchtschirm eines Braun'schen Rohres vorgenommen wird. Das sich anschliessende Frequenzgebiet von 100 kHz–12 MHz wird dagegen mit einer Überlagerungsschaltung erfasst. Auch hier erfolgt die Nullanzeige mittels eines Braunschen Rohres an Hand der Gestalt von Lissajous-Figuren. Der durch die mit der Probe gefüllten Messzelle bewirkte Dämpfungswiderstand wird nach einer Differenzsubstitutionsmethode ermittelt.

Besonders hohe Messempfindlichkeiten lassen sich dann erreichen, wenn eine Überlagerungsschaltung nur für eine bestimmte Festfrequenz aufgebaut wird. Das führte zur Konstruktion des "Dipolmeters", welches zur DK-Messung hochverdünnter Lösungen und einer anschliessenden Berechnung des molekularen Dipolmomentes aus dielektrischen und optischen Daten entwickelt wurde.

Für Routine-Untersuchungen kommt dagegen eine robuste Resonanzschaltung unter Nullanzeige mit einem Leuchtquarz in Betracht. Praktische Bedeutung kommt auch registrierenden Geräten zur Messung der Dielektrizitätskonstanten zu. Für Zwecke der Betriebskontrolle wurde der "Elograph" entwickelt.

Eine kurze Betrachtung von Messzellen zur Untersuchung von Flüssigkeiten, Pulvern, Platten und Folien schliesst die Arbeit ab. [Fr.Oe.]

1295 – High-frequency methods for chemical analysis (in German). Friedrich Oehme (Institut z. Entwicklung chem.-phys. Analysenmethoden, Weilheim/Obb., Deutschland). *Jahrb. Chem. Ind. (Solothurn/Schweiz)*, 10 (1961/1962) 44.
An Hand der Schaltung des Hochfrequenz-Titrimeters HFT (WTW, Weilheim/Obb.) wird die Funktion des Gerätes zur Bestimmung von Blind- und Wirkkomponenten besprochen. Es wird gezeigt, dass sich das Gerät sowohl zur Bestimmung von Dielektrizitätskonstanten und von Leitfähigkeiten als auch zur tan δ-Messung (aus der Halbwertsbreite einer aufgenommen Resonanz-

kurve) eignet. Als Zellen kommen dabei entweder die in der DK-Messung üblichen Kondensatortypen oder die kontaktlosen Zellen der ,,Hochfrequenz-Titration" zur Anwendung. Anschliessend wird ein Überblick über neue Anwendungsmöglichkeiten des Hochfrequenz-Titrimeters gegeben. Dabei handelt es sich um registrierende Leitfähigkeitsmessungen zur Untersuchung der Abbindegeschwindigkeit von Gipsansätzen und zur Prüfung von Fermentreaktionen im Zusammenhang mit dem Kohlenhydratstoffwechsel. Weiterhin wird die DK-Messung an stärker leitenden Proben besprochen und mit der Untersuchung des Dispersionszustandes einer Ichthyolsalbe als Beispiel belegt. Bedeutung kommt auch den registrierenden DK-Messungen zu, speziell im Zusammenhang mit der Eluatkontrolle chromatographischer Säulen für die Lösungsmittelreinigung. Verlustmessungen schliesslich eignen sich zur Untersuchung des Debye-Verhaltens. Debye-Verluste sind auch für die Schweissbarkeit von Folien im Hochfrequenzfeld verantwortlich zu machen. Für eine Messfrequenz von 27 MHz können diese Verluste unter Anschluss einer Spezialmesszelle für Folien mit dem Hochfrequenz-Titrimeter ebenfalls gemessen werden. [Author]

1296 – The titration-beaker HTB 3 as a new cell for micro-titrations with the high-frequency titrator HFT 30 C (in German). Friedrich Oehme (Institute for the Development of Phys.-Chem. Analysis Methods, Weilheim/Obb., Germany). *Mitt. Inst. Entwicklung chem.-physik. Analysenmeth., Weilheim/Obb.*, 1 (1961) 9.
Zunächst werden kurze Betrachtungen über die Grössen angestellt, welche zellenseitig die Ansprechempfindlichkeit einer kontaktlosen Messzelle für die Durchführung von Hochfrequenz-Titrationen bestimmen. Zellen nur kleinen Flüssigkeitsbedarfes lassen sich demgemäss nur unter Verwendung von Zellenbaustoffen hoher Dielektrizitätskonstante realisieren. Da Glas hierbei ausscheidet, konnte auf fertige Formkörper aus ,,Degussit ZR 23" (Zirkondioxyd mit einer Dielektrizitätskonstante von 24) zurückgegriffen werden. Auf diesem Wege konnte eine Zelle aufgebaut werden, welche bereits mit einem Flüssigkeitsvolumen von 2.5 ml einwandfreie Titrationen zulässt. [Author]

1297 – A potentiograph and automatic recording titration apparatus (in German). K. Hädicke (Deutsche Metrohm Fuisting & Co. K.G., Essen, Germany). *Fette, Seifen Anstrichmittel*, 62 (1960) 584–586.
An instrument to record changes in mV or current is described. It records the measured quantities against the volume of non-aqueous solutions added. It can be used for titrations in which the change of the electric tension is small. Titration curves for fatty acids are given. The error in the determination of pure compounds is ± 1% and that of a mixture of seven components is ± 3%. [Gio.Ser.]

1298 – Capillary behaviour in high sensitivity polarography. W. D. Cooke, M. T. Kelley and D. J. Fisher (Department of Chemistry, Cornell University, Ithaca, N.Y., (first author) and Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A. second and third authors). *Anal. Chem.*, 33 (1961) 1209–1215.
Factors conditioning the sensitivity of polarography with dropping mercury (DM) electrodes have been evaluated: mechanical features of the DM capillary have a primary influence. A description is given of a modified DM capillary designed to eliminate capillary "noise". Highly stable backgrounds are obtained with this modified DM capillary. By the use of the modified DM electrode, applications of the polarographic method can be extended to more dilute solutions than those allowed for by conventional DM electrodes. Polarograms of Cd, In, Pb, Ni, Th and Zn were run in different supporting electrolytes. For Zn^{2+}, a detectable limit of 0.006 µg of Zn^{2+} per ml has been reached. [Su.Mo.Ce.]

1299 – The graphite electrode: an improved technique for voltammetry and chronopotentiometry. P. J. Elving and D. L. Smith (University, Ann Arbor, Mich., U.S.A.). *U.S. Atomic Energy Comm.*, (1960).
The use of the graphite electrode in voltammetry is greatly improved by pre-wetting the electrode with a solution of a wetting agent.
The electrode has been used for cathodic and anodic chronopotentiometry and for voltammetric determinations, and the ferri–ferro-cyanide and quinone–quinol systems, as well as with adenine, ascorbic acid, sulphanilamide and tetra-phenylborate. Chronopotentiometric data have an error of ± 3%. The results obtained by automatic recording voltammetry are similar, and do not differ from those obtained with platinum electrodes. [Gio.Ser.]

1300 – Electronic methods in chemistry. III. Electronic regulation of higher wattages (in Czech). J. Pokorný and J. Bukovnický (Institute of Chemical Technology, Prague, Czechoslovakia). *Chem. listy*, 55 (1961) 1294–1296.

A regulator equipped with thyrathrons is described. It is useful mainly for the regulation of transformers, and is suitable for the automation of analytical apparatus. [Ot.So.]

1301 – On the influence of the dimensions of the cathode and anode on curves of polarometric titration with two indicating electrodes (in Russian). O. A. Songina and I. S. Savickaja (Kazachian State University, U.S.S.R.). *Zavodskaya Lab.*, 27 (1961) 1068–1074.
On the basis of experimental proof of the influence named in the title, a correction of Kolthoff's equation is given, which takes the ratio of the electrode dimensions into account and makes it possible to calculate the true diffusion current from experimental data. It is shown that asymmetric curves can be caused by an inequality of electrode dimensions, irreversibility of the system, and also by inequality of concentrations of the oxidised and reduced forms. (Corrections are tabulated). [Ot.So.]

1302 – Thin membrane micro glass electrode. Milton T. Bush (Department of Pharmacology, School of Medicine, Vanderbilt University, Nashville, Tenn., U.S.A.). *Microchem. J.*, 4 (1960) 216–217.
A glass–calomel cell is described for rapid pH measurements on a small drop of solution. [Su.Mo.Ce.]

1303 – Probe micro glass electrode. Milton T. Bush (Department of Pharmacology, School of Medicine, Vanderbilt University, Nashville, Tenn., U.S.A.). *Microchem. J.*, 5 (1961) 159–162.
A very simple and versatile apparatus containing a probe-type glass electrode and a small calomel reference electrode is described, with full details. The apparatus can handle large volumes in beakers, or very small volumes (0.05 ml or less) in air or under oil. [Su.Mo.Ce.]

1304 – An apparatus for the measurement of conductivities using a difference principle (in German). E. Seelos (Inst. for the Development of Phys. Chem. Analysis Methods, Weilheim/Obb., Germany). *Mitt. Inst. Entwicklung chem.-physik. Analysenmeth., Weilheim/Obb.*, 1 (1961) 5.
Es wird gezeigt, dass durch Anordnung je einer Leitfähigkeitsmesszelle in zwei benachbarte Brückenzweige einer üblichen Wheatstone-Brücke der Indikatorstrom des Brückenausganges ein Mass für die Leitfähigkeitsdifferenz, der in den Messzellen befindlichen Proben dienen kann. Es besteht die Möglichkeit, Leitfähigkeitsdifferenzen bis zu 2 Zehnerpotenzen auszuwerten. Das Gerät hat im Zusammenhang mit der Gasbeladung bzw. Entgasung von Wasser und bei der Eluatkontrolle von Austauschersäulen Bedeutung aufzuweisen. [Fr.Oe.]

1305 – A method for determining ion mobilities in dielectric liquids. O. Czowski and J. Terlecki (Physics Department, Engineering College and Physics Department, Academy of Medicine, Gdansk, Poland). *Acta Phys. Polon.*, 18 (1959) 191–198.
A direct method of measuring the mobility of ion carriers based on measurement of the time employed by an ion-layer (formed in the liquid which fills an ionization chamber, by means of an X-ray beam) to reach the electrodes is described. If two experiments are performed where an ion layer is generated at two different positions, the ion velocities are directly computable. In hexane it has been found that the values are $4.1 \cdot 10^{-4}$ and $1.3 \cdot 10^{-3}$ cm^2/V sec for positive and negative ions respectively. [Ca.Cas.]

1306 – Continuous antidromic electrophoresis. Samuel Natelson and others (Biochemistry Laboratories, Jewish Hospital of Brooklyn and Roosevelt Hospital, New York, N.Y., U.S.A.). *Microchem. J.*, 4 (1960) 145–154.
Substances with very close electrophoretic mobilities are continuously separated by anti-dromic electrophoresis. Description of the procedure and instrument (with and without cooling) is given. The supporting medium (paper or plastic film-supported gel) is mechanically and continuously moved in the opposite direction to the migration movement of the ions; in this way, the ions are kept in the electric field for a long period. Separation of the eighteen most common amino acids is readily obtained. [Su.Mo.Ce.]

1307 – A miniature electrostatic precipitator for sampling aerosols. Theory and operation. Myron Robinson (U.S. Army Chemical Corps, Fort Detrick, Frederick, Md., U.S.A.). *Anal. Chem.*, 33 (1961) 109–113.
The theory of a miniature electrostatic sampler for a suspended solid or liquid constituent of an aerosol is described. The theory assumes mono-disperse spherical particles, being subject to the same limitations as other precipitation theories. The experimental precipitator is described; an aluminum cylinder of 60 cm length and 3.65 cm radius, encloses an axial electrode of tungsten

wire, which is maintained positive at 17 kV. The theoretical results are tested experimentally using air carrying 3.25 μ diameter spherical particles of polystyrene latex. [Su.Mo.Ce.]

1308 – Apparatus for rapid serial pH and pCl micro determinations (in English). D. V. Varsányi (Department of Biochemistry, State Institute for Dermato-Venereology, Budapest, Hungary). *Mikrochim. Acta*, 1961 (770–776).
A cell assembly is described for the determination of pH and pCl in a volume of 0.5 ml. The calomel comparison electrode makes contact with the solution *via* a double salt bridge, one filled with saturated KCl, the other with saturated KNO_3. The connections between them are formed by asbestos fibres. Both solutions can easily be replaced in order to prevent diffusion of chloride into the measuring electrode compartment. [H.L.Ki.]

1309 – Hydrogen electrodes for pH determination and potentiometric titration (in Russian). L. N. Davydov. *Lab. Delo*, 6 (1960) 54–57.
A hydrogen micro-electrode is described. It is composed of a pump and of an electrode with two chambers, one for holding the test solution and the other for saturating the platinum black surface of the electrode with H_2. The rotation of a piston controls the H_2 supply and the same piston is used to fill the electrode with the test solution. The solution is saturated by shaking the electrode. A comparison is made of the results obtained with different electrodes in the determination of pH of blood and of buffer solutions. An electrode is described for use in potentiometric macrotitrations. [Gio.Ser.]

1310 – Reference electrode for potentiometric silver titrations. George Matsuyama (Research Department, Union Oil Co. of California, Brea, Calif., U.S.A.). *Anal. Chem.*, 32 (1960) 886.
A special type of calomel comparison electrode was prepared from commercially available parts, to overcome diffusion and other practical problems in its use for potentiometric silver titrations. A description of the new type of calomel electrode is given. [Su.Mo.Ce.]

1311 – Use of solid electrodes for the amperometry of molybdenum and tungsten (in Russian). S. K. Chirkov and L. S. Studenskaya (Institute Chern., Metallov., U.S.S.R.). *Byull. Nauch.-Tekh. Inform. Ural'sk. Nauch.-Issled.*, 6 (1959) 113–120.
By measuring the oxidation current of Pb^{2+} with two identical platinum wire electrodes at 1.2–1.5 V, WO_4^{2-} can be amperometrically titrated with $Pb(NO_3)_2$ in acetate buffer, pH 4–5. Ions reduced on a Pt cathode do not interfere, but ions oxidized in these conditions do. Mo and W are separated by precipitation of W as tungstic acid. The method is suitable for the analysis of ferromolybdenum, iron alloys and steel. [Gio.Ser.]

1312 – Analysis of quartz–feldspar mixtures by means of dielectric constant measurements (immersion method) (in German). F. Oehme (Institute for the Development of Physico-Chemical Analytical Methods, Weilheim/Obb., Germany). *Keram. Z.*, 11 (1959) 180–182.
A description of a practical method for analysis of quartz, feld-spar and their mixtures by means of dielectric constant measurements (immersion method) is given. Possible interferences arising from adsorption phenomena on the surface of the sample under investigation are discussed. [Ca.Cas.]

1313 – Distortion-free electrophoresis in starch gel. B. Paletta (Medizinisches Chemisches Institut und Pregl.-Laboratorium der Universität, Graz, Österreich). *Clin. Chim. Acta*, 5 (1960) 490–496.
The separation of protein bands in paper electrophoresis can be greatly improved by uniform cooling of the strip and applying a very homogeneous electric field. An apparatus is described which enables these conditions to be satisfied. [Gio.Ser.]

1314 – Microelectrophoresis in agar gel (in Russian). R. Portokale and W. Bojeru (Institute for Virus Research, Rumanian Academy of Sciences, Rumania). *Voprosy Med. Khim.*, 5 (1959) 310–316.
Results in good agreement with the "classical" electrophoresis method are obtained by means of a micromethod, utilizing a film of agar gel on an ordinary microscope slide; bands are developed usually by means of bromophenol blue and quantitatively evaluated by means of an automatic photometer together with a photographic recorder. The method can also be applied to other substances, such as carbohydrates, lipoproteins, nucleoproteins and nucleic acids, as well as to immunoelectrophoretic techniques. [Ca.Cas.]

See also abstracts nos. 1281, 1337, 1506.

3. Polarography

1315 – Electroanalytical methods (in Dutch). J. A. C. van Pinxteren (Farmaceutisch Laboratorium der Rijksuniversiteit, Utrecht, The Netherlands). *Pharm. Weekblad*, 96 (1961) 846–854.
A survey is given of the principles underlying polarography. This is followed by an explanation of amperometric methods using one or two indicator electrodes. [H.L.Ki.]

1316 – Determination of carbon content in biological substances by means of a recording conductometric apparatus (in German). W. Schneider (Institute for Animal Nutrition, Agricultural High School, Stuttgart-Hohenheim, Germany). *Landwirtsch. Forsch.*, 12 (1959) 214–218.
The sample is burnt in a stream of O_2 (supplied by means of a dosing pump) and the CO_2 formed is pumped into the measuring cell which is connected to a recorder. The C content is then calculated from a calibration curve. [Ca.Cas.]

1317 – Theory of alternating current polarography. W. H. Reinmuth and D. E. Smith (Department of Chemistry, Columbia University, New York 27, N.Y., U.S.A.). *Anal. Chem.*, 33 (1961) 964–966.
A letter to the Editor, in which some points are clarified regarding the theory of alternating current polarography. The works of Bauer and coworkers on this subject (*J. Electroanal. Chem.*, 1 (1959) 2; *J. Am. Chem. Soc.*, 82 (1960) 2091; *ibid.*, 82 (1960) 2094; *U.S. Atomic Energy Comm.* Rept. No. 58, Contract AT(11–1)–70, Project 8, July 1960) are severely criticized. [Su.Mo.Ce.]

1318 – Study of the double-layer by a.c. polarography. B. Breyer, H. H. Bauer and J. R. Beevers (Faculty of Agriculture, Sydney University, Australia). *Australian J. Chem.*, 14 (1961) 479–486.
Possible influences of the structure of the double-layer on a.c. polarographic phenomena are discussed. Results obtained in the reduction of zinc and uranium at values of the electric tension more negative than the e.c.m., and of copper at values of the electric tension more positive than the e.c.m., were explicable in terms of double-layer effects. It has been found that a.c. polarograms sometimes provide evidence for changes in double-layer structure much more clearly than do double-layer measurements *per se*, suggesting the use of a.c. polarography specifically for double-layer studies. [H.H.Ba.]

1319 – General equation for oscillographic polarography, reversible processes in anodic and cathodic polarization (in Russian). J. P. Gochstein (Vernasky Institute for Geochemistry and Analytical Chemistry, Academy of Sciences, U.S.S.R.). *Doklady Akad. Nauk*, 126 (1959) 598–601.
A generalized form of Abel's equation is deduced, by means of which the variation of the concentration of a given initial substance submitted to oscillographic polarography can be calculated as a function of the distance from the electrode surface, between zero and time t. The equation is used to calculate the electric tension and the current as functions of time in some particular cases (constant, linearly variable and periodically variable electric tension). [Ca.Cas.]

1320 – Influence of the solvent in polarography (in German). K. Schwabe (Technical High School, Dresden, Germany). *Angew. Chem.*, 73 (1961) 628.
(A summary of a lecture held in Stuttgart, Germany).
Untersuchungen mit quartärnen Ammonium-Verbindungen als Leitelektrolyte ergaben, dass die Fussspannungen mit der Grösse der Alkylreste im allgemeinen ansteigen. Bei $N(C_8H_{17})_4^+$ liegt der Wert bei —3.15 V (gegen ges. Kalomelelektrode). Auf diese Weise liess sich z.B. die polarographische Reduktion des Cyanamids und Azetons genauer untersuchen. Cyanamid wird bei —2.33 V, Azeton bei —2.56 V in $N(C_4H_9)_4OH$ -Lösung reduziert. Beim Cyanamid lässt sich aus der pH-Abhängigkeit der Stufenhöhe folgern, dass die Reduktion über die Diiminform geht. Beim Azeton verschiebt sich die Halbstufenspannung mit dem pH Wert und es bildet sich *iso*-Propanol. Stark adsorbierbare Kationen verschieben im allgemeinen die Halbstufenspannung in positive, stark kapillaraktive Anionen in negative Richtung. Organische Lösungsmittel schieben im allgemeinen die Halbstufenspannungen in negative Richtung. Im Falle der Trichloressigsäure verschiebt sich die Halbstufenspannung exponentiell mit der Dielektrizitätskonstante des Lösungsmittelgemisches. Bei der reversibelen Reduktion des Chloranils lässt sich die Verschiebung durch das Lösungsmittel aus der mit Glaselektrode gemessenen pH-Änderung berechnen. [J.Inc.]

1321 – Preliminary investigations of the nature of the capacity peaks observed with organic

compounds at the dropping Hg electrode in an alternating field. S. L. Gupta and S. K. D. Agarwal (Department of Physical Chemistry, Birla College of Science, Pilani, Rajasthan, India). *Kolloid-Z.*, 163 (1959) 136–138.
A study of some surface-active agents (sodium lauryl *p*-toluidine sulfonate, Cerfak, *iso*-propanol, toluene, ether, amyl alcohol, camphor, bromo-cresol purple, thymol blue, methyl orange, methylene blue, methyl violet, cetyl-pyridinium bromide) was made. The influence of KCl, KI and KNO_3 on their alternating-current 50 Hz 45 mV polarograms was followed by measuring the electric tension and the height of the tensammetric maxima. In the cases of low molecular weight surface active agents, the percentage increase in the capacitive current is practically independent of the drop-dimensions and drop-life times. Three types of maxima are observed: 1) chemically-controlled ones whose position and amplitude are not affected by the nature of the electrolyte; 2) desorption maxima, with variable amplitude, and constant electric tension; 3) difficultly classifiable ones. The method is recommended for studying the nature of the capacity peaks. [Ca.Cas.]

1322 – Applications of cathode-ray polarography in the field of oceanography. G. C. Whitnack (Chemistry Division, U.S. Naval Ordnance Test Station, China Lake, Calif., U.S.A.). *J. Electroanal. Chem.*, 2 (1961) 110–115.
Some applications of cathode-ray polarography in the field of oceanography are discussed in this paper. Apparatus is described. Materials used in this work were synthetic and natural sea-water samples. The behavior of chloride ion, some trace elements, and dissolved oxygen in sea water were studied by this method. The advantages of rapidity, specificity, sensitivity and adaptability to solid electrode systems and direct reading instrumentation for continuously recording these constituents found in sea-water, have been pointed out. [Fra.Cla.]

1323 – Development of surface polarography (in German). A. Braunwalder, A. Grubenmann and F. Hügli (Technicum de Winterthur, Zürich, Suisse). *Chimia*, 15 (1961) 461.
Les auteurs effectuent la polarographie au moyen d'un capillaire recourbé dont le coude a été limé et repose sur un papier filtre renfermant l'échantillon à doser. Ce papier filtre est posé sur une feuille poreuse d'acétate de cellulose qui renferme les constituants d'une électrode de calomel saturé. Il leur est ainsi possible de doser des substances à des concentrations allant jusqu'à 10^{-6} *M*. [De.Mo.]

1324 – Methods and applications of d.c. polarography. I. Apparatus, methods and electrodes. II. Theory of polarographic curves (in German). H. W. Nürnberg and M. von Stackelberg (Max-Planck Institut für Eisenforschung, Dusseldorf; Institut für physikalische Chemie, Universität, Bonn, Deutschland). *J. Electroanal. Chem.*, 2 (1961) 181–229.
First and second parts of a rather extensive review of d.c. polarography, dealing with the following topics: conventional d.c. polarography, test-polarography, pulse-polarography, conventional derivative polarography, methods for eliminating the "teeth" of the polarographic curve, impulse methods, differential polarography, dropping mercury electrodes, Hg-pool electrodes, rapidly dropping electrodes, rotating Hg-electrodes, jet electrodes, moving solid electrodes, rotating disc electrodes and other materials for electrodes. In the second part the following topics are dealt with: the limiting diffusion current, rigid electrodes, the form of the polarographic curve, the half wave value of the electric tension. [Red.]

1325 – Polarographic test for solvent quality. R. C. Propst (Du Pont de Nemours, Savannah River Laboratory, Aiken, S.C., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 2492, *Abstract no.* 19248.

1326 – Some applications of the rotating disc electrode (in German). R. Landsberg, W. Geissler and S. Müller (Institute of Physical Chemistry, Technical College, Leuna-Merseburg, Germany). *Z. Chem.*, 1 (1961) 169–174.
Der Aufbau rotierender Scheibenelektroden aus Platin oder Graphit-Azobenzol wird beschrieben und ihre Eignung zur Konzentrationsbestimmung bei 12.5 Umdrehungen pro Sekunde geprüft, wobei Linearität zwischen Oxidationsstrom und Manganatkonzentration erhalten wird. Danach wird die Reaktion: $MnO_4^- + OH^- \xrightarrow{k_1} MnO_4^{2-} + \dot{O}H$ verfolgt und die Kinetik mit OH-Radikal als stationärem Zwischenprodukt aufgeklärt. Da die Graphit–Azobenzol-Elektrode keine Passivierungserscheinungen zeigt, hat sie sich gut zur Reduktion von Cl_2, Br_2, I_2 und zur Oxydation von I_2, I^-, Br^-, NO_3^- und zur Bestimmung des Diffusionskoeffizienten von H_3O^+ geeignet. Für letzteren Fall wurde erhalten (25°): KCl (Mol/l): 1.5, 1.0, 0.1, 0.01, 0.001; $D.10^5$ (cm^2sec^{-1}): 6.6_5, 7.2_2, 8.6_1, 9.2_3, 10.9. In 1 *N* KNO_3-Lösung diffundieren OH^--Ionen mit $D = 4.45 \cdot 10^{-5}$ cm^2 sec^{-1}. [He.Be.]

1327 – Polarographic determination of complex-equilibria (in German). A. Tockstein (Technical College for Chemistry, Pardubice, C.S.S.R.). *Z. Chem.*, 1 (1961) 3–14, 34–47.

Die theoretischen Grundlagen der polarographischen Stufe und ihre Änderungen infolge der Teilnahme des Depolarisators an einem Komplexgleichgewicht werden erläutert und mit Beispielen illustriert. Im ersten Teil werden Komplexe, hauptsächlich von Aminen, mit Schwermetallionen diskutiert, welche bei der Reduktion Amalgam bilden, und zwar in Abhängigkeit vom pH-Wert und von der Konzentration des Komplexbildners. Der zweite Teil enthält Ableitungen für Komplex–Gleichgewichte, bei denen aufgrund der Durchtrittsreaktion lediglich ein Wertigkeitswechsel des Zentralatoms erfolgt und dabei ein neuer Komplex entsteht. Unter Berücksichtigung der Ligandendissoziation werden die Halbstufenspannungsverschiebungen berechnet. Weiterhin werden Beispiele von Doppelstufen und die aus deren Teilstufenhöhen zu konstruierenden Dissoziationskurven unter Berücksichtigung kinetischer Ströme ausführlich beschrieben. Schliesslich werden Austauschreaktionen (nach Schwarzenbach und Brill): $\overline{\mathrm{Me}}\mathrm{Y} + \mathrm{Me} \rightleftarrows \mathrm{MeY} + \overline{\mathrm{Me}}$ vom polarographischen Standpunkt untersucht und die Ergebnisse verschiedener Autoren verglichen. Die Polarographie vermag danach auf folgende 3 Arten, Komplexgleichgewichte zu analysieren: (1), Verschiebung der Halbstufenspannung; (2), Änderung der Stufenform; (3), Änderung des Diffusionsstromes. [He.Be.]

1328 – Influence of foreign electrolyte concentration in square-wave polarography (in English). F. v. Sturm and M. Ressel (Research Laboratory, Siemens Schuckertwerke A.G., Erlangen, Germany). *Microchem. J.*, 5 (1961) 53–65.
In square-wave polarography, peak currents are markedly dependent on the foreign electrolyte concentration; a pronounced effect is due to the double layer structure. Examples of this concentration effect are given for reversible and irreversible polarographic reductions. These observations are particularly important for microchemical and trace analysis applications. Charging current waves at a high resistance of the cell circuit are described. [Su.Mo.Ce.]

1329 – Investigations of catalytic hydrogen waves in polarography. I. The dependence of the height of catalytic waves on the dilution of the buffer solution (in Hungarian). E. Pungor and Gy. Farsang (Institute for Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 293–297.
Es wurde die Abhängigkeit der katalytischen Wasserstoffstufe von der Konzentration und vom pH-Wert der Pufferlösung, an Methylenblau, Thiamin und Nikotinsäureamid als Modellsubstanzen untersucht. Auf Grund der Ergibnisse wurde gefunden, dass die in der Umgebung der Electrodenoberfläche auftretenden Konzentrationsverhältnisse bei der Bildung der katalytischen Stufe eine bedeutende Rolle spielen. [J.Inc.]

1330 – Investigations of catalytic hydrogen waves in polarography. II. The dependence of catalytic hydrogen waves on the concentration of non-buffer electrolytes (in Hungarian). E. Pungor and Gy. Farsang (Institute for Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 325–327.
Es wurde die Einwirkung fremder, nicht als Pufferkomponente dienender Elektrolyte auf die katalytische Stufe untersucht. Die Versuche ergaben eindeutig, dass die Höhe der katalytischen Stufe durch indifferente Elektrolyte erniedrigt wird. Diese Wirkung ist auf die Verschiebung des sich auf der Elektrodenoberfläche ausgebildeten adsorptiven Gleichgewichtes zurückzuführen. (See preceding abstract). [J.Inc.]

1331 – Investigations of catalytic hydrogen waves in polarography. III. The effect of tetraethyl-ammonium salts on the catalytic waves of organic substances, in the absence of cobalt containing systems (in Hungarian). E. Pungor and Gy. Farsang (Institute for Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 328–330.
Es wurde die Wirkung des Tetraäthylammoniumbromids auf den katalytischen, polarographischen Strom untersucht. Auf Grund der theoretischen Erklärung, der aus experimentellen Ergebnissen erhaltenen Funktion, wurde nachgewiesen, dass das Tetraäthylammoniumbromid die Protonenkonzentration an der Elektrodenoberfläche erhöht und somit bei niedrigen Salzkonzentrationen eine Erhöhung der katalytischen Stufe verursacht. Bei Erhöhung der Salzkonzentration wird diese Wirkung überkompensiert, was sich über einer bestimmten Salzkonzentration in der Abnahme der Funktion äussert. (See preceding two abstracts). [J.Inc.]

1332 – Polarography in a sodium chloride–potassium chloride melt using tungsten-in-Vycor microelectrodes. Donald L. Maricle and David N. Hume. (Department of Chemistry, and Laboratory for Nuclear Science, Massachussetts Institute of Technology, Cambridge 39, Mass., U.S.A.). *Anal. Chem.*, 33 (1961) 1188–1192.
Polarographic reduction waves of silver(I), nickel(II), iron(II) and copper(I) have been obtained with a new type of microelectrode (tungsten sealed in Vycor) in a sodium chloride–potassium

chloride melt at temperatures as high as 740°. Limiting currents i_{lim} were directly proportional to the concentration; the effect of the electrode area on i_{lim} cannot be predicted, the effect of scan rate and temperature on i_{lim} has been investigated. Wave shapes have been analyzed: for the polarograms of silver(I), iron(II) and copper(I) the slopes were in reasonable agreement with the theoretical ones. Nickel reduction showed an anomalous linear segment which is, as yet, unexplained but which does not affect the proportionality between i_{lim} and concentration. Analytical and research applications are suggested. [Su.Mo.Ce.]

1333 – The determination of gold in mill products by means of a cathode-ray polarograph. K. J. Cathro (C.S.I.R.O. Chemical Research Laboratories, Box 4331, G.P.O., Melbourne, Australia). *Analyst*, 86 (1961) 657–664.

In a medium containing 0.5 *M* ethylenediamine tartrate and 0.1 *M* potassium pyrophosphate and of pH 5.8, Au gave a smooth peaked wave on the C.R. polarograph, with linear relation between peak heights and concentration, from 2–50 μg/ml of Au. Peak tension was —0.17 V *vs.* the saturated calomel electrode. On derivative operation, a non-linear, but analytically usable, relationship was found. Cu(II) gave a peak tension of —0.32 V and interfered with gold determination at ratios above 0.5 : 1 (direct operation) or 3 : 1 (derivative operation). Fe(III), Ag, As(III), Te(IV), Se(IV) or Sb(III), in ratios of 10 : 1 with gold did not interfere.

Gold was separated from cyanide solutions by precipitation in the presence of Te with $SnCl_2/HCl$. Adding known amounts of gold to a mill solution showed that this method gave recoveries in the range 98–106%. Addition of alkaline hypobromite before acidification prevented coprecipitation of Cu with gold. After precipitation the precipitate was washed, dried and calcined at 500–600°, dissolved in 1 : 1 v/v HNO_3 : HCl and the solution evaporated to dryness. The final residue was dissolved in the above mentioned supporting electrolyte, made up to known volume with supporting electrolyte, and polarographed. [P.O.Ka.]

1334 – Determination of micro-amounts of zinc by the method of amalgam polarography (in Russian). E. M. Rosenblat and Kh. Z. Brainina (Chemical Reagents Research Institute, U.S.S.R.). *Zavodskaya Lab.*, 27 (1961) 1197–1199.

The electrode is a mercury drop, electro-deposited on a platinum wire of 0.2 mm diameter. Oxygen is removed by a stream of nitrogen, the medium being 0.1 *N* KCl, and $E_{\frac{1}{2}} = -1.2$ V. To determine Zn in sodium sulphate, 1 g of the sample is dissolved in 50 ml water, 5 ml conc. HCl is added, and the solution is evaporated to dryness. The rest is dissolved in 20 ml water, and if the pH of this solution is less than 5 the evaporation procedure is repeated. A polarogram is then registered under the above-mentioned conditions, and evaluated by use of a calibration curve. Sensitivity is $1 \cdot 10^{-8}$ *M*; the error is not more than 20% in the presence of a large excess of foreign ions. [Ot.So.]

1335 – Polarography in liquid ammonia above its critical temperature (in English). W. Hubicki and M. Dabrowska (Department of Inorganic Chemistry, Mariae Curie Sklodowska University, Lublin, Poland). *Anal. Chem.*, 33 (1961) 90–92.

Results of polarographic measurements obtained using $LiClO_4$–*N* NH_3 as a solvent at different temperatures are given for Ca^{2+}, Zn^{2+} and Pb^{2+} salt solutions. The liquid ammoniate of $LiClO_4$ makes possible investigations with liquid ammonia under normal pressure at temperatures higher than its critical temperature. [Su.Mo.Ce.]

1336 – Amperometric titration of mercury by EDTA using a rotating tantalum electrode (in Russian). V. A. Khadeev and A. T. Bazarbev (State University, Tashkent, U.S.S.R.). *Uzbek. Khim. Zhur.*, [5] (1960) 38–45.

It has been found possible to titrate mercury directly by EDTA volumetric solutions using a rotating tantalum microelectrode. The concentration of free sulphuric or nitric acid in the titrated solution must be 0.1–0.5 g equiv/l. Anodic titration at an electric tension of the Ta electrode +1.2 V (S.C.E.) gives a steady current before the end-point, which after equivalence rises sharply. The cathodic titration at +0.35 V may also be used, giving an L-shaped curve. The anodic method is highly selective. The method may also be used to titrate, in the same solution, first mercury by EDTA, then silver by potassium iodide solutions. [Ot.So.]

1337 – The anodic capacity of a mercury electrode in aqueous sodium fluoride solutions. M. J. Austin and Roger Parsons (Department of Physical and Inorganic Chemistry, The University, Bristol, Great Britain). *Proc. Chem. Soc.*, (1961) 239–240.

It has been suggested (Watts-Tobin, *Phil. Mag.*, 61 (1961) 133) that the sharp rise of the capacity of a mercury electrode dipped in an aqueous solution of NaF, at electric tensions more than 0.5 V positive from the zero point, is due to hydroxyl ion adsorption. The authors have measured the capacity of a dropping mercury electrode using a mercury pool as a counter-electrode, and varying the pH of the NaF solution between 7–12. Results obtained are represented in a graph of capacity *vs.* electric tension. Very little effect on the capacity is observed for variation of pH from 7–11: this leads to the conclusion that it is improbable that the anodic capacity rise is due to hydroxyl ion adsorption. At pH 12 a marked rise of the anodic capacity is observed, but further work is necessary to interpret this fact. [Su.Mo.Ce.]

1338 – The distribution of metal concentration inside a mercury drop in electrolytic separation on a stationary mercury electrode (in Russian). L. N. Vasileva and E. N. Vinogradova (M.V. Lomonosov State University, Moscow, U.S.S.R.). *Zavodskaya Lab.*, 27 (1961) 1078–1086.
The intrusion of the reduced substance into the volume of the mercury drop has been studied under conditions of amalgam formation and reversibility of the process. The time is estimated at which concentration of the metal in the drop begins to rise linearly with the time of inclusion of the metal into the drop, with a relative error of 1%. Further, the time is estimated at which, in any place in the drop, the concentration differs by less than 1% from the mean concentration. Under the given conditions, the metal is distributed homogeneously in the drop at the time of anodic dissolution and depends linearly on the time of inclusion. [Ot.So.]

1339 – The polarography of glycine–metal complexes and the determination of stepwise formation constants. H. A. McKenzie and D. P. Mellor (Department of Biophysical Chemistry, Australian National University, Canberra; and Chemistry School, University of New South Wales, Sydney, Australia). *Australian J. Chem.*, 14 (1961) 562–576.
The polarography of metal–glycine complexes was studied, particularly to measure the stability and step-wise formation constants. Equations permitting the calculations, from data obtained at constant ionic strength, are presented. Problems in the use of maximum suppressors and buffer ions are discussed.
Stoichiometric stepwise stability constants for the glycine complexes of copper(II) and cadmium (II) were determined polarographically, and also by a pH titration method (Irving and Rossetti, *J. Chem. Soc.*, (1958) 2904, 2910), values by the two methods being in good agreement. Hydrolysis and precipitation supervened with lead(II), and anomalous polarographic behaviour was observed with zinc(II). [H.H.Ba.]

1340 – Polarography of aluminium and its alloys. D. S. Turnham (7 Holland Park, Clacton-on-Sea, Essex, Great Britain). *J. Polarog. Soc.*, 7 (1961) 43–55.
This paper is divided into two parts. In the first, the polarographic behaviour and polarographic determination of aluminium is reviewed, both in pure solution and as a minor constituent in ferrous, copper-based, magnesium and zinc alloys. In the second part, the determination of other minor constituents in aluminium alloys is reviewed. The elements discussed include copper, iron, lead, nickel, zinc, cadmium, sodium, chromium and tin. Separation methods are considered in several cases and the determination of trace impurities in high-purity metals is discussed. 38 references are given. [G.F.Rey.]

1341 – Polarographic investigations of aluminium alloys (in Hungarian). Gy. Farsang and E. Pungor (Institute for Inorganic and Analytical Chemistry, Eötvös University, Budapest, Hungary). *Magyar Kém. Folyóirat*, 67 (1961) 344–346.
Es wurde ein Verfahren für die polarographische Bestimmung der Schwermetallkomponenten von Aluminiumlegierungen von derselben Probelösung entwickelt.
Arbeitsvorschrift: Man löst 0.5–1 g Metallspäne in 12 ml destillierter Salzsäure. Nach Zugabe von 1–1.5 ml Wasserstoffperoxyd kocht man 5–10 Min. Die abgekühlte Lösung fügt man in 50 ml Messkolben und füllt bis Marke. Von der Lösung pipettiert man 5 ml heraus und vermischt sie mit 4 ml 50% Kalium-Natriumtartrat Lösung, 2 ml NH_4OH und 2 ml 0.5% Gelatine-Lösung. Nach Vertreiben des Sauerstoffes wird polarographiert. Aus dem erhaltenen Polarogramm sind Kupfer, Zink, Mangan und Eisen mit der sogenannten Additionsmethode bestimmbar. Das Nickel wird nach Zugabe von 2 ml alkalischer KCN-Lösung (16 g KCN + 20 g NaOH/100 ml) polarographiert. [J.Inc.]

1342 – On the polarographic behaviour of indium in the presence of large amounts of cadmium in pyrophosphoric acid solutions containing chlorides (in Russian). D. I. Kurbatov and M. S. Rusakova (Ural Department, Academy of Sciences, U.S.S.R.). *Izvest. Sibir. Otdel. Akad. Nauk, S.S.S.R.*, [7] (1960) 67–72.
In the presence of large amounts of chloride, indium forms a well-developed wave; limiting concentrations are proportional to concentration in a large range. In solutions of pyrophosphoric acid not containing chlorides, indium is not reduced. In 19 *M* pyrophosphoric acid solutions indium forms insoluble compounds, which are precipitated, and indium cannot be reduced. A suitable medium is 19 *M* pyrophosphoric acid containing 2 g ions chlorine for 1 g ion cadmium. [Ot.So.]

1343 – Polarographic determination of indium in the presence of lead, tin and cadmium (in Czech). M. Kvaček and P. Kühn (Institute of Mineral Raw Materials, Kutná Hora; and Department of Mineralogy, Mining Institute, Ostrava, Czechoslovakia). *Chem. listy*, 55 (1961) 1296–1299.
A method is described for the direct determination of indium in the presence of a fifty-times larger excess of Pb and Sn, and large amounts of Cd. The determination is carried out in 2 *M* HCl, which is also 2 molar in KBr. The method has been used for analysis of sphalerites and Zn concentrates. [Ot.So.]

1344 – Polarographic determination of the lanthanides by means of azo dyestuffs. T. M. Florence and L. E. Smythe (Atomic Energy Commission Research Establishment, Lucas Heights, New South Wales, Australia). *Nuclear Sci. Abstr.* 15 (1961) 2494, *Abstract no.* 19272.

1345 – Simultaneous polarographic determination of indium and tin. Sidney L. Phillips and Evan Morgan (Research Laboratory, International Business Machines Corp., Poughkeepsie, N.Y., U.S.A.). *Anal. Chem.*, 33 (1961) 1192–1193.
A polarographic method for the simultaneous determination of tin and indium in concentrations from 1–10 mg per 50 ml is described. Supporting electrolyte is 0.1 *M* NH_4SCN and 0.017 *M* pyrogallol; optimum pH value is 1.0. The effect of pyrogallol concentration and pH value on the polarographic waves is investigated. Half-wave electric tensions for tin(IV), tin(II) and indium (III) *vs.* S.C.E. are —0.16, —0.42 and —0.56 V, respectively. [Su.Mo.Ce.]

1346 – The reduction of thallium(I) at the dropping mercury electrode (in English). R. Tamamushi and N. Tanaka (Department of Chemistry, Tohoku University, Sendai, Japan). *Z. physik. Chem.*, (*Frankfurt*), 28 (1961) 158–167.
In several supporting electrolytes the reduction of Tl^+ was investigated by d.c. polarography, and measurements of Faradaic impedance. Tl^+ is adsorbed at the mercury surface and the adsorbability is increased by adsorbed anions of the supporting electrolyte in the order: ClO_4^-, $SO_4^{2-} < NO_3^- < Cl^-$. In 1 *M* KNO_3 and 1 *M* HNO_3 the log-plot of the d.c. polarogram only became strictly linear, when the concentration of polyoxyethylene lauryl ether (LEO) was higher than $2 \cdot 10^{-6}$ *M*, because the LEO-molecules with their greater adsorbability are replacing the adsorbed Tl^+ ions. [H.W.Nür.]

1347 – Adsorption controlled anodic process of the graphite electrode: application to the determination of minute amounts of nonionic surfactants P. J. Elving and D. L. Smith (Michigan University, Ann Arbor, Mich., U.S.A.). *Nuclear Sci. Abstr.*, 15(1961)2499, *Abstract no.* 19299.

1348 – Trace analysis of purest silicon (in German). F. A. Pohl and W. Bonsels (A.E.G.-Forschungsinstitut, Frankfurt/M., Germany). *Mikrochim. Acta*, (1960) 641–649.
After the mechanical and chemical preparation, traces of Fe and Tl are separated from the others (Pb, Cd, In, Cu, Ni, Zn and Bi) by extraction with di-*iso*-propylether. Fe and Tl are determined in tartrate as supporting electrolyte after reduction with $NH_2OH.HCl$. Bi, Pb, Zn, and In are polarographed also in a tartrate medium, while the supporting solution for the determination of Cu, Cd, Ni and Zn is 6 *M* NH_4OH. The relative errors amount to less than 20% in the range of $10^{-6}\%$. [H.L.Ki.]

1349 – Polarographic investigations in water-free dimethylsulfoxide. II (in German). V. Gutmann, P. Heilmayer and G. Schöber (Institut für anorganische und allgemeine Chemie, Technische Hochschule, Wien, Österreich). *Monatsh. Chem.*, 92 (1961) 240–245.
The polarographic behaviour of silicon fluoride, bis(dimethyl sulfoxide), ethyl-trichlorosilane, phenyl-trichlorosilane, diphenyl-dichlorosilane and silicon fluoride ammoniate was investigated in dimethyl sulfoxide, to which tetra-ethylammonium perchlorate or nitrate was added. Each substance shows two waves respectively at about —0.52 V and —1.09 V (S.C.E.), both diffusion controlled. The number of electrons transferred was equal to one in each case. Trichlorosilane shows a third wave just before the final rise of the current at —2.70 V. Regarding the mechanism of the reduction, the authors presume an ionisation under the influence of the homogeneous field around the dropping electrode. [H.L.Ki.]

1350 – Polarographic investigations in water-free ethylenediamine. IV. (polarographic anion-effect) (in German). G. Schöber and V. Gutmann (Institut für anorganische und allgemeine Chemie, Technische Hochschule, Wien, Österreich). *Monatsh. Chem.*, 92 (1961) 292–295.

In non-aqueous solutions the dissociation constant of a salt will be dependent on the type of anion. This brings about a shift in the half-wave value of the electric tension as it is observed by the authors for $CdCl_2$, $Cd(NO_3)_2$ and $Cd(ClO_4)_2$. Owing to the absence of multiple waves auto-complexing is highly improbable. [H.L.Ki.]

1351 – Mechanism of reduction of tetravalent germanium on the mercury drop electrode (in Russian). N. V. Stashkova and A. I. Zelyanskaya (Ural Department, Academy of Sciences, U.S.S.R.). *Izvest. Sibir. Otdel. Akad. Nauk, S.S.S.R.*, (1961) 72–81.
Reduction of Ge(IV) has been investigated in a supporting medium of sodium acetate of various pH values. It was found that in 0.2 *M* CH_3COONa at pH 6–10 well defined germanium waves are obtained. In 7 ml of a solution of 0.2 *M* Na acetate, 0.5 *M* Na_2SO_3, 0.001% gelatin and $5–7 \cdot 10^{-7}$ *M* Ge it was found that germanium is reduced by a four-electron process. It is shown that the particular properties of germanium reduction on the mercury drop electrode *i.e.* lowering of the diffusion current with increasing pH and increasing Ge concentration, positive shift of the half-wave value with increasing temperature, and decrease of the ratio $I/\sqrt{h}$ at high Ge concentrations, may be explained by slow dissociation of penta-germanium ions. [Ot.So.]

1352 – *Ortho*-diphenolgermanic acids (in German). N. Konopik (Institut für physikalische Chemie, Universität, Wien, Österreich). *Monatsh. Chem.*, 92 (1961) 8–21.
The complex compounds formed between germanic oxide and pyrogallol, and also 2,3-dihydroxynaphthalene-6-sulfonic acid show the same behaviour as the complex with pyrocatechol previously examined. The author investigated the reduction wave at a mercury electrode with respect to the pH (in the region 0.4–4.0), the height of the mercury reservoir, the ionic strength and the concentrations of both components. The limiting current appears to be diffusion controlled. The reduction required 4 electrons per atom of germanium. A ratio for the composition of the compound is: Ge : *o*-diphenol = 1 : 3. [H.L.Ki.]

1353 – Polarographic determination of germanium *via* its complex with pyrocatechol (in German). N. Konopik (Institut für anorganische und physikalische Chemie, Universität, Wien, Österreich). *Monatsh. Chem.*, 91 (1960) 717–728.
o-dihydroxy compounds form strong two-basic complexes with Ge(IV). These complexes show polarographically a flat maximum, the height of which is strongly dependent on the concentration of the supporting electrolyte $NaClO_4$. The influence of the pH was studied in a medium of $HClO_4$ for pH between zero and 1.5, and in a buffer of glycine for solutions with pH between 1.5–4.0; in both cases the ionic strength was maintained at about 1 by addition of $NaClO_4$.
The half-wave value of the electric tension decreases linearly with increasing pH; the wave height decreases also, but sigmoidically, until the height becomes zero at about pH 4. For analytical applications a buffer solution of pH 1.5 is recommended, the concentration of pyrocatechol being 0.9 *M*. The relation between wave height and concentration of Ge is strictly linear for concentrations from 0.025–5 m*M*. As(III) gives a double wave at nearly the same value of the electric tension. The presence of Si has no disturbing effect. [H.L.Ki.]

1354 – Polarographic determination of tin in stainless steel K. R. J. Cottell (U.K.A.E.A. Research Group Chemistry Division, Chatham Outstation, Great Britain). *Nuclear Sci. Abstr.*, 15 (1961) 2491, *Abstract no.* 19243.

1355 – Use of inverse polarography; determination of microgram amounts of lead in zinc, gallium, antimony and arsenic (in Czech.). J. Provazník and J. Mojžíš (A. S. Popov Research Institute, Prague, Czechoslovakia). *Chem. listy*, 55 (1961) 1299–1303.
The determination of $3 \cdot 10^{-5}–1 \cdot 10^{-3}$ % Pb in very pure Zn, and of $6 \cdot 10^{-5}–2 \cdot 10^{-3}$% Pb in Ga, Sb and As purified for use in semiconductors is described. The influence of the basic material is eliminated in the case of Zn and Ga by suitable choice of the electric tension in electrolysis; in the analysis of Sb and As these are removed by distillation with bromine. [Ot.So.]

1356 – The normal amount of Pb in human blood (in German). L. Jenšovský and Z. Roth (Institut für Arbeitshygiene und Berufskrankheiten, Prag, Tschechoslowakei). *Naturwissenschaften*, 48 (1961) 382–383.
Nach Fällung von einigen ml Heparin-Blut mit 20% Trichloressigsäure und Abzentrifugierung wird in der deproteinierten Lösung Blei mit der "anodic stripping polarography" bestimmt. (Konzentrationsbereich µg/100 ml). Aus Versuchsdaten wird die interindividuelle und intraindividuelle Streuung des Bleigehaltes im Blut der Patienten errechnet. [H.W.Nür.]

1357 – Approximate thermodynamic formation constants of some complexes of lead(II) and thallium(I) from polarographic data. C. J. Nyman, D. K. Roe and R. A. Plane (Depart-

ments of Chemistry at Washington State University, Pullman, Washington; and Cornell University, Ithaca, N.Y., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 323–326.
The relation for the polarographic half-wave electric tension for a complex ion may be used at any ionic strength, provided activity coefficients are available, and a combination of polarographic half-wave electric tension and activity coefficient data may be utilized for the calculation of thermodynamic formation constants. The authors have used the polarographic data of Vlcek (*Collection Czechoslov. Chem. Communs.*, 20 (1955) 400) and estimates of activity coefficients from the Guggenheim equation to calculate the formation constants of the aqueous complex species $PbNO_3^+$, $Pb(OH)_3^-$, $TlNO_3$, and TlCl. The values obtained are 1.08, 13.90, 0.38, and 0.46, in log units respectively. These data are in agreement with other determinations which involve consideration of activity coefficients. Experimental polarographic data at a constant ionic strength of 1.0 *M* yields a formation constant for TlCl of 0.64. [R.Mur.]

1358 – Polarographic investigation on the monocarboxylate-complexes of lead. I. Stability constants. V. Klemenčić and I. Filipović (University of Zagreb, Jugoslavia). *Croat. Chem. Acta*, 31 (1959) 3–22.
According to De Ford and Hume, the stability constants of the monocarboxylate-complexes of Pb with the following acids have been measured polarographically: formic, ($K_1 = 27$; $K_2 = 47$; $K_3 = 42$); acetic, ($K_1 = 180$; $K_2 = 750$; $K_3 = 1350$); monochloroacetic acid, ($K_1 = 22$; $K_2 = 40$; $K_3 = 42$); propionic acid, ($K_1 = 180$; $K_2 = 1320$; $K_3 = 2200$); butyric acid ($K_1 = 190$; $K_2 = 1000$; $K_3 = 2000$; $K_4 = 1800$); *n*-valeric acid, ($K_1 = 190$; $K_2 = 1500$; $K_3 = ?$; $K_4 = 5358$); *i*-valeric acid, ($K_1 = 190$; $K_2 = 1500$; $\mathrm{K}_3 = ?$; $K_4 = 3770$). Complex-stability increases with ligand radius and basicity. [Ca.Cas.]

1359 – Polarographic investigation on the monocarboxylate complexes of lead. II. Influence of monocarboxylate concentration on diffusion current. V. Klemenčić and I. Filipović (University of Zagreb, Jugoslavia). *Croat. Chem. Acta*, 31 (1959) 23–28.
If the monocarboxylate concentration is higher than 1 *M* the following relationship has been found between diffusion current (i_d) and viscosity coefficient (η) : $i_d = K\eta^{-\frac{1}{2}}$. Hydration and the formation of higher complexes interfere when dealing with lower complexes. [Ca.Cas.]

1360 – Polarographic behaviour of lead in iodide solutions. V. Klemenčić and I. Filipović (University of Zagreb, Jugoslavia). *Croat. Chem. Acta*, 31 (1959) 29–32.
Two waves are observed when Pb (as nitrate) is polarographed in NaI solutions (0.10–1.5 *M*), the first (lower) wave is due to the formation of a monomolecular layer of PbI_2 and disappears (owing to more soluble complex formation) as the I^- concentration rises above 1.5 *M*. [Ca.Cas.]

1361 – Indirect polarographic determination of nitrates in food products. E. Davídková and J. Davídek (Central Research Institute, Food Industry, Prague, Czechoslovakia). *Průmysl potravin*, 11 (1960) 385–387.
The reaction between nitrates and 2,4-xylenol yields a yellowish-red product (6-nitro-2,4-xylenol) which can be determined polarographically in 0.4 *M* NaOH with a half-wave value of —0.82 V. After removing nitrites by distillation of the methyl derivatives, and precipitation of proteins by means of tungstosilicic acid solution (20%), 20 ml H_2SO_4 (85%) saturated with Ag_2SO_4 are added to 5 ml of solution containing 100–500 μg of nitrites. 1 ml of 2% 2,4-xylenol in acetone is added. After 20 min, H_2O is added and 45 ml are distilled into a 50 ml flask containing 5 ml of 4 *M* NaOH. After addition of gelatin the polarogram is recorded. [Gio.Ser.]

1362 – Polarography of niobium(V) in (ethylenedinitrilo)-tetraacetic acid and citric acid media. John H. Kennedy (Explosives Department, Experimental Station Laboratory, E. I. du Pont de Nemours and Company, Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 33 (1961) 943–946.
A reversible polarographic wave of a 0.001 *M* Nb(V)–EDTA complex has been obtained at pH 3, representing a one-electron reduction; the half-wave electric tension in 0.03 *M* EDTA was—0.593 V *vs.* S.C.E. Information on Nb–citrate complexes was obtained from polarographic data. When the concentration of the citric acid media is lower than 0.2 *M*, a non-reducible niobium complex is formed. With higher citrate concentration and pH 3.0, a reducible Nb(V) complex is obtained, which gave a polarographic wave at —0.951 V *vs.* S.C.E., and which is suitable for analytical application. A method is described for the determination of quantities from 0.5–50 mg of Nb(V) per 100 ml, in the presence of phosphate ion, tantalum, tungsten, molybdenum and thallium. A third, non-reducible, complex was obtained by boiling 1 *M* citric acid solutions (pH 3) containing niobium; this third Nb-complex was more stable than the first two. [Su Mo.Ce.]

1363 – Polarographic determination of niobium in zirconium base alloys. D. P. Stricos

(Knolls Atomic Power Laboratory, Schenectady, N.Y., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 2496, *Abstract no.* 19282. [Red.]

1364 – Amperometric bismuth titration by an anodic complexometric method using a tantalum electrode (in Russian). A. K. Zhdanov, V. A. Khadeev and S. D. Ishankhodzhaev (V. I. Lenin University of Central Asia, U.S.S.R.). *Uzbekh. Khim. Zhur.*, [3] (1960) 29–35.
About 2 g of the alloy sample are dissolved in HNO_3 1 : 1, made up to 500 ml, and an aliquot taken. Acidity is thus sufficient to prevent hydrolysis. The solution is titrated by Trilone B volumetric solution using a rotating tantalum micro-electrode. The oxidation current of the reagent at an applied electric tension of 1.2 V is used for indication. Errors are about 0.5% rel. Phosphates, oxalates, fluorides and large amounts of chlorides interfere, also the cations, Mn(II), Fe(III), Pb(IV) and Hg. [Ot.So.]

1365 – Developments in the use of the wide bore dropping mercury electrode for determining dissolved oxygen and oxygen in gases. R. Briggs and G. Knowles (Water Pollution Research Laboratory, Stevenage, Herts., Great Britain). *Analyst*, 86 (1961) 603–608.
Since the introduction of the wide-bore dropping mercury electrode (Briggs, R., Dyke, G. V., and Knowles, G., *Analyst*, 83 (1958) 304) improvements in technique have been devised. A downward pointing assembly suitable for use in bottles or in flowing systems is described. The previous comparison electrode, a zinc rod dipping into an acetate buffer, has now been replaced by an Ag/AgCl electrode. The wide-bore electrode is coated internally with oven-baked silicone. The assembly for flowing systems shows an increase of only 3% in the polarographic current for flow rates of several hundred ml/minute. A cell is described for the determination of oxygen in gases, based on equilibration of the gas with a Na_2HPO_4–KCl buffer. The temperature coefficient of the calibration is negligible. For measurements on a wide variety of water samples the addition of a reagent containing 1.5% sodium hexametaphosphate, 22.3% NaCl, 6.3% K_2CO_3, 2.7% KCl, 7.3% KNO_3, 4.3% glycine and 1.8% sodium starch glycollate is recommended. Adding 0.5 ml of this reagent per 100 ml of sample brings the pH to a standard value of 8, eliminates maxima and prevents precipitation of $CaCO_3$. [P.O.Ka.]

1366 – Polarographic behaviour of some chromocomplexes. I. The hexa-rhodanochromate (III) ion (in German). E. Fischerová and O. Fischer (Purkyně University, Brno, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 26 (1961) 2570–2585.
The behaviour of the hexa-rhodanochromate(III) ion and the corresponding complexes of divalent chromium have been investigated in various supporting electrolytes. The reduction of the ion named to Cr(II) complexes takes place in most media at a slight overvoltage and in concentrated rhodanide solutions, reversibly. In dilute solutions of supporting electrolytes, the reduction is slowed down by electrostatic repulsion of the depolariser from the electrode, which is seen from horizontal parts of the limiting current curves. Cr(II) complexes speed up hydrolysis of the hexa-rhodanocomplex in the vicinity of the electrode. The products of alkaline hydrolysis are adsorbed on the surface of the mercury drop, and influence in great measure the shape of polarographic and oscillographic curves. [Ot.So.]

1367 – Polarographic behaviour of selenium. IV (in English). G. S. Deshmukh and O. P. Asthana (Banares Hindu University, India). *Naturwissenschaften*, 48 (1961) 477.
With selenous acid and alkali selenites in 1.0 *M* CH_3COONH_4 (+0.005% gelatin) two well-defined waves are observed ($E_{\frac{1}{2}}$ — 0.81 and —1.33 V *vs.* S.C.E.). They are proportional to concentration up to $3 \cdot 10^{-3}$ *M* Se(IV) and correspond to a two electron reduction in both steps (Se(IV) → Se(II) → Se). Only the first wave is completely reversible. [H.W.Nür.]

1368 – Cathodic action of the uranyl–EDTA complex at the dropping mercury electrode (in English). Tsai-Teh Lai and Teh–Liang Chang (Analytical Chemistry Laboratory, Cheng Kung University, Tainan, Taiwan, China). *Anal. Chem.*, 33 (1961) 1193–1196.
The first wave of U(VI) to U(V) reduction (in a solution 0.2 *M* $NaClO_4$ and 0.005% gelatin) was applied to the investigation of the uranyl–ethylene-dinitrilo-tetra-acetate (EDTA) chelate. After addition of EDTA to this solution a new reversible wave due to the reduction of the uranyl–EDTA complex to the U(V) state was obtained, over the pH range 3.3–9.3. The electrode reaction has been proved to be diffusion-controlled. Half wave electric tension for a solution $1.10 \cdot 10^{-3}$ *M* $UO_2(ClO_4)_2$ in $9.03 \cdot 10^{-2}$ *M* EDTA is — 0.37 V *vs.* S.C.E. for the pH range 5.7–6.8. For higher and lower values of pH the half wave electric tension is pH dependent, showing that one hydrogen or hydroxyl ion is involved in the reaction. The diffusion current for uranyl ion concentrations from $2.20 \cdot 10^{-4}$ *M* to $2.4 \cdot 10^{-3}$ *M* in $7.13 \cdot 10^{-2}$ EDTA, 0.2 *M* $NaClO_4$ and 0.005% gelatin at pH 5.50 is proportional to concentration, within the experimental error (1–2%). The electrode reaction is formulated for three diffentent pH ranges. [Su.Mo.Ce.]

1369 – Polarography in water and water–ethanol. I. U(VI) in chloride and perchlorate media in one molar acid. Williams Ves Childs and Edward S. Amis (University of Arkansas, Fayetteville, Ark., U.S.A.). *J. Polarog. Soc.*, 7 (1961) 30–42.
The polarographic reduction of uranium(VI) has been studied in 1 *M* acid solution, in water, in various water–ethanol mixtures, and also *M* in acid up to 92.2% ethanol. The acids employed were hydrochloric and perchloric, and the results are presented as functions of ethanol concentration, chloride concentration and uranyl ion concentration. In solutions of high ethanol concentration $E_{\frac{1}{2}}$ U(VI) was shown to be very dependent on chloride concentration. Similarly, diffusion coefficients were found to be dependent on both ethanol and chloride concentrations in solutions of high ethanol content. [G.F.Rey.]

1370 – Rapid polarographic determination of iron and manganese in minerals. M. Ionescu and D. Dumitrescu. *Rev. chim. (Bucharest)*, 11 (1960) 483–485.
0.2 g of mineral are evaporated to dryness with 5 ml HCl (1 : 1). The residue is taken up in 5 ml HNO_3–HCl (3 : 1) and evaporated again to dryness. The residue is dissolved in 6 ml HCl. Minerals not dissolved by the above procedure are fused with alkali, the residue is dissolved in acid and treated with H_2O_2. Excess O_2 is boiled off. In both cases, the solution is diluted to 100 ml, 5 ml are treated with 5 ml 0.5 *M* triethanolamine and 5 ml of 5 *M* NaOH. After shaking, 3 drops of Na_2SO_3 and 4 drops of 0.5% gelatin solution are added. After 0.5–2 h the polarogram is registered. Standards are prepared under the same conditions. The half-wave potentials are —0.49 V for Mn and —1.08 V for Fe. [Gio.Ser.]

1371 – Amperometric titration of redox systems without external electric tension. I. Titration in reversible-irreversible systems (in Polish). E. Michalski and N. Pawluk (Department of Inorganic Chemistry, University, Łódź, Poland). *Chem. anal. (Warsaw)*, 6 (1961) 489–500.
The amperometric method, without external electric tension, was used to detect the end-point in some redox titrations. The following systems were investigated: (1), ferrous–permanganate; (2), ferrous–dichromate; (3), iodine–thiosulphate; (4), iodine–arsenite. As an indicator electrode the platinum wire was used and as comparison electrodes the following electrodes were used: (a), saturated calomel electrode; (b), platinum electrode in 0.1 *N* Ce $(ClO_4)_4$; (c), platinum electrode in saturated $Hg_2(NO_3)_2$. Depending on the comparison electrode, the indicator electrode worked as a cathode or as an anode. The equivalence point could be estimated graphically when the titrant or titrate was electroactive. When electroactive products were formed in the course of the reaction end-point determination was impossible unless the reaction product was bound into a complex. Successful titrations of (1) and (2) with (b) comparison electrode, and of (3) and (4) with (a) electrode were performed. In the case of (1) and (2) and (a) electrode, or (c) electrode it was necessary to add phosphate or fluoride for binding the ferric ions. [Ad.Hu.]

1372 – Amperometric cerimetric titration of iron(II) with ferroin as indicator (in English). I. M. Kolthoff and B. B. Bhatia (School of Chemistry, University of Minnesota, Minneapolis, Minn., U.S.A.). *Microchem. J.*, 4 (1960) 451–457.
Amperometric titration of ferrous iron in 1 *N* sulfuric acid solution is carried out at an electric tension of 0.65 V (*vs.* S.C.E.) with standard ceric cerium solution and 10^{-4} *M* ferrous phenanthroline as indicator. A rotating platinum wire is used as indicator electrode. For solutions of ferrous iron more concentrated than $5 \cdot 10^{-5}$ *M*, the titration is accurate and precise within 1%. Arsenic(III), in concentrations up to $2 \cdot 10^{-2}$ *M* does not interfere. [Su.Mo.Ce.]

1373 – Investigation of the mechanism of reduction of the $Fe(CN)_6{}^{3-}$ anion on the mercury drop electrode (in Russian). O. A. Petrii and N. V. Nikolaeva-Fedorovitsh (M.V. Lomonosov State University, Moscow. U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 1999–2009.
The effect of composition of the solution and of temperature on the rate of electro-reduction of $Fe(CN)_6{}^{3-}$ on a dropping Hg electrode has been investigated. It has been shown that the rate, after reaching a minimum, increases by about 30–40% on further increase of the electric tension. With increase in concentration of the supporting electrolyte, the reaction rate increases proportionately to the concentration of univalent cations by a power of 3.0–3.2. Based on the results obtained, it has been concluded that the rate of $Fe(CN)_6{}^{3-}$ reduction is determined by the slow annexation of an electron by the $Fe(CN)_6{}^{3-}$ particle within the boundary of the double layer. [Ot.So.]

1374 – Mechanism of the peroxidatic activity of iron(III)–EDTA in the catalyzed reaction of hydrogen peroxide with *p*-amino-N,N-diethylaniline. Paul M. Mader (Kodak Research Laboratories, Rochester, New York, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 2956–2961.
Polarographic kinetic studies on the iron(III)–EDTA complex-catalyzed reaction of hydrogen peroxide with *p*-amino-N,N-diethylaniline have been carried out in the pH range 9.67–10.54.

The reactions were performed in the presence of 4-chloro-1-naphthol which removes the interfering oxidation product of *p*-amino-N,N-diethylaniline. The kinetic data are explained on the basis of an oxidation of the diamine by the iron complex, with regeneration of the iron(III) complex by a more rapid reaction with hydrogen peroxide. The equilibrium constant for the reversible oxidation of the diamine by the iron complex has been determined at several pH values. [R.Mur.]

1375 – Amperometric titration of small quantities of Fe^{3+} by means of a solution of NaH_2PO_4 (in Russian). I. L. Teodorovic and M. K. Abramov (Institute of Chemistry, Academy of Sciences of the Usbek S.S.R.). *Doklady Akad. Nauk Usbek S.S.R.*, (1959) 29–31.
Satisfactory results, even in presence of Sn, Mn, Cd, Al, Cu, Cr, Co, Ni, Zn, or Ba, are obtained by means of a rotating Pt electrode, without external electric tension, and a saturated calomel electrode, NaH_2PO_4 being the titrating agent. In order to ensure a constant composition of the precipitated $Fe_3(PO_4)_2$ it is advisable to add to 30 ml of the solution to be titrated (at pH 3.4–3.6), 10 ml of a suitable buffer (20.5 g NaCl, 127 ml of 0.2 *N* HCl and 45 g glycine per litre). [Ca.Cas.]

1376 – Polarographic behavior of Ni ion in non-complexing media (in French). J. Dandoy and L. Gierst (Laboratoire de chimie analytique, Faculté des Sciences, Université Libre de Bruxelles, Belgique). *J. Electroanal. Chem.*, 2 (1961) 116–127.
The authors study the polarographic behavior of Ni ions in perchloric media, which is known for its non-complexing properties. Two types of measurements were used for this investigation: polarographic measurements and galvanostatic measurements. The behavior of Ni ions is explained in terms of dehydration kinetic current, and the influence of the electrochemical double-layer is discussed. [Fra.Cla.]

1377 – A polarographic study of rhodium in thiocyanate solutions (in English). Danilo Cozzi and Francesco Pantani (Institute of Analytical Chemistry, University of Pisa and Florence, Italy). *J. Electroanal. Chem.*, 2 (1961) 230–236.
The authors have carried out a wide investigation to obtain some information on the polarographic behaviour of rhodium, and hence of complex forms, in solution. Thiocyanate solutions are investigated and a well defined irreversible step is obtained from solutions. The process is a three electron reduction from Rh^{3+} to the metal. The effects of varying the maximum suppressors, temperature, Rh^{3+} and CNS^- concentrations are widely investigated. The irreversibility of the wave was analysed using Delahay's method. Some other experiments were carried out to characterize the complexes in solution; study of absorption spectra, the behaviour towards ion exchange resins and extraction with *iso*-amyl alcohol. [Fra.Cla.]

1378 – The use of polarography in organic analysis (in Russian). I. A. Korshunov and A. I. Kalinin. *Zavodskaya Lab.*, 27 (1961) 1323–1328.
A review in which the purification of reagents for polarographic analysis, use of non-aqueous solvents, use of oscillographic, alternating-current, and square-wave polarography, and finally, the use of indirect methods are dealt with. The review is supplemented by a bibliography including 132 references. [Ot.So.]

1379 – Anodic voltammetry to +2.0 volts. Application to hydrocarbons and oxidation stability studies. J. West Loveland and Glenn R. Dimeler (Research and Engineering Department, Sun Oil Company, Marcus Hook, Pa., U.S.A.). *Anal. Chem.*, 33 (1961) 1196–1201.
The use of a rotating platinum micro-electrode, with acetonitrile as solvent and 0.5 *N* sodium perchlorate as the electrolyte, is investigated in the study of the voltammetric behaviour of several aromatic hydrocarbons and non-hydrocarbons. Anodic voltammograms at +2.0 V *vs.* Ag/Ag^+ are obtained. The standard deviation for peak currents and $E_{\frac{1}{2}}$ were found to be 4.3% and 0.005 V respectively. Observations of the effect of structure on ease of anodic oxidation are made. The technique is used for the study of the oxidation stability of oils. Application in qualitative and quantitative hydrocarbon and non-hydrocarbon analysis is suggested. [Su.Mo.Ce.]

1380 – Polarometric determination of organic substances and of hexavalent chromium in solutions of chromic acid (in Russian). V. I. Ginsburg (Research Institute of the Polygraphic Industry, U.S.S.R.). *Zavodskaya Lab.*, 27 (1961) 1337–1339.
Titration is by a 0.005 *N* Mohr's salt solution at $E = 0.75$–0.80 V making use of the oxidation current of iron. The relative error is not higher than 5%. For the determination of organic substances the sample is heated with a solution of 75 g $K_2Cr_2O_7$ and 150 ml H_2SO_4 (s.d. 1.84) for 1.5 h. After cooling and diluting an aliquot is titrated as above. [Ot.So.]

1381 – The influence of proteins on the polarographic behaviour of acetaldehyde in ferment-

ing media (in Russian). V. M. Elgort, A. L. Markman and I. E. Elpiner (Polytechnic Institute of Central Asia, U.S.S.R.). *Uzbek. Khim. Zhur.*, [5] (1960) 76–84.
It has been found possible to determine acetaldehyde directly in fermenting, as well as nonfermenting, young beer and in nutritive media provided that the sample is not saturated with proteins. Proteins, when interacting with acetaldehyde, become polarographically active. It has also been found that in fermenting there is present, beside acetaldehyde and pyruvic acid, a third (unknown) substance containing a carbonyl group. For the quantitative determination of acetaldehyde, formed in the fermenting process as well as added, the sample must be diluted 10–20 times and polarographed in a medium of 0.1 N $(CH_3)_4NI$ in a vessel with a mercury pool. Evaluation is by addition of a standard solution, the amount of which must be such as to increase the total diffusion current 1.5 times. The relative error of the determination is within the limits of the polarographic determination of organic substances, being 3–5%. [Ot.So.]

1382 – Etude des aldéhydes aliphatiques en milieu anhydre (in French). A. Kirrmann, J. M. Saveant and N. Moe (Laboratoire de chimie de l'école normale supérieure, 24 rue Lhomond, Paris 5e, France). *Comptes rend.*, 253 (1961) 1106–1108.
La réduction polarographique des aldéhydes saturés contenant de 2–3 atomes de carbone a été étudiée dans le diméthylformamide (DMF). Tous ces composés sont caractérisés par une tension électrique de demi vague égal à —2 V, la hauteur du palier étant anormalement faible. Cette hauteur augmente en présence d'eau ou de phénol, tous deux donneurs de protons. Les auteurs admettent finalement les étapes suivantes:

$$RCHO + HA \rightleftharpoons R{-}CH{-}O\ldots HA$$
$$R{-}CH{=}O\ldots HA + e \rightleftharpoons R{-}\dot{C}H{-}OH + A^-$$
$$R{-}\dot{C}H{-}OH + e \rightleftharpoons [R{-}CHOH]^-$$
$$[R{-}CHOH]^- + HA \rightleftharpoons R{-}CH_2OH + A^-$$

La seconde réduction étant plus facile que la première, il en résulte une seule vague à deux électrons. [Bad.Lam.]

1383 – Polarographic method for the analysis of solutions obtained in the manufacture of glyoxal (in Russian). V. G. Brudz and others (Research Institute of Chemical Reagents, U.S.S.R.). *Zavodskaya Lab.*, 27 (1961) 1087–1090.
A polarographic analysis has been developed for the mixtures obtained in the manufacture of glyoxal. The accuracy of the determination is 3–5% for glyoxal, 3% for glycolaldehyde and glyoxalic acid and 5% for formaldehyde. 1 ml of the sample is weighed and diluted with water to 50 ml. An aliquot is diluted with 0.05 N LiOH, bubbled with hydrogen, and a polarogram is registered from which a calibration curve is prepared. The wave at $E_{\frac{1}{2}} = -1.9$ V gives the glycolaldehyde concentration, the difference between this and the wave at $E_{\frac{1}{2}} = -1.7$ V gives formaldehyde concentration. Glyoxal is determined in phosphate buffer at precisely pH = 10.4 where, in the presence of gelatin, a wave at —1.58 V corresponds to the sum of glyoxal, glycolaldehyde and formaldehyde. [Ot.So.]

1384 – Polarographic resolution of mixtures of complexans. W. Hoyle and others (Chemistry Department, Birmingham University, Great Britain). *J. Electroanal. Chem.*, 2 (1961) 166–173.
In this paper, a modified polarographic method is described for the resolution of many mixtures of known complexans, without the necessity of previous isolation or group separation by electrophoresis. The solution of complexans is treated with just sufficient copper sulphate to form the Cu(II) chelates of all complexans present and a derivative polarogram is recorded for the mixture. Resolution is possible when the $E_{\frac{1}{2}}$ values differ by only *ca.* 50 mV. The influence of proportion of components on the resolution is examined. A good proportionality exists between peak height and the amount of complexan present, and a semi-quantitative analysis is possible where reasonable resolution is obtained. [Fra.Cla.]

1385 – Polarographic determination of dinitrophenylamino-acids (in Russian). I. A. Vaĭntraub (State University, Kishinev, U.S.S.R.). *Biokhimiya*, 25 (1960) 688–692.
Dinitrophenylamino acids are separated by chromatography and the chromatograms are sectioned and eluted with Britton–Robinson or borate buffer pH 8.2. After addition of Na_2SO_3 to remove O_2, a polarogram is recorded, using a cell with external S.C.E., thermostatically controlled at 25° ± 0.1°, and an electronic integrating–differentiating polarograph. Bis(dinitrophenyl)histidine forms three waves, while all other dinitrophenylamino acids display a two step reduction, thus permitting the determination of histidine in the presence of an 80-fold excess of the other amino-acids. [Gio.Ser.]

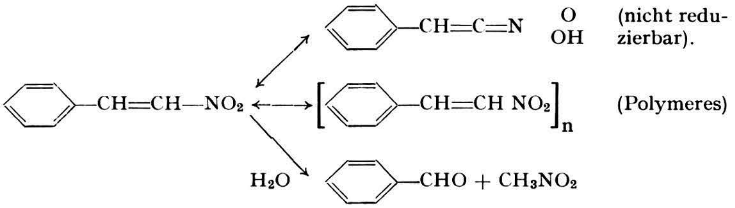
1386 – A contribution to protein polarography. V. Podrouzek (Psychiatric Clinic of the Charles University, Prague, Czechoslovakia). *Ceskoslov. fysiol.*, 8 (1959) 120–122.
Blood plasma proteins can be determined by means of polarography (electric tension 150 m V, drop-fall time 3 sec., sensitivity 1/50, start at 1.5 V, capacity $3000\,\mu F$, $4000\,\Omega$): the sample must be diluted 1 : 25 with physiological NaCl solution, and Ag plates are used as auxiliary electrodes.
[Ca.Cas.]

1387 – Polarography of maleic acid aryl- and alkylimides (in German). A. Němečková, M. Maturová, M. Pergál and F. Šantavý (Institute of Chemistry, Medical Faculty, Palacký University, Olomouc, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 26 (1961) 2749–2753.
The substances named are reduced by two electrons in the acid range, in a medium of Britton-Robinson buffer solutions. With increasing pH values two one-electron reductions take place. In alkaline medium, hydrolysis and reduction of the corresponding amides of maleic acid occurs. With increasing numbers of carbon atoms in the radical, polarographic reproducibility decreases.
[Ot.So.]

1388 – Amperometric determinations of SH-groups in haemoglobin of horned cattle. H. Schiller (Physikalisches Chemisches Institut, Humboldt-Universität, Berlin, Deutschland). *Z. physik. Chem. (Leipzig)*, 216 (1961) 87–91.
An der rotierenden Pt–Elektrode (1500 rev/min) werden in Trioxymethylaminomethan als Lösungsmittel reduziertes Hämoglobin, Oxyhämoglobin und Methämoglobin mit salpetersaurer $AgNO_3$–Lösung bei —0.1 V (N.C.E.) amperometrisch titriert. Beim Oxyhämoglobin schwankt die SH-Gruppenzahl pro Molekel zwischen 4.25–5.54 während sie beim reduzierten Hämoglobin um bis zu 0.6 grösser ist. Das zeigt, dass die beiden Redoxsysteme des Hämoglobins (Fe(III)/Fe(II) und Disulfid/Sulfhydryl) im Gleichgewicht miteinander stehen. [H.W.Nür.]

1389 – On the amperometric titration of sulfhydryl groups by means of $AgNO_3$ (in Russian). W. O. Belitzer and O. W. Lobatschevska (Institute of Biochemistry, Academy of Sciences of the Ukrainian S.S.R., Kiev, U.S.S.R.). *Ukrain. Biokhim. Zhur.*, 31 (1959) 579–588.
By means of a suitable ammoniacal buffer made from 0.25 *M* NH_4NO_3 (and 0.1 *M* NH_4OH containing 0.5 *M* $Ca(NO_3)_2$ and 10% alcohol), formation of complexes between Ag^+ and the products of $AgNO_3$ titration of SH groups is avoided. Correct results are obtained as experiments on cysteine, 2-mercapto-ethanesulfonate and 2,3-dimercapto-propanesulfonate show. [Ca.Cas.]

1390 – Polarographic analysis of the reduction and stability of ω-nitrostyrene (in German). L. Holleck and D. Jannakoudakis (Institut für physikalische Chemie, Universität Hamburg, Deutschland). *Z. Naturforsch.*, 16 B (1961) 396–398.
Die Reduktion der $—NO_2$ Gruppe verläuft unter Aufnahme von 4-Elektronen zum Hydroxylamin, wonach in stärker sauren Lösungen noch 2 Elektronen aufgenommen werden. In alkalischer Lösung erfolgt Zersetzung mit Auftreten neuer Stufen, deren Zuordnung getroffen wird. Daraus ergibt sich folgendes Schema ($pH > 7$):



[He.Be.]

1391 – Polarographic examination of methyl-phenyl-dodecyl-trimethyl-ammonium (désogène). L. Robert, G. Goldstein and J. Polonovski (Service de chimie biologique, 45 Rue des Saints Pères, Paris, France). *Mikrochim. Acta*, (1959) 318–321.
Désogène gives, in 0.1 *M* tetramethyl-ammonium hydroxide or 0.1 *M* LiCl, a normal polarogram with a half-wave electric tension of —1.75 V (S.C.E.) which corresponds to a two-electron reduction and follows Ilkovič's law until the concentration has become about 500 mg/l. At higher concentrations an adsorption maximum preceded by a prewave appears. [H.L.Ki.]

1392 – Polarographic determination of 2,4-diamino-4′-ethoxyazobenzene (urokarmin). L. Faith (State Institute for Control of Drugs, Bratislava, Czechoslovakia). *Farmácia*, 29 (1960) 286–288.

2,4-Diamino-4'-ethoxyazobenzene (I) yields a two electron wave at pH 4.2 with a half-wave value of —0.30 V *vs.* the S.C.E. The sample is dissolved in ethanol (40 ml) and diluted to 50 ml. 0.5 ml of this solution, containing 0.5 μg of (I) are mixed with acetate buffer (pH 4.2) and diluted to 10 ml. After gassing out O_2, the polarogram is recorded and compared with a calibration curve. The error is ±3%. [Gio.Ser.]

1393 – Use of chloramine T in amperometry (in Russian). V. A. Khadeev and others (V. I. Lenin State University, Tashkent, U.S.S.R.). *Uzbek. Khim. Zhur.*, [6] (1960) 28–37.
The polarographic behaviour of chloramine T has been investigated in acid, neutral and weakly alkaline media on a platinum micro-electrode at anodic and cathodic polarisation. It has been found that well developed waves are obtained in all cases of cathodic polarisation, but no anodic waves are obtained in either of the media. The following determinations have been worked out. As(III): 0.1–4 mg are titrated in the presence of 1 g $NaHCO_3$ and 2 ml 1 *M* acetate buffer, final volume 40 ml, relative error 0.7%. Sb (III): 0.4–19 mg are titrated in the presence of sodium tartrate with an error of 0.8%, either in the presence of potassium iodide or without, in this case at an electric tension equal to +0.1 V. Further titrations mentioned are: Sn(II), thiosulphates, sulphites, bisulphites, ferrocyanides, iodides, hydrazine salts, ascorbic acid and *o*-oxyquinoline. [Ot.So.]

1394 – Polarographic investigations of some triphenylmethane derivatives (in Hungarian). I. Rusznák and others (Institute for Practical Chemistry, Technical University, Budapest, Hungary). *Magyar Kém. Lapja*, 16 (1961) 287–289.
Es wurden zehn verschiedene Triphenylmethan-Derivate bei pH 3.02 polarographisch untersucht um den Zusammenhang zwischen Struktur und Halbstufenspannung aufzuklären. Mit Hilfe der Heyrovsky–Ilkovič'schen Gleichung wurde die Elektronenzahlveränderung der Reduktionsvorgänge bestimmt und für eins gefunden. Das entspricht einen Vorgang woran freie Radikale beteiligt sind. Die Reihenfolge der Halbstufenspannungen lässt sich durch die Elektroneneffekte der Substituente ableiten. [J.Inc.]

1395 – Reduction with zinc amalgam and determination of triphenylmethyl phenyl sulphide (in Italian). T. Tarantelli (Institute of General Chemistry, University of Camerino, Italy). *Ann. chim. (Rome)*, 51 (1961) 1174–1177.
Triphenylmethyl phenyl sulphide is quantitatively reduced by amalgamated zinc to triphenylmethane and thiophenol. After addition of ammonia buffer to the reduced solution, an amperometric titration can be performed by using, as a titrating agent, $AgNO_3$ in ethyl alcohol and a rotating silver wire as indicator electrode. [Fr.Pan.]

1396 – Phthalides and indandiones-(1,3). VIII. Meerwein-Pondorf's reduction of 2-(*p*-X-aryl)-indandiones-(1,3) and its polarographic evaluation (in Slovakian). P. Hrnčiar and V. Podaný (Departments of Organic Chemistry and Analytical Chemistry, Komenský University, Bratislava, Czechoslovakia). *Chem. Zvesti*, 15 (1961) 713–719.
Work was done on a Heyrovsky Polarograph (type V 301), with a vessel according to Kalousek, and with a separate calomel electrode. For a determination, 10 ml Britton–Robinson buffer solution, 4 ml of the corresponding derivative and 4 ml ethanol are taken and after bubbling nitrogen for 5 minutes, a polarogram was registered. pH values used were 5.5 and 11.9. $E_{\frac{1}{2}}$ values are tabulated. [Ot.So.]

1397 – Sur le comportement polarographique et spectrophotométrique de certains dérivés nitrés du pyrrole. P. Fournari, M. Person et Mme G. Watelle-Marion (Faculté des Sciences de Dijon, France). *Compt. rend.*, 253 (1961) 1059–1060.
Les auteurs ont étudié le comportement polarographique et spectrophotométrique du méthyl-1-nitro-4 pyrrole aldéhyde-2 ($C_6H_6O_3N_2$) fondant à 158–160° et du méthyl-1 nitro-5 pyrrole aldéhyde 2, fondant à 69–70°. La méthylation à l'azote a peu d'influence sur la valeur de la tension électrique de demi vague de la vague à quatre électrons du groupement nitré. La réduction est cependant facilitée en milieu alcalin. [J.Bad.Lam.]

1398 – Polarographic determination of pyridoxol in pharmaceuticals (in German). O. Manoušek and P. Kočová (Zentral Forschungsinstitut der Lebensmittelindustrie, Prag, Tschechoslowakei). *Mikrochim. Acta*, (1961) 754–761.
In a supporting solution of 0.1 *M* NH_4OH and NH_4Cl buffer (pH 8.5) pyridoxol (3-hydroxy-4,5-dioxymethyl-2-methylpyridine) gives a single wave, $E_{\frac{1}{2}} = -1.7$ V (S.C.E.), which is diffusion controlled and corresponds to a two electron reduction. At the same pH, but using a 0.1 *M* veronal buffer, the normal wave is succeeded at a slightly more negative potential by a catalytic wave. The procedure is as follows: 0.05 g pyridoxol is dissolved in water to a volume of 250 ml. When necessary the solution is filtered. 5 ml of the prepared solution is mixed with an equal volume of

0.2 *M* ammonia buffer. After having removed the oxygen the polarogram is registered. The same method can be used for estimating 3-hydroxy-5-oxymethyl-2-methylpyridine. [H.L.Ki.]

1399 – Polarography of 2-ethyl-4-thiocarbamoylpyridine. P. O. Kane (Research Laboratories, May and Baker Ltd., Dagenham, Essex, Great Britain). *J. Electroanal. Chem.*, 2 (1961) 152–160.
Experimental details and results are given. To aid the interpretation of the polarographic properties of 2-ethyl-4-thiocarbamoylpyridine (ethionamide), polarograms of 4-thiocarbamoylpyridine were also recorded. Polarograms may be divided into three regions of electric tensions: one oxidation wave and two reduction waves, depending on pH at the dropping mercury electrode over the pH range 0–13. One of the reduction waves is kinetically controlled. A discussion is included on the nature of the electrode reaction products and an interpretation of these reactions is presented. [Fra.Cla.]

1400 – Polarographic determination of caprolactam (in Russian). Ya. I. Turyan and B. P. Zhantalai (Institute for Nitrogen Industry Research, Lisitshansk, U.S.S.R.). *Zavodskaya Lab.*, 27 (1961) 1211–1214.
A sample containing about 0.1 g of the product to be determined is placed in a 100 ml flask. 5.0 ml 10 *N* NaOH are added and distilled water to 50 ml volume. The mixture is boiled carefully for 60 min. After cooling, the mixture is neutralised by 10 *N* H_2SO_4 to neutral red. 50 ml 1 *M* $NaHCO_3$ and a known amount of formaldehyde are added to give a 1.5% solution. The solution is made up to volume with water and polarographed. ($E_{\frac{1}{2}} = 1.12$ V). [Ot.So.]

1401 – Polarographic determination of nitrocyclohexane in caprolactam production (in Russian). Ya. I. Turyan and P. M. Zaitsev (Institute of the Nitrogen Industry, Lisitshansk, U.S.S.R.). *Zavodskaya Lab.*, 27 (1961) 1329–1331.
The influence of the components of mixtures resulting in caprolactam production on the polarographic determination of nitrocyclohexane has been investigated. 10 ml of aqueous or alcoholic-aqueous acetate buffer solution, pH 4.65 are placed in the polarographic vessel, and bubbled with nitrogen for 10 minutes. 1 ml of the analysed sample is introduced, and after another minute of nitrogen bubbling a polarogram is registered. Precision is 3%, the limit of determination is 0.0003%. [Ot.So.]

1402 – Polarographic determination of adrenochrome semicarbazone. M. Sterescu and M. Popa. *Rev. chim. (Bucharest)*, 11 (1960) 489.
0.02 g of adrenochrome semicarbazone are dissolved in 100 ml of 10% LiCl and 1 ml of 1% gelatin is added. After bubbling N_2 to remove O_2 the polarogram is recorded between 0 and —1.0 V. The error is ±1%. [Gio.Ser.]

1403 – Polarography of astraphloxin (in German). H. Berg and W. Böckel (Institute of Microbiology and Experimental Therapy, Jena, Germany). *Monatsber. deut. Akad. Wiss. Berlin*, 3 (1961) 32–40.
Die polarographischen Eigenschaften von Astraphloxin (Indoleninrot) werden durch Gleichspannungspolarographie (auch am stationären Tropfen), Dreieckspannungsoszillographie, Wechselstrompolarographie, Umschalter u.a. analysiert. Danach erfolgt die Elektronenaufnahme im mittleren und hohen pH-Bereich ohne zusätzliche Protonen. Die Reoxydierbarkeit des schwerlöslichen Leukofarbstoffes wird durch Deckschichtenbildung verhindert. Der Hauptstufe bei $\pi_{\frac{1}{2}} = -1.01$ V sind kleinere Teilstufen vor- und nachgelagert, woraus auf komplizierte Elektrodenprozesse geschlossen wird. Die endgültige Lösung des Problems hängt wesentlich von einem günstigeren Lösungsmittelsystem ab. [He.Be.]

1404 – Kinetics of tryptophan metabolites. 1. Polarographic behaviour of kynurenic acid and its ethyl ester and N-oxide (in Italian). E. Fornasari and others (Polarographic Center, Padova, Italy). *Gazz. chim. ital.*, 91 (1961) 1105–1111.
In acid or alkaline solutions, kynurenic acid yields an irreversible polarographic step corresponding to a two-electrons reduction. A sharp variation of $E_{\frac{1}{2}}$ with pH is observed; in neutral solutions two steps are obtained. The ethyl ester of this acid yields only one step at any pH. The N-oxide is firstly reduced to kynurenic acid, which undergoes the above mentioned reduction. [Fr.Pan.]

1405 – Polarographic determination of biotin (in German). J. Davídek (Institut für Chemie und Lebensmitteluntersuchung, Chemisch-technische Hochschule, Prag-Dejvice, Tschechoslowakei). *Naturwissenschaften*, 48 (1961) 403.
Erstmalig gelang nach Nitrosierung mit Alkalinitrat im sauren Milieu die polarographische Bestimmung des Nitrosoderivates. ($E_{\frac{1}{2}} = -0.83$ V (S.C.E.) in 0.5 *M* CH_3COONa, diffusionsbedingte Stufe). 10^{-5} Mol/l können mit ±3% Fehler noch bestimmt werden. [H.W.Nür.]

1406 – Investigation of methylene blue solutions by cyclic voltammetry on the hanging mercury drop electrode (in Polish). W. Kemula,and others (Department of Inorganic Chemistry, University, Warsaw, Poland). *Roczniki Chem.*, 35 (1961) 1009–1020.
During reduction of methylene blue, riboflavin and thionine on the hanging mercury drop electrode (HMDE) in voltammetric conditions, adsorption maxima were observed, their size depending on the electrode surface. Using cyclic polarisation of HMDE, adsorption cathodic maxima as well as anodic desorption minima occurred. A detailed study of methylene blue solutions by cyclic voltammetry has shown that, in more dilute solutions than $2 \cdot 10^{-5}$ *M*, only adsorption effects were observed. Especially sensitive is the desorption minimum, which can be observed in 10^{-8} *M* solutions, if pre-electrolysis at constant electric tension was applied in order, to accumulate the leucomethylene blue adsorbed on the electrode surface. This procedure can be used for the determination of extremely small quantities of the dye. The maximum and minimum value of the electric tension depends, to some extent, on the concentration of the solution. In more concentrated solutions a second redox system can be observed at more negative values, which is exclusively a diffusion system. In acid medium $E_{\min}-E_{\max} = 35$ mV, but the relationship is more complicated at pH $\geqslant 7$. The adsorbed layer of leucomethylene blue covers the electrode surface but does not prevent electrode processes occurring. The properties and oxidation electric tension of this layer depend on the kind of previous electrode polarisation. Similarly, this adsorbed layer does not prevent the electrode reactions of cadmium ions. On the other hand, the structure of this layer is changed by addition of small quantities of gelatin (0.01%), preventing the electrode reactions of methylene blue and cadmium ions. [Ad.Hu.]

See also abstracts nos. 1298, 1299, 1301, 1302, 1311, 1478, 1507.

4. Potentiometry

1407 – Theory of chronopotentiometry with cylindrical electrodes. III. Successive electrochemical reactions. Dennis G. Peters and James Lingane (Chemistry Department, Harvard University, Cambridge, Mass., U.S.A.). *J. Electroanal. Chem.*, 2 (1961) 249-258.
The theoretical transition–time equation for successive electrochemical reactions has been derived for the case of cylindrically symmetrical diffusions. The case of only two electroactive substances is considered for simplicity of discussion. Chronopotentiometric data for the successive reductions of ferric and cupric ions at a platinum wire cathode in hydrochloric acid have served to establish the validity of this relation. For the first substance the corresponding electrode reaction proceeds with 100% current efficiency, while for the second, the current efficiency will be less than 100%, and the transition time for the second inflection will be greater than it would be in the absence of the first substance. Furthermore, the cylindrical effect becomes larger as the transition times increase. [Fra.Cla.]

1408 – High temperature electromotive force measurements (final report). J. V. Vanghen (Stetson University, De Land, Fla., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 2871, *Abstract no.* 22278. [Red.]

1409 – L'application du calcul d'erreur dans la détermination des constantes de stabilité des complexes par la méthode du pH (in German). G. Anderegg (Laboratoire de chimie inorganique de l'Ecole Polytechnique Fédérale, Zürich, Suisse). *Helv. Chim. Acta*, 44 (1961) 1691.
L'auteur entreprend une étude approfondie de la titration avec électrode de verre dans le but de calculer les constantes de couples acide–base et de déterminer les causes d'erreur et la précision des valeurs obtenues. Il utilise ensuite les résultats de ce travail dans l'étude des équilibres des complexes métalliques, et montre que l'emploi de la méthode des moindres carrés conduit aux valeurs les plus satisfaisantes. Il applique sa méthode à la détermination des constantes des complexes métalliques d'un certain nombre de métaux divalents (Co, Ni, Cu, Zn), avec le glycinate. [De.Mo.]

1410 – Substitution en milieux hydro-organiques d'une électrode de verre à l'électrode à H_2 d'une pile comprenant une électrode Ag–AgCl (en français). J. P. Morel, P. Seguela and J. C. Pariaud (Laboratoire de chimie physique, Faculté des Sciences de Clermont-Ferrand, Puy-de-Dôme, France). *Compt. rend.*, 253 (1961) 1326–1327.

Les auteurs ont comparé à 25° les tensions électriques des deux piles définies par les schémas suivants: Pt, H_2(HCl (M) solvant X) AgCl Ag.
Electrode de verre (HCl (M) solvant X) AgCl Ag. Les solvants utilisés sont l'eau, des mélanges eau–éthanol (95%), eau–méthanol (90%), eau–acétone (33%). Pour les électrodes de verre employées, les auteurs montrent qu'il est possible d'utiliser la relation thermodynamique de Nernst: ces électrodes se comportant comme l'électrode à hydrogène. [Bad.Lam.]

1411 – Electrodes for pH measurements. Roger G. Bates (National Bureau of Standards, Washington, D.C., U.S.A.). *J. Electroanal. Chem.*, 2 (1961) 93–109.
In this paper the author defines the operational pH value, according to almost universal acceptance, as follows:

$$\mathrm{pH} = \mathrm{pH}(S) + \frac{E - E_s}{(RT(\ln_{10}))/F}$$

E and E_s are, respectively, the electromotive force of a pH cell of the usual design, containing first the unknown solution, and secondly, a standard solution of known pH, namely pH(S). The pH cell consists of a reference electrode, a liquid junction and an electrode including that at the liquid junction, which is assumed to remain unchanged while measurements of E and E_s are being made during the time interval between these measurements.
Four indicator electrodes are described: the glass electrode, the hydrogen electrode, the quinhydrone electrode and the antimony electrode. The advantages, limitations and accuracy of each one are discussed. [Fra.Cla.]

1412 – The glass electrode as indicator electrode for potentiometric titrations in non-aqueous solutions (in German). H. Frind and A. Busch (Cassella Farbwerke Mainkur A.-G., Frankfurt am Main, Germany). *Chemiker-Ztg.*, 84 (1960) 568–569.
A review, with 19 references, of the titration in non aqueous media of a great number of inorganic compounds. [Gio.Ser.]

1413 – Comparison electrode working up to 1300° (in French). M. Rey and G. Danner (Société electrochimique, St. Ouen, France). *Silicates inds.*, 25 (1960) 19–22.
Known comparison electrodes work up to 300° (Ag/Ag salts); for AgAg SO_4 (diluted in potassium and lithium sulfates) a working temperature of 535° can be reached, while electrodes made from alumina with fused Ag may reach a temperature as high as 960°, and even higher temperatures are reached by means of a fused Ag drop in fused alkali sulfates; reproducibility is of the order of 25 mV and the mean life about 100 h (at higher temperature both fall off very rapidly). By this means polarization curves for NaCl, vanadium and lead-glasses are measured in the range 800–1200°. [Ca.Cas.]

1414 – Etude de l'adsorption de l'hydrogéne sur le nickel de Raney par une méthode potentiométrique. H. Kagan (Laboratoire d'electrolyse du C.N.R.S., Bellevue, Seine et Oise, France). *Compt. rend.*, 253 (1961) 1050–1052.
La concentration de l'hydrogène produit par coulométrie à une cathode de platine plongeant dans une solution alcaline (NaOH) peut être suivie par potentiométrie à une électrode de platine platiné. La présence de nickel Raney dans cette solution retarde l'apparition de l'hydrogène en solution et le saut potentiométrique (caractérisant l'apparition d'hydrogène) est obtenu pour une quantité d'électricité (génératrice de H_2) beaucoup plus importante qu'en l'absence de nickel Raney. Les auteurs utilisent cette méthode pour étudier les catalyseurs pulvérulents. [J.Bad.Lam.]

1415 – Oxidimetric determination of *n*-butyl-lithium in hydrocarbons using vanadium pentoxide. Peter F. Collins, Conrad W. Kamienski, Donald L. Esmay and R. B. Ellestad (Research Laboratories, Lithium Corporation of America, Inc., Bessemer City, N.C., U.S.A.). *Anal. Chem.*, 33 (1961) 468–470.
A potentiometric titration of *n*-butyl-lithium in hydrocarbon solvents is described. Vanadium pentoxide is added to a solution of *n*-butyl-lithium in *n*-heptane in an atmosphere of argon; a rapid reaction takes place and the reduced vanadium is titrated with standard sulfato-ceric acid. End-point is determined potentiometrically using a bright platinum indicator electrode and a normal calomel or silver–silver chloride comparison electrode. The presence of large amounts of alkoxide does not alter the reasonable accuracy of the method. [Su.Mo.Ce.]

1416 – Application of potentiometry to the determination of potassium/guaiacolsulphonate (in Polish). J. Płotkowiak and Z. Płotkowiakowa (Department of Pharmaceutical Chemistry, Academy of Medicine, Poznań, Poland). *Acta Polon. Pharm.*, 18 (1961) 319–323.

Determination of guaiacolsulphonates was based on titration of the phenolic groups. The preparation consists of a mixture of monopotassium 4-, and 5-guaiacolsulphonate (A) and di-potassium 4-guaiacolsulphonate (B). Titration in *n*-propanol: *n*-pentane: water (30 : 5 : 5) solution using platinum electrode–salt bridge–saturated calomel electrode system with 0.2 *N* NaOH indicates the amount of (A). When the sample prior to titration was titrated with 0.01 *N* H_2SO_4 the amount of (B) was obtained and subsequent titration with 0.2 *N* NaOH gave the total content of A + B. [Ad.Hu.]

1417 – Studies on the behaviour of uni-bivalent salts in aqueous solution. II. Sodium oxalate and determination of standard electrode tension of $Ag/Ag_2C_2O_4,C_2O_4^{2-}$. S. C. Sircar and B. Prasad (Ravenshaw College, Cuttack, India). *J. Indian Chem. Soc.*, 38 (1961) 361.
The study of the cells of the type:

(a) $Ag/Ag_2C_2O_4,Na_2C_2O_4//Satd.\ KCl//Na_2C_2O_4,Ag_2C_2O_4/Ag$

indicates that sodium oxalate is completely dissociated in the concentration range of 0.0083–0.0395 moles/litre. The study of the cells:

(b) $Ag/Na_2C_2O_4,Ag_2C_2O_4//Satd.\ KCl//Hg_2Cl_2,NaCl//Hg$

(c) $Ag/Na_2C_2O_4,Ag_2C_2O_4/Hg_2Cl_2,NaCl/Hg$

shows that the standard electric tension of the $Ag/Ag_2C_2O_4,Na_2C_2O_4$ electrode is —0.4591 V. Other cells of similar type were studied in order to know the extent of dissociation of sodium oxalate, and to find the standard electric tension, E_0 for the half cell $Ag/Ag_2C_2O_4,C_2O_4^{2-}$. [R.S.Sa.]

1418 – Sodium ion activity determination in disperse systems (in Russian). N. A. Komarova and P. A. Kriukov (Dogushaiev Soil Institute of the U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.). *Kolloid. Zhur.*, 21 (1959) 189–194.
Wet soils, or their extracts, gave the same values for Na^+ activity in nearly all the cases tested (sometimes slightly higher values were found when dealing with extracts); reliability tests were carried out on 65 alumino- or boro-silicate glass electrodes by measuring the electrode response in Na^+ solutions (0.0001–1.0 *N*); most electrodes gave a response which was a function of Na^+ concentration and was independent of the type of the anion involved [Ca.Cas.]

1419 – Stability relationships among the rare earth dipicolinates. Ingmar Grenthe (Department of Chemistry, Pennsylvania State University, University Park, Pa., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 360–364.
The stepwise formation constants for the complexes formed between the dipicolinate ion and copper, yttrium, and the rare earth metals have been evaluated at 20° by potentiometric measurements utilizing a copper–rare earth–dipicolinate competition system in aqueous perchlorate media of ionic strength 0.5 *M*. [R.Mur.]

1420 – Coordination compounds of labile metals with ethylenimine. Tatiana B. Jackson and John O. Edwards (Metcalf Chemical Laboratories of Brown University, Providence, R. I., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 355–360.
The complexes of ethylenimine (aziridine) with divalent copper, nickel, cobalt, manganese, and mercury have been prepared, isolated, and the aqueous successive formation constants for complexes formed with copper, zinc, silver, and mercury ions evaluated by means of pH measurements and Bjerrum calculations. It has been noted that the ethylenimine nitrogen acts as a typical amine nitrogen in the formation of metal–nitrogen bonds, but with an apparently lower bond strength. This bonding is quite similar to that in ammonia and amino complexes; colors, vapor pressures and other properties are parallel. It is believed that the maximum co-ordination number is the same as that for ammonia complexes of these ions; the steric effect of the ring may prevent the attainment of this maximum number. The ethylenimine ring is quite stable when the complex is in the solid state. The temperature dependency of ethylenimine ionization is expressed by the equation: $pK_a = 2438\ (1/T) — 0.244$, from which the value of $\Delta H°$ of 11.6 kcal./mole^{-1} is obtained. [R.Mur.]

1421 – Chelating tendencies of some α-mercaptoacetamides with bivalent-metal ions. Dean F. Martin (W. A. Noyes Laboratories, University of Illinois, Urbana, Ill., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 1076–1078.
The acid association constants of six α-mercaptoacetamides of the type ArNHCOCH(SH)R have been measured by potentiometric titrations in water–dioxane mixtures at 30°. The acid association constants are linear functions of mole fraction of dioxane; the data are correlated with the struc-

tural characteristics of the α-mercaptoacetamides. Successive formation constants for complexes formed in seventy-five volume % dioxane at 30° with the bivalent ions uranyl, beryllium, zinc, nickel, and manganese have been determined for the six ligands. Very stable chelates are formed with the first three of this group, the complex with nickel has a lesser stability. Precipitation occurred in the cases of copper and cobalt. [R. Mur.]

1422 – Stabilities of bivalent metal complexes of β-ketoimines. Dean F. Martin, Gaile A. Janusonis and Barbara B. Martin (W. A. Noyes Laboratories, University of Illinois, Urbana, Ill., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 73–75.
The acid dissociation constants of eight β-ketoimines of the type $RCOCH_2C(=NAr)R'$ have been determined by potentiometric titrations in dioxane–water mixtures. The relationship between pK_D and mole fraction of dioxane is approximately linear with some deviation toward lower pK_D being noted at low mole fractions of dioxane. The formation constants of these β-ketoimines have been determined with a number of metal ions; copper, beryllium, uranyl, nickel, cobalt, zinc, and manganese. A discussion and comparison of the acid dissociation and formation constants is given. [R.Mur.]

1423 – Stability of complexes of several 8-substituted quinoline derivatives formed with bivalent metals (in English). M. Yasuda (Chemical Institute, Nagoya University, Nagoya, Japan). *Z. physik. Chem. (Frankfurt)*, 29 (1961) 377–379.
At 25° the stability constants of complexes of 8-aminoquinoline, 8-aminoquinaldine, 8-methoxyquinoline, 8-methoxyquinaldine, quinoline-8-carboxylic acid and quinaldine-8-carboxylic acid with Cu, Ni, Zn, Cd and Pb in aqueous solutions at constant ionic strength (0.1 M $NaClO_4$) have been evaluated with the help of acid dissociation constants of the amino compounds determined from pH-measurements with a glass electrode. Complexes with ligands having 2-methyl substituents have less stability. Compared with the other investigated metals, Pb forms complexes of relatively high stability with ligands containing carboxyl groups, while the stability with ligands having amino groups is relatively low. [H.W.Nür.]

1424 – Some lower n-alkanoate complexes of bivalent metals in aqueous solutions. Copper mono-aceto and zinc mono-aceto complexes (in English). A. K. Rai and R. C. Mehrotra (Chemistry Laboratory, University of Glorakhpur, India). *Z. physik. Chem. (Frankfurt)*, 29 (1961) 237–247.
Mixtures of $CuCl_2$ and $ZnCl_2$ with acetic acid were prepared according to Job's method of continued variation, and the pH was measured using a glass electrode. The results show that monoacetate complexes $(CuAc)^+$ and $(ZnAc)^+$ are formed, and their dissociation constants have been determined at several ionic strengths. Extrapolation to zero ionic strength gives the thermodynamic dissociation constants of these monoacetate complexes (for $(CuAc)^+$, $K = 2.512 \cdot 10^{-2}$ and for $(ZnAc)^+$, $K = 4.467 \cdot 10^{-2}$). [H.W.Nür.]

1425 – Complexes of Cu^{2+} with ethylidene-tetrathioacetic acid (in Italian). G. Saini, G. Ostacoli, E. Campi and N. Cibrario (Institute of Analytical Chemistry, University of Turin, Italy). *Gazz. chim. ital.*, 91 (1961) 904–913.
In aqueous solutions of Cu^{2+} and ethylidene-tetrathioacetic acid (H_4A) several complexes are formed with a metal to ligand ratio 1 : 1 and 2 : 1. The logarithms of the stability constants, determined potentiometrically at 20° with ionic strength 0.1, gave these results: $\log K_{CuH_3A} = 2.64$; $\log K_{CuH_2A} = 3.24$; $\log K_{CuHA} = 4.08$; $\log K_{CuA} = 5.00$; $\log K_{Cu_2A} = 2.33$. The pK's of H_4A were determined: $pK_1 = 3.24$; $pK_2 = 3.56$; $pK_3 = 3.99$; $pK_4 = 4.93$. The structure of the complex forms is also discussed. [Fr.Pan.]

1426 – A study of Ca–K ion exchange equilibrium with the help of membrane electrodes. S. K. Bose (City College, Calcutta, India). *J. Indian Chem. Soc.*, 37 (1960) 465.
The suitability of membrane electrodes having different mobility ratios for the same pair of cations for the determination of individual ion activities in a mixture has been demonstrated. The following reaction system has been selected for which the forward as well as the reverse reactions have been investigated: $Ca(clay)_2 + 2KCl \rightleftharpoons 2K\text{-clay} + CaCl_2$. From the electric tension between KCl and a mixture of KCl and $CaCl_2$ solutions of known ionic activities using membrane electrodes, the mobility ratio is calculated from the relationship:

$$E_{obs} = \frac{RT}{2F} \log \frac{a_k{}^{1}}{a_k{}^{II} + 2a_{Ca}{}^{II} \cdot U_{Ca}/U_K}$$

where a stands for the activity of the ion and U_{Ca}/U_K is the mobility ratio. [R.S.Sa.]

1427 – NH_4^+, Mg^{2+} and Ba^{2+} activities in colloidal clays in relation to the concentration of the dispersed phase. Amalesh Chatterji (University College of Science, Calcutta, India). *J. Indian Chem. Soc.*, 37 (1960) 457.

The variation of the activity of NH_4^+, Mg^{2+} and Ba^{2+} ions in clays with the concentration of the latter has been calculated using clay membrane electrodes with the help of the following cell:

$$Hg/Hg_2Cl_2/NH_4(Mg \text{ or } Ba)\text{chloride/membrane}/NH_4(Mg \text{ or } Ba)\text{clay}/Hg_2Cl_2/Hg$$

Using the Nernst equation: $E = RT/nF \log \frac{a_{\text{solution}}}{a_{\text{clay}}}$, curves have been plotted showing the variation of ionic activities with concentration of clay suspension in g/100 g. The percentage dissociation of respective ions has been calculated from the observed activity a and the total concentration c of the ion present in the base saturated clay. [R.S.Sa.]

1428 – Electrochemical investigations on bentonite suspensions. III. Potentiometric and conductometric titration of electrodialyzed suspensions of askangel with alkaline hydroxides (in Russian). I. A. Usskow and J. T. Usskova (Shevteshenko University, Kiev, U.S.S.R.). *Kolloid. Zhur.*, 21 (1959) 231–237.
Potentiometric and conductometric titrations of askangel suspensions, performed immediately after addition of Na, K, Rb and Cs hydroxides were characterized by a single inflection point at pH 8–8.5, while with LiOH, another break-point appeared at pH 10.4 which disappeared after 24 h. The first inflection point shows a time-dependence, it being shifted toward greater quantities of base consumed. From the angle of the first part of the titration curve the variation of electrical conductivity of suspensions of the gel, as a function of added alkali, can be calculated; in the case of Li, Rb and Cs this angle decreases with time and an increasing dissociation in the order $Cs < Rb < K < Na$ is deduced. That cations enter into crystal lattices and are adsorbed can be deduced from the above measurements. [Ca.Cas.]

1429 – Electrometric study on arsenites of copper as a function of the pH (in English). R. S. Saxena and G. P. Saxena (Chemistry Laboratory, Government College, Kota, India). *Z. physik. Chem. (Frankfurt)*, 28 (1961) 220–228.
By potentiometric titration of $NaAsO_2$ with $CuSO_4$ the formation of three copper arsenites was observed ($CuO.As_2O_3$; $2CuO.As_2O_3$; $3CuO.As_2O_3$) at the three specific pH values; 9.85, 11.25 and 12.28. In these precipitated, heavy metal arsenites, the proportion of CuO increases with the decrease in hydrogen ion concentration. [H.W.Nür.]

1430 – Determination of added borates in mixed fertilisers. H. N. Wilson and G. V. M. Pelligrini (Imperial Chemical Industries Ltd., Billingham Division, P.O. Box No. 6, Billingham, Co. Durham., Great Britain). *Analyst*, 86 (1961) 517–519.
This method was based on the conversion of boric acid to mannito-boric acid and titration of this with sodium hydroxide using an "identical-pH" end-point method. 2.5 g of sample were dissolved in 50 ml 4% HNO_3 and PO_4^{3-} was precipitated from the warm solution with $Bi(NO_3)_3$. The heterogeneous mixture was made up to a volume of 250 ml and then filtered through a dry paper. To 100 ml NaOH solution was added to the bromo-thymol blue end-point, the solution was filtered and to the filtrate and washings 5% HNO_3 was added to pH 5, and the solution was warmed and stirred vigorously to remove CO_2. After cooling, the solution was adjusted to exactly pH 6.3 using a pH-meter, using first 10% NaOH then 0.02 *N* NaOH. 10 g mannitol was added and the solution was titrated with 0.02 *N* NaOH to pH 6.3. This process was repeated until the addition of 10 g mannitol no longer decreased the pH from 6.3. A blank was obtained using a similar sample of fertiliser containing no BO_3^{3-}. If A and B (ml) were the NaOH titres of the sample and blank then B content (%) = $0.0216\ (A\text{-}B)$ [P.O.Ka.]

1431 – Studies on the citrate complex of aluminium(III). R. K. Pattnaik and S. Pani (University College of Engineering, Orissa, India). *J. Indian Chem. Soc.*, 38 (1961) 379.
Aluminium(III) reacts with citric acid at low pH, forming a neutral complex and liberating three protons simultaneously. At high pH (above pH 3.1), the complex C behaves like a dibasic acid and dissociates to form complex C_1^- and C_2^{2-} in two steps. The equilibrium constants of the reactions:

$$Al^{3+} + H_3Cit \rightleftharpoons C + 3H^+;\ C \rightleftharpoons C_1^- + H^+ \text{ and } C_1^- \rightleftharpoons C_2^- + H^+$$

are $1.948 \cdot 10^{-5}$, $3.225 \cdot 10^{-4}$ and $1.616 \cdot 10^{-7}$, respectively. The citrate ligand occupies the three coordination positions and the other three coordination positions are occupied by three water molecules. [R.S.Sa.]

1432 – The chemistry of the solvated metal chelates. IV. 8-quinolinol chelates of scandium

(III), thorium(IV), and uranium(VI). James H. Van Tassel, Wesley W. Wendlandt and Edward Sturm (Department of Chemistry, Texas Technological College, Lubbock, Texas, U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 810–812.
The authors report X-ray powder and non-aqueous titration data obtained during studies of the normal and "solvated" 8-quinolinol (HQ) chelates of scandium(III), thorium(IV) and uranium(VI). X-ray powder data for the complexes $UO_2(Q)_2.HQ$, $UO_2(Q)_2$, $Sc(Q)_3.HQ$ and $Th(Q)_4$ showed that the "solvated" chelates are of triclinic symmetry, while the normal chelates are of monoclinic symmetry. Unit cell dimensions were calculated on the assumption of one molecule per unit cell. The $Th(Q)_4.HQ$ sample was apparently amorphous and attempts to prepare the normal chelate $Sc(Q)_3$ were not successful. Non-aqueous titrations of $UO_2(Q)_2.HQ$ in acetonitrile with potassium methoxide titrant produced a clear inflection; comparison with direct titrations of HQ indicated the solvated chelate to be a stronger acid. $UO_2(Q)_2$ displayed no acid character. No clearly defined inflection points were obtained on titration of $Sc(Q)_3.HQ$ and $Th(Q)_4.HQ$. Attempts to prepare mixed chelates of HQ and substituted derivatives of HQ were unsuccessful. [R.Mur.]

1433 – Electrode properties of a scandium membrane electrode (in Russian). A. P. Samodělov. *Izvest. Sibir. Otdel. Akad. Nauk S.S.S.R.*, (1961) 43–47.
A strongly acid, non-expanding polystryene cationite KU-2 (containing as active group HSO_3^-) in the form of a 200 mesh powder was saturated with scandium, mixed with polystyrene powder, dissolved in toluol and formed into membranes. The cationite content varied from 50–80%. The membrane was fixed with polystyrene glue to the end of a polystyrene tube which was filled with 0.1 *M* $ScCl_3$ solution. A silver-chloride electrode was inserted thus forming a "membrane electrode". In the concentration range 0.05 *M*–1.0 *M* dependence of the membrane electrode tension on —log $a_{\pm ScCl_3}$ is near to linear and corresponds well to Nernst's equation. The membrane electrode is reversible. [Ot.So.]

1434 – Potentiometric titration of nitrogen-containing organo-silicon compounds in non aqueous media (in Russian). A. P. Kreshkov, V. A. Drozdov and E. G. Vlasova. *Izvesto Vysshykh Ucheb. Zavedeniĭ, Khim. i Khim. Tekhnol.*, 3 (1960) 80–84.
Nitrogen-containing organo-silicon compounds can be titrated with $HClO_4$ in methyl cyanide, methyl nitride or mixtures of them with benzene or dioxan. The *N* was attached directly to the Si as well as contained in an organic radical. The end-point can be estimated by indicators or potentiometric methods. The potentiometric end-point is sharper in methyl nitrite than in methyl cyanide. The titrant added is proportional to the number of N atoms contained by the compound. The average error is *ca.* 1.5%. [Gio.Ser.]

1435 – Potentiometric titration of individual alkyl-chlorosilanes with organic bases in methyl cyanide (in Russian). A. P. Kreshkov, V. A. Drozdov and E. G. Vlasova. *Izvesto Vysshykh Ucheb. Zavedeniĭ, Khim. i Khim. Tekhnol.*, 3 (1960) 85–87.
$(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, CH_3SiCl_3 and $SiCl_4$ have been titrated by visual and potentiometric methods. Crystal violet, dimethyl-aminoazobenzene, bromocresol purple, methyl orange, bromophenol blue, and gallo sea blue (C. I. Mordant Blue 14) have been used as indicators. A new cell has been used for the potentiometric titration in solvents of low dielectric constant. 0.05 *N* phenazone or nitron have been used for the titration in methyl cyanide and amido-pyridine in benzene. The error was ±0.3%. [Gio.Ser.]

1436 – Potentiometric determination of the solubility product of lead carbonate (in English). Reino Näsänen, Paavo Meriläinen and Kaarina Leppänen (Department of Chemistry, University of Helsinki, Finland). *Acta Chem. Scand.*, 15 (1961) 913–918.
A simple potentiometric pH method has been employed in the determination of the solubility product of lead carbonate. The method gave consistent values for the solubility product on both precipitation and dissolution of lead carbonate. The effect of added potassium nitrate on the solubility equilibrium was also investigated. The results are discussed on the assumption that the complex ion $PbNO_3^+$ is formed. Values of the first acid dissociation constant of carbonic acid in potassium nitrate solutions were determined. Extrapolation to zero ionic strength gave the value $10^{3.55}$ (25°; I = O) for the equilibrium constant of the reaction: $Pb\ CO_3(s) + 2\ H^+ \rightleftarrows Pb^{2+} + CO_2(aq) + H_2O$. The solubility product of lead carbonate was calculated to be $10^{-13.13}$ (25°; $I = 0$). [G.Ekl.]

1437 – Potentiometric determination of the solubility of lead phosphate (in Polish). E. Szyszko (Department of Food Research, State Department of Hygiene, Warsaw, Poland). *Roczniki Państwowego Zakladu Hig.*, 12 (1961) 339–345.
The solubility of lead phosphate was determined by means of a potentiometric method with lead electrodes. The determination was performed by titration of 0.03 *M* lead acetate with 0.2 *M*

Na_2HPO_4 at pH = 6.3, and using the same solutions in the presence of 0.075% acetic acid, neutralized to pH 6.0, and with the addition of 0.001% of tyloze. The latter conditions correspond to those existing in amperometric titrations of phosphate. The resulting solubility is equal to $8.12 \cdot 10^{-3}$ g/l and therefore the error of amperometric titration due to solubility of lead phosphate is negligible. [Ad.Hu.]

1438 – The hydrolytic behavior of thorium(IV)-pyrocatechol-3,5-disulfonate. Yukito Murakami and Arthur E. Martell (Department of Chemistry, Clark University, Worcester, Mass., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 5605–5607.
The results of potentiometric titrations performed on aqueous 0.1 *M* potassium nitrate solutions containing mole ratios of Tiron (disodium pyrocatechol-3,5-disulfonate) and thorium(IV) of 4 : 1, 3 : 1, 2 : 1 and 1 : 1 are described. The titration data indicate that for mole ratios of 1.5 : 1, or greater, the same compound is formed initially in the titration (pH lower than 5), regardless of the quantity of excess ligand. The spectrophotometric method of continuous variations was utilized to verify the existence of a 1.5 : 1 compound. Extensive hydrolysis of the metal chelate, but no precipitation, occurred at higher pH for all mole ratios studied. [R.Mur.]

1439 – Potentiometric precipitation reactions and complex-forming reactions using a platinum indicating electrode (in Russian). V. M. Tarayan (State University, Yerevan, U.S.S.R.). *Izvest. Akad. Nauk Armyan. S.S.R. Khim. Nauki*, 13 (1960) 333–342.
Thorium has been determined using a platinum indicating electrode and adding a drop of freshly prepared 1 *N* $FeCl_2$ solution, forming thus an indicating system Pt/Fe^{3+}, Fe^{2+}. The comparison electrode was a saturated calomel electrode. Titrations were carried out at room temperature in an atmosphere of CO_2 in 60–70 ml volume. Titrants used were sodium fluoride, oxalate and pyrophosphate. Titrating with sodium fluoride, the pH is kept at 2.1 – 3.5. Two steps are observed, corresponding to ThF_4 and ThF_6^{2-} formation. The second is suitable for end-point indication. Oxalate is used as a 0.02–0.2 *N* solution at pH 2.0–2.5. A medium of 50% ethanol is suitable. Pyrophosphate was used as an 0.2–0.25 *N* solution at pH 2.0–4.0. [Ot.So.]

1440 – Electrometric studies on the precipitation of arsenites of lead as a function of the pH (in English). Ram Sahai Saxena and Gyan Prakash Saxena (Chemical Laboratories, Government College, Kota, India). *J. Electroanal. Chem.*, 2 (1961) 242–248.
In this paper a detailed and systematic study is published of the formation of arsenites of lead by the interaction of $Pb(NO_3)_2$ and $NaAsO_2$ at a definite H^+ ion concentration of the medium, by applying electrometric methods which have provided more conclusive evidence on the composition of complexes. Three definite arsenite compounds are formed having the molecular formulae $PbO.As_2O_3$, $2PbO.As_2O_3$ and $3PbO.As_2O_3$ at pH 9.85, 11.25 and 12.28, respectively. The proportion of PbO increases with the concentration of alkali used in the preparation of sodium arsenite and the formation of lead arsenites is thus a function of H^+ ion concentration. The potentiometric curves are regular in shape, and the results are accurate and reproducible. [Fra.Cla.]

1441 – An electromotive force investigation of the product of the solution of antimony in liquid antimony tri-iodide. John D. Corbett and Frank C. Albers (Institute for Atomic Research and Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa, U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 533–535.
The nature of the product of the oxidation-reduction process occurring upon the dissolution of antimony metal in liquid antimony tri-iodide has been investigated by measurements of the electric tension in suitable concentration cells. A half-cell containing liquid antimony tri-iodide "saturated" with antimony metal was used as comparison; the working half-cell contained varying quantities of dissolved antimony metal. Analysis of the mole fraction of dissolved antimony *vs.* electric tension data indicates that the product of the number of electrons involved in the reduction of antimony tri-iodide and the number of antimony atoms in the final neutral product of the reaction has a value of two. Of the two products consistent with this observation, Sb_2I_4 and SbI, the former catenated product is considered more likely because of the diamagnetism of the solution. The value obtained for the mole fraction of antimony metal in the "saturated" solution ($2.48 \cdot 10^{-2}$) compares favorably with results from earlier direct solubility measurements. [R.Mur.]

1442 – Studies on the hydrolysis of metal ions. The hydrolysis of the ion $Bi_6(OH)_{12}^{6+}$ in perchlorate medium. Åke Olin (Department of Inorganic Chemistry, The Royal Institute of Technology, Stockholm 70, Sweden). *Acta Chem. Scand.*, 13 (1959) 1791–1808.
The hydrolysis of the ion $Bi_6(OH)_{12}^{6+}$ has been studied at 25° in 0.5 *M* sodium perchlorate medium by means of the cells: Bi–Hg|S| comparison; glass|S| comparison, where S had the general composition B *M* Bi(III), H *M* H^+, (0.1–3B–H) *M* Na^+, 0.1 *M* ClO_4^-. The measurements were carried out as potentiometric titrations keeping the total bismuth concentration constant in each

run and varying the actual hydrogen ion concentration by adding acid or base. The low solubility of the hydrolysis products necessitated the low concentration of the neutral salt. To keep the activity factors constant, the total metal ion concentration had to be reduced accordingly. B was varied between 4–0.5 m*M*. The data may be explained by the equilibria:

$$1.5\ Bi_6(OH)_{12}^{6+} + 2H_2O \rightleftarrows Bi_9(OH)_{20}^{7+} + 2H^+;\ \log K = -3.5 \pm 0.1;$$

$$Bi_9(OH)_{20}^{7+} + H_2O \rightleftarrows Bi_9(OH)_{21}^{6+} + H^+;\ \log K_1 = -3.2 \pm 0.2:$$

$$Bi_9(OH)_{21}^{6+} + H_2O \rightleftarrows Bi_9(OH)_{22}^{5+} + H^+;\ \log K_2 = -2.6 \pm 0.2.$$

[G.Ekl.]

1443 – Studies on the hydrolysis of metal ions. 34. The hydrolysis of the indium(III) ion, In^{3+}, in 3 *M* (Na^+) Cl^- medium (in English). George Biedermann, Norman C. Li and Judy Yu (Department of Inorganic Chemistry, The Royal Institute of Technology, Stockholm 70, Sweden, and Department of Chemistry, Duquesne University, Pittsburg 19, Pa., U.S.A.). *Acta Chem. Scand.*, 15 (1961) 555–564.

The hydrolysis equilibria of In(III) have been studied at 25° in the ionic medium 3 *M* (Na^+)Cl^- by measuring the hydrogen ion concentration with a glass electrode. The [In(III)] ranged from $1 \cdot 10^{-3}$ *M* to $4 \cdot 10^{-2}$ *M* and the hydrogen ion concentration was varied from values high enough for the hydrolysis to be negligible to those low enough for a precipitate to be formed. The data could be explained by assuming the equilibria:

$$In^{3+} + H_2O \rightleftarrows In(OH)^{2+} + H^+;\ \log K_{a1} = -6.9 \pm 0.1:$$

$$2\ In^{3+} + 2\ H_2O \rightleftarrows In_2(OH)_2^{4+} + 2\ H^+;\ \log \beta_{22} = -10.15 \pm 0.1.$$

[G.Ekl.]

1444 – Studies on the hydrolysis of metal ions. 36. An estimate of the formation constants of $CaOH^+$, $SrOH^+$ and $BaOH^+$ in 3 *M* $NaClO_4$ (in English). Birgitta Carell and Åke Olin (Department of Inorganic Chemistry, the Royal Institute of Technology, Stockholm 70, Sweden). *Acta Chem. Scand.*, 15 (1961) 727–734.

The formation constants of $CaOH^+$, $SrOH^+$ and $BaOH^+$ have been estimated from measurements at 25°, of the electric tension of the cells: Pt/H_2, B *M* B^{2+}, (3-2 B) *M* Na^+, A *M* OH^-; (3-A) *M* ClO_4^-/ comparison; Ag, AgCl(AgBr)/B *M* B^{2+}, (3-2B) *M* Na^+; X *M* Cl^-(Br^-), (3-x) *M* ClO_4^-/comparison; where B^{2+} stands for Ca^{2+}, Sr^{2+} or Ba^{2+} and the comparison half cell was (3 *M* $NaClO_4$/2.99 *M* Na^+, 0.01 *M* Ag^+, 3 *M* ClO_4^-) Ag, AgCl.

From the measured values of *E*, [OH^-] was calculated using the relationship $E = E° + 59.15 \log [OH^-] - 9.3\ B - 8\ [OH^-]$. The following formation constants were obtained:

$$Ca^{2+} + OH^- \rightleftarrows CaOH^+;\ \log K_1 = 0.642 \pm 0.015:$$
$$Sr^{2+} + OH^- \rightleftarrows SrOH^+;\ \log K_1 = 0.225 \pm 0.015:$$
$$Ba^{2+} + OH^- \rightleftarrows BaOH^+;\ \log K_1 = 0.004 \pm 0.015.$$

[G.Ekl.]

1445 – Specific interaction between Np(V) and U(VI) in aqueous perchloric acid media J. C. Sullivan, J. C. Hindman and A. J. Zielen (Chemistry Division, Argonne National Laboratories, Argonne, Ill., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 3373–3378.

A specific interaction between the oxygenated cations Np(V) and U(VI) has been shown to exist in an acidic aqueous medium by means of spectrophotometric, potentiometric and proton relaxation measurements. Spectral evidence for the complex is the appearance of a new absorption band at 9925 Å (in addition to the original band at 9800 Å) upon the addition of U(VI) to perchloric acid solutions of Np(V). Electrochemical evidence is presented by a shift in the electric tension of a cell containing the Np(V)–Np(VI) couple upon the addition of a U(VI) solution. An association constant of 0.66 is calculated from the spectral data and a very similar value of 0.691 is calculated from the potentiometric data. Limited data on proton spin relaxation times is in qualitative agreement with the proposal of a complex between these two species. An improved value of 1.13638 ± 0.00016 V has been determined for the formal electric tension of the Np(V)–Np(VI) couple in 1 *M* perchloric acid at 25°. [R.Mur.]

1446 – Salicylate and 5-sulfosalicylate complexes of chromium(II). Robert L. Pecsok and William P. Schaefer (Department of Chemistry, University of California, Los Angeles, Calif., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 62–65.

The composition of the complexes of chromium(II) with salicylate and 5-sulfosalicylate have been investigated by means of pH titrations in aqueous 3 *M* sodium perchlorate. The data indicate the complex to be composed of two ligands per metal ion. Calculations of successive association constants for the two complexes yield values of $pK_1 = 8.41$ and $pK_2 = 6.95$ for the salicylate complex and $pK_1 = 7.14$ and $pK_2 = 5.74$ for the 5-sulfosalicylate complex. Polarographic studies of the salicylate complex have shown the presence of an anodic wave, the half-wave electric tension of which is pH-dependent and salicylic acid concentration-independent. The diffusion current constant of this complex in 3 *M* sodium perchlorate at pH 12 is —1.05, and $E_{\frac{1}{2}}$ is —1.33 V (*vs.* S.C.E.). Analysis of the current–electric tension wave indicates a close approximation to reversibility although the corresponding cathodic wave for the chromium(III) complex was not observed. Preliminary polarographic studies on a chromium(II) ethylenediaminetetra-acetate complex show that this species is an even more powerful reducing agent, having $E_{\frac{1}{2}} = —1.48$ V at pH 12. [R.Mur.]

1447 – Electrometric study on acid–molybdate system and the formation of polyanions (in English). R. S. Saxena and G. P. Saxena (Chemistry Laboratory, Government College, Kota, India). *Z. physik. Chem. (Frankfurt)*, 29 (1961) 181–187.
By potentiometric pH titrations and conductometric titrations of Na_2MO_4 with HCl, the successive formation of three kinds of polymolybdate ions at certain pH ranges was confirmed: $(Mo_6O_{21})^{6-}$ at pH = 4.9–5.5; $(Mo_6O_{21}H_2)^{4-}$ at pH = 4.1–4.8, and $(Mo_6O_{21}H_3)^{3-}$ at pH = 2.8–4.0. No formation of octa-molybdate could be observed. [H.W.Nür.]

1448 – Electrode for simplified field determination of chloride in ground water. W. Back (U.S. Geological Survey, Washington, D.C., U.S.A.). *J. Am. Water Works Assoc.*, 52 (1960) 923–926.
A silver–silver chloride electrode is used in connection with an S.C.E. and a conventional pH meter. After standardisation 20 samples per h can be measured. The limitations of the method and its errors are discussed in terms of its theory. [Gio.Ser.]

1449 – Electrometric methods for the determination of Te(IV) (in Russian). V. K. Khakimova and P. K. Agasyan (M. V. Lomonosov State University, Moscow, and Institute of Chemistry, Academy of Sciences, Uzbekhian S.S.R.). *Uzbek. Khim. Zhur.*, [6] (1960) 21–28.
The rate of reaction of the oxidation of Te(IV) by bichromate has been investigated, and it was found that for quantitative results 30 min are required at an acidity of $\geqslant 2$ *N* HCl or H_2SO_4, and a ratio of Te : $Cr_2O_7^{2-} \leqslant 1:1.2$ (mequiv.). A potentiometric method has been developed in which Te(IV) is oxidised by excess potassium bichromate, with back-titration by Mohr's salt, for Te amounts of 0.20 mg and higher in 30 ml solution, with a mean absolute error of 0.02 mg. A saturated calomel electrode and a platinum foil indicating electrode are used. This same method has been applied also to the coulometric determination of 0.08 mg and more with an error of 0.01 mg. The potentiometric method may be used also in the presence of thousand-fold excess of Se, whereas the coulometric method is not suitable in the presence of Se. [Ot.So.]

1450 – New methods for the determination of free acid in the presence of large amounts of uranyl salt (in English). Sten Ahrland (Eurochemic, Mol-Donk, Belgium; and Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Sweden). *Acta Chem. Scand.*, 14 (1960) 2035–2045.
Two new methods have been developed for the determination of free acid in solutions containing large amounts of uranyl salt. Both methods are based upon the weakening of the acidic properties of the uranyl ion which is brought about by its bonding to sulphate ions. By utilizing this complex formation it is possible to arrive at a titration curve of two distinct steps. According to the first method the free acid is determined by potentiometric titration to the easily determined point of inflexion between these steps. For low concentrations of acid, however, when a titration is not practicable the free acid is determined by direct measurement of pH, according to the second method described. [G.Ekl.]

1451 – Influence of diverse ions on the determination of manganese. A study of the Lingane–Karplus method. William G. Scribner and Richard A. Anduze (Research and Engineering Division, Monsanto Chemical Co., Dayton 7, Ohio, U.S.A.). *Anal. Chem.*, 33 (1961) 770–773.
The application of the Lingane–Karplus method (oxidation of Mn(II) to Mn(III) by permanganate in neutral pyrophosphate medium, end-point detected potentiometrically), is extended to a variety of manganiferous materials. The influence of every available element in the periodic classification has been considered by the authors. Experimental results and a summary of prior knowledge are presented by periodic groups. The method has proved to be extremely versatile. The few interfering substances can be removed by prior chemical separation. [Su.Mo.Ce.]

1452 – Potentiometric determination of chloride in milk. B. L. Herrington and D. H. Kleyn (Cornell University, Ithaca, N.Y., U.S.A.). *J. Dairy Sci.*, 43 (1960) 1050–1057.

The sample (10 ml) is acidified with 20 ml HNO_3 (6 ml conc. HNO_3/litre) to eliminate the interference of proteins. The Cl^- is then titrated with $AgNO_3$ (4.882 g /litre) with an Ag electrode until an electric tension of +250 mV *vs.* S.C.E. is reached. An S.C.E. with a filter tip of asbestos is necessary to avoid the diffusion of Cl^-. [Gio.Ser.]

1453 – Direct potentiometric determination of chlorides in concentrated (electrolytic) baths. J. Pradilla-Sorzano (University Ind. de Santander, Bucaramanga, D.C., U.S.A.). *Rev. univ. ind. Santander,* 2 (1960) 45–48.
The electric tension of a cell made with two Ag–AgCl electrodes, one immersed in a standard solution of Cl^- in 1–2 *M* H_2SO_4 and the other in a mixture of equal volumes of the test solution and of standard AgCl solution, is measured. A relationship is derived correlating the measured electric tension with the Cl^- concentration of the test solution. [Gio.Ser.]

1454 – The aluminium electrode as an indicator of chloride concentration. S. R. Jones (Knolls Atomic Power Laboratory, Schenectady, N.Y., U.S.A.). *Nuclear Sci. Abstr.,* 15 (1961) 2867, *Abstract no.* 22247.

1455 – The oxidation states of astatine in aqueous solution. Evan H. Appelman (Department of Chemistry and Lawrence Radiation Laboratory, University of California, Berkeley, Calif., U.S.A.). *J. Am. Chem. Soc.,* 83 (1961) 805–807.
The 1—, 0, ?+ and 5+ oxidation states of astatine have been identified in aqueous solution by study of various co-precipitation reactions. No evidence was found for the 7+ state. The reduction–oxidation equilibria of this element were studied by observations of the reactions of the several oxidation states with other reversible redox couples, and from this the following electric tensions (*vs.* N.H.E.) were deduced: $At^- \overset{-0.3\text{ V}}{\rightleftarrows} At(O) \overset{-1.0\text{ V}}{\rightleftarrows} At(?+) \overset{-1.5\text{ V}}{\rightleftarrows} AtO_3^- \overset{<-1.6\text{ V}}{\rightleftarrows} At(7+)(?)$
The photochemical oxidation of At(O) by VO_2^+ and by Fe^{3+} was observed. The experimental data indicate that the predominant At(O) species is neither At_2 nor At; a reaction of At(O) with organic impurities is postulated. [R.Mur.]

1456 – Comportement d'électrodes inattaquables d'oxydoréduction en présence d'oxygène. E. Lewartowicz (Laboratoire d'électrolyse du C.N.R.S., Bellevue, Seine et Oise, France). *Compt. rend.,* 253 (1961) 1260–1262.
Le système ferreux–ferrique se comporte à une électrode d'oxyde de platine comme un système relativement lent. La tension électrique à courant nul est relativement mal définie et dépend de nombreux facteurs (agitation de la solution, teneur de la solution en impuretés oxydantes ou réductrices, épaisseur de la couche d'oxyde). L'auteur a mis cette propriété à profit pour étudier l'influence de l'oxygène dissous sur la valeur de cette tension électrique. La tension électrique d'équilibre de ce même système ferreux–ferrique étant par contre stable et bien défini à une électrode d'or (en particulier insensible à l'oxygène), il est possible de doser l'oxygène en mesurant la tension électrique existant entre une électrode de platine pré-anodisée et une électrode d'or, plongeant dans une solution ferreuse–ferrique dans laquelle barbotte le mélange gazeux à analyser. L'oxyde de platine est régénéré périodiquement par oxydation anodique. Limite de sensibilité: quelques dizaines de parties par million d'oxygène dans le mélange gazeux. [Bad.Lam.]

1457 – Studies on the citrate complex of cobalt(II). R. K. Pattnaik and S. Pani (University College of Engineering, Orissa, India). *J. Indian Chem. Soc.,* 38 (1961) 364.
The citrate complex of cobalt(II) has been studied by pH titration methods in the pH range 2.5–6.8. The results are confirmed qualitatively by measurement of specific conductance. Cobalt reacts with citric acid at lower pH, forming a complex C, liberating two protons simultaneously. The equilibrium constant of the reaction: $Co^{2+} + H_3Cit \rightleftharpoons C + 2H^+$ is $8.40 \cdot 10^{-5}$. The neutral complex then dissociates at a higher pH range in two steps to complexes C_1^- and C_2^{2-}. The equilibrium constants of the reaction $C \rightleftharpoons C_1^- + H^+$ and $C_1^- \rightleftharpoons C_2^{2-} + H^+$ are $6.835 \cdot 10^{-5}$ and $1.05 \cdot 10^{-8}$ respectively. The formation constant of the complex C according to $Co^{2+} + HCit^{2-} \rightleftharpoons C$ is found to be $1.438 \cdot 10^3$. The equilibrium constant of the reaction $Co^{2+} + Cit^{3-} \rightleftharpoons C_2^{2-} + H^+$ is found to be $3.38 \cdot 10^{-6}$. The hydrolysis constant of the hydrolysis of Co^{2+} according to $Co^{2+} + H_2O \rightleftharpoons CoOH^+ + H^+$ is calculated to be $4.285 \cdot 10^{-5}$. [R.S.Sa.]

1458 – Acid hydrolysis of $[PtCl_4]^{2-}$ and $[PtCl_3(H_2O)]^-$. Charles I. Sanders and Don S. Martin, Jr. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Ia., U.S.A.). *J. Am. Chem. Soc.,* 83 (1961) 807–810.
The authors have utilized aqueous potentiometric titrations with a base to evaluate the equilibrium constant at 25° for the acid hydrolysis reaction of $[PtCl_4]^{2-}$ to yield $[PtCl_3(H_2O)]^-$, and for

the hydrolysis of the latter species to yield $[PtCl_2(H_2O)_2]$. Values of $K_1 = 3.0 \cdot 10^{-2}$ ($\mu = 0$) and $K_1' = 1.5 \cdot 10^{-2}$($\mu = 0.318$, $NaNO_3$ added) were obtained for the former hydrolysis reaction, and $K_2 = 1.0 \cdot 10^{-3}$ ($\mu = 0$) and $K_2' = 5.4 \cdot 10^{-4}$($\mu = 0.318$) for the latter reaction. Computations performed by least squares on a titration curve obtained at $\mu = 0.318$ produced a tentative value of $pK_{11}' = 7.0(\pm 0.1)$ for the acid dissociation constant of $[PtCl_3(H_2O)]^-$ and tentative values of $pK_{21}' = 5.2(\pm 0.8)$ and $pK_{22}' = 8.3(\pm 0.8)$ for the first and second acid dissociation constants, respectively, of $[PtCl_2(H_2O)_2]$. [R.Mur.]

1459 – Deposition electric tension of Tc 99 from alkaline solution and its application to a standard pure source on metallic foil (in Japanese). N. Matunnura and H. Yumoto (Tokyo University, Tokyo, Japan). *Nuclear Sci. Abstr.*, 15 (1961) 2879 *Abstract no.* 22344.

1460 – The application of plutonium in investigations of electric tension on free surfaces (in German). B. Kamieński, J. Mikulski, J. Pawełek and L. Stroński (Institute of Nuclear Physics, Kraków, and Institute of Physical Chemistry, Polish Academy of Sciences, Kraków, Poland). *Nukleonika*, 6 (1961) 99–106.
See *Bull. Acad. Polon. Sci., Ser. Sci. Chim.*, 8 (1960) 685. [Ad.Hu.]

1461 – Microtitrations of organic bases in non-aqueous solutions. M. Gutterson and T.S. Ma (Department of Chemistry, Brooklyn College, Brooklyn 10 (N.Y.), U.S.A.). *Mikrochim. Acta*, (1960) 1–11.
The authors compare titrations of perchloric acid with weak bases or their halide salts (in which case mercuric acetate has to be added) in different solvents: acetic acid, acetic anhydride, formic acid and propionic acid. The end-point was determined visually or potentiometrically. The amounts taken were about 40 μ/equiv. The limit of determination was in acetic acid, $pK_b < 12$; in acetic anhydride, $pK_b < 13.5$. The use of formic acid, although having a higher levelling effect, is not recommended because of instability, while propionic acid has the disadvantage that it is difficult to obtain water free samples. [H.L.Ki.]

1462 – Titrimetric determination of hexahydro-1,3,5-trinitro-s-triazine (RDX) and octahydro-1,3,5,7-tetranitro-s-tetrazine (HMX) with ferrous sulfate (in English). Jaromír Šimeček (Military Academy A. Zápotocký, Brno, Czechoslovakia). *Anal. Chem.*, 33 (1961) 260–262.
The determination of RDX and HMX is based on the liberation of nitric groups by sulfuric acid hydrolysis; ferrous sulfate is used for their estimation by colorimetry, or as a titration reagent for a potentiometric technique using Pt/stainless steel electrodes. The reactions which lead to the liberation of nitric acid are studied; the amount of nitric acid set free is dependent on the concentration of sulfuric acid. Optimum conditions for this acid hydrolysis are established. [Su.Mo.Ce.]

1463 – Oxydimetric carbonyl determination *via* hydroxylamine (in German). B. Budešínský and J. Körbl (Forschungsinstitut für Pharmazie, Prag, Tschechoslowakei). *Mikrochim. Acta*, (1959) 922–931.
10 ml of 0.1 *M* $NH_2OH.HCl$ and 0.4–0.5 mequiv. of the carbonyl compound are mixed. After the solution has become clear 0.5–5 ml 10 *M* KOH are added, the amount being dependent on the reactivity of the oxo-compound. The reaction is usually complete after 30 min. Thereafter, further 10 *M* KOH is added until its total amount corresponds to 100 mequiv. The excess of $NH_2OH.HCl$ is titrated potentiometrically with 0.1 *M* $K_3Fe(CN)_6$ after dilution with 10 ml H_2O. A blank solution is also titrated. [H.L.Ki.]

1464 – Produits d'autoprotolyse de l'éthanol, du *n*-propanol et de l'*iso*-propanol. A. Teze and R. Schaal (Laboratoire de chimie, IV, P.C.B., 11 rue Pierre Curie, Paris Ve, France). *Compt. rend.*, 253 (1961) 114–116.
Les auteurs utilisent la chaine d'électrodes suivante: $Pt,H_2 \mid ROLi, LiCl$ dans le solvant $\mid AgCl|Ag$ pour déterminer le produit d'autoprotolyse. $K_s = \mid ROH_2^+ \mid \cdot \mid RO^- \mid$ de trois solvants: éthanol, propanol, et *iso*propanol. Pour évaluer la valeur de ces constantes à force ionique nulle, les auteurs utilisent la méthode d'extrapolation de Harned. Les valeurs numériques de K_s sont fournies en molalité ou en molarité. Pour l'éthanol à 20°, $pK_s = 19.15$ (mole^2 l^{-2}) et 18.95 (mole^2 kg^{-2}), et à 25°, $pK_s = 18.88$ (mole^2 l^{-2}), et 18.67 (mole^2 kg^{-2}). Pour le propanol à 20° $pK_s = 19.52$ (mole^2 l^{-2}) et 19.33 (mole^2 kg^{-2}), et à 25° $pK_s = 19.43$ (mole^2 l^{-2}) et 19.24 (mole^2 kg^{-2}). Pour l'isopropanol à 20° $pK_s = 21.05$ (mole^2 l^{-2}) et 20.84 (mole^2 kg^{-2}), et à 25° $pK_s = 20.80$ (mole^2 l^{-2}) et 20.58 (mole^2 kg^{-2}). [J.Bad.Lam.]

1465 – Etude des variations d'acidité de quelques β-dicétones aliphatiques en fonction de la température. Mme L. Laloi and P. Rumpf (Centre d'études et de recherches de chimie or-

ganique appliquée, C.N.R.S., Bellevue S & O, France). *Bull. soc. chim. France*, (1961) 1645–1653.
Les auteurs présentent ici le résultat de leurs recherches sur la détermination des pK de l'acétyl-acétone et de certains composés substitués. Ils comparent la méthode potentiométrique (électrode de verre) et la méthode spectrophotométrique. En particulier, pour la méthode potentiométrique, on insiste sur les conditions nécessaires pour obtenir une bonne précision. Il faut que: (a) les activités des ions soient voisines dans la solution étalon et dans la solution inconnue; (b) les nombres de transport soient très voisins dans les deux solutions (ce qui implique que quand il y a beaucoup d'ions H^+ ou HO^- la comparaison se fasse avec des solutions étalons de pH très voisins); (c) les températures des deux solutions soient égales. Même si ces conditions sont remplies, le pH ne peut être déterminé à mieux de 5/100 d'unité.
Pour les deux méthodes les pK_c (apparents) et pK_a (absolus) sont déterminés à plusieurs températures (de 10–45°) pour l'acétyl-acétone (pK_a (25°) $= 9.03$), la méthyl-2 hexanedione 3–5 (pK_a,(25°) $= 9.43$), la diméthyl-2,2 hexanedione 3–5 (pK_a, (25°) $= 10.01$), la méthyl-3 pentanedione 2–4 (pK_a 25° $= 10.87$) et l'éthyl-3 pentanedione 2–4 (pK_a, (25°) $= 11.34$). Les résultats obtenus par les différentes méthodes se recoupent dans la limite de précision indiquée plus haut. De ces déterminations de pK, les auteurs déduisent les chaleurs d'ionisation et les entropies d'ionisation.
[J.Des.]

1466 – Use of anhydrous propionic acid as solvent for titration of some alkaloids (in Polish). S. Przyszlakowski (Department of Inorganic Chemistry, Academy of Medicine, Lublin, Poland). *Acta Polon. Pharm.*, 17 (1960) 395–398.
Anhydrous propionic acid was used as a medium for potentiometric titration of some alkaloids. Its application is superior to acetic acid. To show that in the case of titration in propionic acid a greater end-point break can be obtained than in acetic acid a number of alkaloids were titrated with 0.1 N and 0.01 N $HClO_4$ using the glass and calomel electrodes, namely: codeine, narcotine, narceine, heroine, quinine, veratrine and brucine. [Ad.Hu.]

1467 – Acetamide as non-aqueous ionizing solvent. II. Electric tension measurements and potentiometric titrations in molten acetamide. G. Jander and G. Winkler (Institute of Inorganic Chemistry, Berlin, Germany). *J. Inorg. Nuclear Chem.*, 9 (1959) 32–38.
By means of a Mo electrode (which acts as a hydrogen-electrode) potentiometric titrations can be performed, and for the ionic product of pure acetamide, a value of $3.2 \cdot 10^{-11}$ is found at 94°, while direct measurements of electric tension give $1.3 \cdot 10^{-11}$. The auto-dissociation mechanism $2\ CH_3CONH_2 \rightleftarrows CH_3CONH_3^+ + CH_3CONH^-$ is thus corroborated. [Ca.Cas.]

1468 – A new volumetric method for the estimation of thiocarbamide. P. C. Gupta (Banaras Hindu University, India). *J. Indian Chem. Soc.*, 37 (1960) 213.
It is reported that thiocarbamide can be estimated using iodine in the presence of a bicarbonate buffer and the end-point of the reaction was observed: (a) visually by disappearance of the iodine colour itself or the blue colour with starch solution: (b) potentiometrically, when there is a sharp fall of the electric tension at the equivalence point, and (c) by employing excess of oxidant and back titrating the excess iodine with standard arsenious oxide solution potentiometrically. The results are accurate to 0.5%. [R.S.Sa.]

1469 – Determination of instability constants of complex compounds from oxidation–reduction electric tensions (in Russian). M. V. Shulman and T. V. Kramareva (Institute of Inorganic Chemistry, Siberian Department of the Academy of Sciences, U.S.S.R.). *Izvest. Sibir. Otdel. Akad. Nauk S.S.R.*, [1] (1960) 55–65.
The redox systems thiourea–diamino, imino, methyl disulphide were titrated with 1 M cadmium nitrate. Titrated solutions also contained $KBrO_3$, 0.2 M $HClO_4$, and were kept at $\mu = 2$. The electric tension of this solution was measured every half hour until it became stable, then the solution was titrated by a 1 M solution of the complex-forming agent. A smooth platinum and a saturated calomel electrode were used. The results agree with those of previous authors. [Ot.So.]

1470 – Methods of investigating crude phthalic anhydride (in Polish). Z. Bellen (Struszyński Analytical Department, Institute of General Chemistry, Warsaw, Poland). *Chem. Anal. (Warsaw)*, 6 (1961) 531–540.
Methods for determining impurities in crude phthalic anhydride, produced from naphthalene, are described. Free dicarboxylic acid was determined by titration with *n*-ethylpiperidine in acetone solution using molybdenum and calomel electrodes. Good results were obtained also when the acetone solution of phthalic anhydride was titrated with an aqueous solution of sodium phthalate using the same electrodes. Another method consists of alkalimetric titration of acids after benzene extraction of the sample. Maleic acid and its anhydride can be titrated manganometrically after

removal of naphthoquinones by benzene extraction. Naphthoquinones and naphthalene can be determined colorimetrically by suitable colour reactions. Naphthoquinones can also be determined gravimetrically after steam distillation from alkaline solution. [Ad.Hu.]

1471 – Ionization constants of some hindered aromatic acids. Melvin S. Newman and Herbert Boden (McPherson Chemistry Laboratory, Ohio State University, Columbus, Ohio, U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 115–116.
The acid dissociation constants of a number of substituted aromatic acids in 50% dioxane–water at 40° have been determined by potentiometric titrations. Steric factors affecting resonance stabilization of the acid and base forms and solvation of the base form are discussed in connection with the data obtained. [R.Mur.]

1472 – Non-aqueous titration of phenolic esters (in English). Bengt Smith and Åke Haglund (Department of Organic Chemistry, Chalmers Institute of Technology, Göteborg, Sweden). *Acta Chem. Scand.*, 14 (1960) 1349–1352.
Potentiometric titration of phenolic esters using tetra-*n*-butylammonium hydroxide in acetone has been found suitable for differentiating between various types of phenolic esters. Esters of aliphatic carboxylic acids can usually be titrated provided that strongly electron-repelling groups are absent in the phenolic ring. Unsubstituted esters of aromatic carboxylic acids do not react, but replacement of hydrogen atoms in the aromatic nucleus by electron-attracting groups can also render the aromatic esters titratable. [G.Ekl.]

1473 – Non-aqueous titrations of polynuclear phenolic compounds. R. P. Mitra and S. K. Chatterji (University of Delhi, India). *J. Sci. Ind. Research*, 20 B (1961) 310.
Potentiometric and conductometric titrations of dinuclear, trinuclear and tetranuclear *o,o'*-dihydroxy-diphenyl methane type of compounds have been carried out in pyridine and acetone using sodium methoxide as the titrant. The potentiometric titration curve of each compound shows inflections, whose number coincides with the number of OH groups in it; their conductometric titration curves show as many breaks. A step-wise neutralisation of all the OH groups in each compound is indicated. The first hydroxyl to be attacked by the base has a much stronger acid character than any other in the same compound, and the conductance changes observed have been explained in terms of ion association and intramolecular hydrogen bond formation between the neighbouring hydroxyl in each compound. [R.S.Sa.]

1474 – Non-aqueous titration of some nitro-compounds containing the dinitrophenyl group (in English). Bengt Smith and Åke Haglund (Department of Organic Chemistry, Chalmers Institute of Technology, Göteborg, Sweden). *Acta Chem. Scand.*, 15 (1961) 675–677.
Various types of nitro compounds obtained in the characterization of such organic compounds as alcohols, phenols, mercaptans and amines can be titrated quantitatively in acetone or pyridine using tetra-*n*-butylammonium hydroxide in benzene–methanol as titrant. Glass and calomel electrodes were used and the titration was followed by means of a potentiometer. [G.Ekl.]

1475 – Nitrobenzene as solvent in potentiometric and high frequency titrations of organic bases with Lewis acids (in Italian). C. Bertoglio-Riolo, T. Fulle Soldi and C. Occhipinti (Institute of General Chemistry, University of Pavia, Italy). *Ann. chim. (Rome)*, 51 (1961) 1178–1186.
The acidic properties of boron, aluminium and antimony tribromide in nitrobenzene appear to be: $BBr_3 > AlBr_3 \gg SbBr_3$. Several organic bases can be titrated with these acids both potentiometrically and by a high frequency method. The molar ratios between the base and the acid at the equivalence point are 1 : 1 with BBr_3, 2 : 1 with $AlBr_3$ and 1 : 2 with $SbBr_3$. By adding an inert solvent in the presence of an excess of the base, precipitates can be obtained with different molar ratios. [Fr.Pan.]

1476 – Quantitative analysis by an automatic potentiometric reaction rate method. Specific enzymatic determination of glucose. H. V. Malmstadt and H. L. Pardue (Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Ill., U.S.A.). *Anal. Chem.*, 33 (1961) 1040–1047.
Oxidation of glucose by glucose oxidase leads to the production of hydrogen peroxide (reaction A) at a rate which is proportional to glucose concentration. The hydrogen peroxide formed reacts immediately with iodide to form iodine, molybdenum(VI) acting as a catalyst (reaction B): changes in iodine concentration are continuously followed by a potentiometric device, using Pt electrodes. Reaction B can be considered instantaneous compared to reaction A which is the rate-determining step. Using a concentration cell, and under standard conditions, $1/t$ is proportional to glucose concentration, t being the time required to produce enough iodine in one half of the cell to

change the chemical tension by a previously fixed amount. A description of the cell and diagrams of the automatic potentiometric instrument, which gives readings of $1/t$ within a minute from the start of reaction, are given. [Su.Mo.Ce.]

1477 – Potentiometric determination of the degree of hydration of 2-ethylanthraquinone (in Russian). I. A. Ivanova and L. M. Shtiphman. *Zavodskaya Lab.*, 27 (1961) 1336–1337.
A known volume of 0.1 N ferric chloride solution, in water–methanol (1 : 30), is placed in the titration vessel, a platinum indicating electrode is introduced, and also an electrolytic connecting bridge leading to a saturated calomel electrode. The analysed sample is placed in a burette, connected to the vessel by a ground joint. The titration is carried out in an atmosphere of nitrogen. Results agree well with results obtained by the permanganate method. [Ot.So.]

1478 – Oxidimetric determination of morphine (in Dutch). J. A. C. van Pinxteren and M. E. Verloop (Farmaceutisch Laboratorium der Rijksuniversiteit, Utrecht, The Netherlands). *Pharm. Weekblad*, 96 (1961) 545–559.
In a boric acid–borax buffer (pH 9.0) morphine is oxidized by potassium ferricyanide to pseudomorphine according to the equation:
$2\,C_{17}H_{19}O_3N + 2\,K_3Fe(CN)_6 + 2\,KOH = C_{34}H_{36}O_6N_2 + 2\,K_4Fe(CN)_6 + H_2O.$
When the quantity of $K_3Fe(CN)_6$ is too large, the oxidation goes beyond the equivalence point. Hence, a redox buffer of equimolar quantities of both ferri-and ferrocyanide was chosen as oxidant and the time was limited to 12 minutes. The presence of pseudo-morphine makes accurate titration of the final quantity of ferrocyanide by $ZnSO_4$ difficult. This can be eliminated by precipitation with silicotungstic acid.
Procedure: 10 ml of a solution containing 2–15 mg morphine hydrochloride are mixed with 5 ml of a boric acid–borax buffer (pH 9.0) and with exactly 10 ml of the redox buffer (0.004 M $K_3Fe(CN)_6$ and 0.004 M $K_4Fe(CN)_6$). After 12 minutes, 10 drops of a $2\frac{1}{2}\%$ solution of silicotungstic acid in 4 N H_2SO_4 are added. Then the ferrocyanide is titrated with a 0.015 M solution of $ZnSO_4$. The end-point is detected potentiometrically, or by the dead stop procedure. For the latter an apparatus is devised with transistor amplification for which the wiring diagram is given.
The morphine content is calculated by reference to a blank. [H.L.Ki.]

See also abstracts nos. 1270, 1272, 1297, 1303, 1308, 1309, 1310, 1483, 1487, 1506.

5. Conductometry

1479 – Molten carbonate electrolytes: physical properties, structure and mechanism of electrical conductance G. J. Janz and M. R. Lorenz (Rensselaer Polytechnic Institute, Troy, N.Y., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 2505, *Abstract no.* 19361.
[Red.]

1480 – Application of electric conductometric measurements to study the radiolysis of water (in German). K. Schmidt (Max Planck-Institute of Biophysics, Frankfurt a.M., Germany). *Z. Naturforsch.*, 16 B (1961) 206–217.
Die Röntgenbestrahlung von hochgereinigtem Wasser, und zwar mit Impulsen und kontinuierlich, wurde durch Leitfähigkeitsmessungen (oszillographische Aufzeichnung) in drei Richtungen verfolgt: 1) Abhängigkeit der Leitwerts–Amplitude (und der Geschwindigkeit des irreversiblen Leitwertanstieges von der Impulsfrequenz; 2) Verlauf des Leitwertes bei Dauerbestrahlung und sein Abklingen nach Aussetzen der Bestrahlung; 3) Abhängigkeit der Effekte 1) und 2) von der Dosisleistung. Die Messungen ergaben eine Proportionalität zwischen Leitwertamplitude (reversibel) und Dosisleistung, desgl. für den irreversiblen Leitwertsanstieg. Im ersteren Fall ergibt sich für die reversible Ionenart eine Lebensdauer von 0.15 s; wahrscheinlich sind es $\dot{O}_2^-$ Radikalionen, entstanden nach $\dot{H} + O_2 \rightarrow H\dot{O}_2 \rightarrow \dot{O}_2^- + H^+$. Der irreversible Anstieg dürfte auf Säurebildung z.B. über $\dot{H} + CO_2 \rightarrow \dot{C}OOH$ zurückzuführen sein. Die Abklingkurven von $\dot{O}_2^-$ werden berechnet und mit Literaturwerten verglichen. [He.Be.]

1481 – Thermodynamics and conductance of simple electrolytes in polar organic solvents. (Rensselaer Polytechnic Inst., Troy, N.Y., U.S.A.). *Nuclear Sci. Abstr.*, 15 (1961) 2489, *Abstract no.* 19229.

1482 – Measurement of Na^+ and Ba^{2+} transference numbers in a melt having the composition $Na_2O.BaO.4SiO_2$ (in Russian). W. I. Malkin and W. W. Pokidshev (Institute of Metal Science and Metal Physics, Central Research Institute of Iron Metallurgy, U.S.S.R.). *Zhur. Neorg. Khim.*, 4 (1959) 2645–2646.
Using radioactive isotopes the mean value 0.87 for Na^+ and 0.11 for Ba^{2+} were found; it also demonstrated that Ba^{2+} plays a less important role than Ca^{2+} in electricity transport under similar conditions. The conclusion that mobility increases with increasing ion radius, found by comparison between Na and K, cannot be generally applied since ionic mobility is lowered by repulsion forces. [Ca.Cas.]

1483 – Citrate complex of copper. R. Das, R. K. Pattanaik and S. Pani (Department of Chemistry, Ravenshaw College, Cuttack, India). *J. Indian Chem. Soc.*, 37 (1960) 59.
Copper(II) reacts with citric acid and forms a neutral complex C at low pH. The results obtained by pH titrations indicate the complex C to be a dibasic acid, dissociating successively in two steps C_1^- and C_2^{2-}. Conductometric titration of a mixture of citric acid and copper nitrate against standard NaOH qualitatively supports the results of pH titrations. The equilibrium constant of the reaction of the formation of C from Cu^{2+} and citric acid with the liberation of two protons, and those of the reactions (i) $C \rightleftharpoons C_1^- + H^+$ and (ii) $C_1^- \rightleftharpoons C_2^{2-} + H^+$, have been calculated. The probable structures of the complex have been discussed. [R.S.Sa.]

1484 – Behaviour of electrolytes in mixed solvents. VII. Conductance of barium chloride and bromide in dioxane water mixture at 35°. P. B. Das and D. Pattannaik (Ravenshaw College, Cuttack, India). *J. Indian Chem. Soc.*, 38 (1961) 411.
The conductance of the solutions of barium chloride and bromide in 10, 20 and 30% dioxane–water mixtures by weight, has been measured at 35°. The effect of the solvent composition on the diameter of the ion pair $BaCl^+$ and $BaBr^+$ has been studied. The dissociation constants K_{BaCl^+} and K_{BaBr^+} have been calculated by the method of Jenkin and Monk. The mean dissociation constants for $BaCl^+$ (K_{BaCl^+}) and its diameter in 10, 20 and 30% dioxane are $10.35 \cdot 10^{-2}$, $5.71 \cdot 10^{-2}$, $2.73 \cdot 10^{-2}$, and 1.12 Å, 1.20 Å and 1.23 Å respectively, whereas the same values for $BaBr^+$ are $23.06 \cdot 10^{-2}$, $10.76 \cdot 10^{-2}$, $8.20 \cdot 10^{-2}$ and 1.428 Å, 1.497 Å and 1.690 Å respectively. [R.S.Sa.]

1485 – Studies in zirconium sols. I. Electrical conductance of zirconium oxide sols. A. M. Trivedi, I. M. Bhatt and M. J. Patani (M. G. Science Institute, Ahemdabad, India). J. *Indian Chem. Soc.*, 38 (1961) 288.
Conductance of zirconium oxide sol has been studied, and it has been concluded that the curve of equivalent conductance against the square root of the concentration passes through the minimum; this behaviour is more marked when the purity of the sol is increased. When diluted sols are allowed to age, the specific conductance increases due to desorption of the adsorbed electrolyte. In the case of concentrated sols, ageing results in the decrease of specific conductance due to the aggregation of the particles. Equivalent conductance of the micelles on dilution first decreases and then increases on further dilution, showing the behaviour of typical colloidal electrolyte. [R.S.Sa.]

1486 – Conductometric determination of thorium. G. Deshmukh, V. D. Anand and P. S. Char (Banaras Hindu University, Varanasi, India). *J. Sci. Ind. Research*, 20 B (1961) 356.
Conductometric titration of thorium with selenious acid in aqueous medium has been proposed as a method for the determination of thorium. Use of alcohol, found necessary in the gravimetric estimation of thorium, leads to the possible formation of another complex. The results obtained in both direct and reverse titrations are fairly accurate. [R.S.Sa.]

1487 – Physico-chemical studies on the composition of bismuth thiosulphate complex. M. S. Bhadravar and J. N. Gaur (Lohia College, Churu, India). *J. Sci. Ind. Research*, 20 B (1961) 504.
The composition of bismuth thiosulphate, obtained by the interaction of bismuth nitrate and sodium thiosulphate, has been determined by means of conductometric and potentiometric techniques and by applying Job's method of continued variation, and has been found to be $Na_3[Bi(S_2O_3)_3]$. The value of the dissociation constant of the complex, calculated using Job's equation, is $4.74 \cdot 10^{-4}$. [R.S.Sa.]

1488 – Methods for the micro-determination of sulphur in organic compounds. Jean P. Dixon (Shell Research Ltd., Thornton Research Centre, P.O. Box I, Chester, Great Britain). *Analyst*, 86 (1961) 597–603.
The method is based on combustion in an oxygen-filled flask, absorption of combustion products in H_2O_2 solution and conductometric titration of SO_4^{2-} with barium acetate solution after addition of 50% v/v *iso*-propanol to give a sharper end-point. Suitable supports are described for

combustion of solids, viscous and non-viscous liquids, volatile liquids and hygroscopic or unstable solids. For metal–organic compounds in which the metal has a soluble sulphate, the solution is ion exchanged using Amberlite IR-120 (H) before titration. If P is present in the compound being analysed, the resultant PO_4^{3-} is removed by precipitation with $AgNO_3$. Before titration the solution is neutralised to methyl red with NH_3 solution. A comparison conductivity cell is used in the reference arm of the Pye conductance bridge used for the titration. Typical analyses showed errors of 1% or less. [P.O.Ka.]

1489 – Physico-chemical research on the system gallium trichloride-nitrobenzene (in Russian). J. A. Fialkov and S. A. Fokina (General and Inorganic Chemistry Institute, Academy of Sciences of the Ukrainian S.S.R., U.S.S.R.). *Zhur. Neorg. Khim.*, 4 (1959) 2611–2616.
Thermal analysis of $GaCl_3$ solutions in nitrobenzene show the formation of 1 : 1 and 1 : 2 molecular complexes (systems containing 50–80% $GaCl_3$ were not investigated, owing to the formation of amorphous insoluble precipitate). Addition of $GaCl_3$ to nitrobenzene enhances conductance, the effect being particularly sharp at the beginning, and when the molar ratio rises above 1 : 1; in the former case, the enhanced conductance is attributed to the 1 : 1 complex while in the more concentrated solutions, the conductance is attributed to particles arising from dissociation of the $GaCl_3$ associated molecules, further strongly solvated by the complex. The present work has confirmed the general fact that conductance of halogenide solutions in non-aqueous media depends on the degree of association.
$GaCl_3$ in nitrobenzene behaves as a weaker electrolyte than $AlCl_3$, particularly at lower concentrations, and darkening of the cathodic electrolyte, which arises during electrolysis of such solutions between Pt electrodes, is explained in terms of formation of colloidal solutions of Ga^{3+} discharge products [Ca.Cas.]

1490 – The microchemical determination of carbonium in isolated parts of structure (in German). H. Malissa, M. Storek and R. Gattringer (Institut für analytische Chemie der Technische Hochschule, Wien, und Fa. Gebr. Böhler & Co AG, Kapfenberg, Österreich). *Arch. Eisenhüttenw.*, 32 (1961) 525–528.
Die gewichtsanalytische, volumetrische und konduktometrische Methode werden verglichen. Nur die beiden letzten Verfahren arbeiten hinreichend genau. [H.W.Nür.]

1491 – Micromethod for rapid determination of carbon in organic substances (in German). W. Stuck (Analytisches Laboratorium, Bayer A.G. Uerdingen, Deutschland). *Mikrochim. Acta*, (1960) 421–428.
The method of Malissa (*Mikrochim. Acta*, (1960) 127) (see following abstract) for the determination of carbon has been further developed. [H.L.Ki.]

1492 – Contribution to micro-elemental analysis (in German). H. Malissa (Max Planck Institut für Eisenforschung, Düsseldorf, Deutschland). *Mikrochim. Acta*, (1960) 127–144.
The gases produced during the combustion are lead through suitable absorption solutions after being freed from interfering components. The water resulting from the combustion is reacted with calcium carbide and the acetylene is then combusted. The change in conductivity of the absorption liquors is a measure of the amount of C, H and S, respectively. [H.L.Ki.]

1493 – Acetamide as a non-aqueous ionizing solvent. I. Conductometric titrations in molten acetamide (in German). G. Jander and G. Winkler (Institute of Inorganic Chemistry, Berlin, Germany). *J. Inorg. & Nuclear Chem.*, 9 (1959) 24–31.
Molten acetamide shows good solvent and dissociating power, the auto-dissociation equilibrium being $2\ CH_3CONH_2 \rightleftarrows CH_3CONH_3^+ + CH_3CONH^-$. Preparation of various compounds of acetamide with metals and with strong acids are described. Their mutual neutralization in molten acetamide can be followed by means of indicators or rough conductometry measurements. This last technique showed the amphoteric behaviour of Ag and Cu acetamide. [Ca.Cas.]

1494 – Conductometric determination of polymethacrylic acid with barium hydroxide (in Polish). Z. Wojtczak (Department of General Chemistry, Copernicus University, Toruń, Poland). *Chem. Anal. (Warsaw)*, 6 (1961) 587–594.
Barium hydroxide has been used for conductometric titration of polymethacrylic acid (PMA). In the range of concentration studied (2.47–483.8 mg/100 ml) reproducible results were obtained with an error less than 1%. Comparative analyses were performed gravimetrically and the difference did not exceed 2.6%. Titration with NaOH instead of $Ba(OH)_2$ gave a titration curve less convenient for end-point determination. When the sample contains methacrylic acid (MA) in addition to PMA their sum can be conveniently determined, but the MA content can only be

approximately estimated. Precise results must be obtained from the bromometric titration of MA. [Ad.Hu.]

1495 – Acetamide as non-aqueous ionizing solvent. III. Conductivity and strength of electrolytes in molten acetamide. G. Jander and G. Winkler (Institute of Inorganic Chemistry, Berlin, Germany) *J. Inorg. & Nuclear Chem.*, 9 (1959) 39–44.
Equivalent conductivities (as functions of the concentration) of the following compounds have been measured in acetamide at 94°: potassium tetra-ethylammonium-iodide; Na salts of picric, benzoic, *o*-hydroxy-benzoic, *o*-nitro-benzoic and 2,4-dinitrobenzoic acids; pyridine hydrobromide; $HClO_4$, HNO_3, HBr, HCl, picric and *p*-toluenesulfonic acid; K and Na salts of acetamide. Dissociation constants are measured for *o*-nitro, 2,4-dinitro, and hydroxy-benzoic acid, for benzoic acid itself and for piperidine. All the data are in agreement with the Debey–Hückel–Onsager equation in the form given by Shedlovsky. The compounds described above exhibit strong, or total, dissocation while the halogenides of Zn, Cd and Hg(II) are weakly dissociated. [Ca.Cas.]

1496 – Acidity of polynitro-benzene derivatives in solutions of ethylenediamine (in Italian). G. Favini and I. R. Bellobono (Institute of Physical Chemistry, University of Milan, Italy). *Ann. Chim. (Rome)*, 51 (1961) 841–856.
Following previous work on this subject (*J.E.C. Abstracts*, 2, (1961) no. 1228), spectra were recorded, and conductometric titrations with sodium amino ethoxide were performed, on polynitro-aryl compounds in anhydrous and aqeous ethylenediamine. The acidic properties, as determined conductometrically, are in a good agreement with the data obtained potentiometrically in the above mentioned paper. [Fr.Pan.]

1497 – Methylglucamine solution as a new standard solution for titrimetric determination of acids by high frequency methods (in Hungarian). L. Balázs and E. Pungor (Institute of Inorganic Analytical Chemistry, Eötvös University, Budapest, Hungary). *Magyar Kém Folyóirat*, 67 (1961) 395–397.
Methylglukamin (1-desoxy-1-methylaminosorbit) Lösung wurde als Masslösung zur Titration von Säuren empfohlen. Methylglukamin ist, ähnlich Ammoniumhydroxyd eine schwache Base, mit Dissoziationskonstante $1.5 \cdot 10^{-5}$ (20°). Sein Hauptvorteil Ammoniumhydroxyd gegenüber besteht darin, dass es in Wasser gut löslich ist, und die davon bereitete Masslösung mit direkter Einwaage herstellbar ist. Laut Messergebnisse sind Salzsäure, Essigsäure, Oxalsäure mit 0.1 *N* Methylglukamin-Masslösung genau bestimmbar. Die Titrationen wurden mit der Hochfrequenzmethode (130 Mc/sec) ausgeführt. [J.Inc.]

1498 – Conductometric analysis of hop bitter substances (in beer). J. R. Hudson and A. H. Cooper (Brewing Industry Research Foundation, Nutfield, Surrey, England). *J. Inst. Brewing*, 66 (1960) 298–301.
After reviewing the available methods a new procedure is described. De-gassed beer is acidified with 6 *N* HCl (15 ml : 100 ml) and treated with pepsin for 20 min. The bitter substances are extracted with light petroleum. The petroleum phase is washed with water and with acidified methanol and dried with anhydrous $MgSO_4$. After evaporating to 5 ml anhydrous methanol is added to 50 ml and the titration performed with methanolic 0.02 *N* nickel acetate. By assuming a molecular weight of 355 for the *iso*-humolones the concentration is given by the formula: (ml of titrant) · 710 · 10/500. [Gio.Ser.]

1499 – Sur la résistivité électrique des suspensions de mycobactéries. F. M. Lévy, Mme D. Zivy and I. Epelboin (Centre International de l'Enfance et Centre National de la Recherche Scientifique, Paris, France). *Compt. rend.*, 253 (1961) 576–578.
Les auteurs caractérisent les suspensions de mycobactéries par les variations de leur résistivité électrique en fonction de la température. On obtient ainsi des informations sur la quantité des germes vivants et sur leur sensibilité à la chaleur. [J.Bad.Lam.]

1500 – Conductometric studies on murexide (in English). N. A. Ramaiah and R. K. Chaturvedi (National Sugar Institute, Kanpur, India). *Z. physik. Chem. (Leipzig)*, 216 (1961) 184–186.
By conductivity measurements of murexide in conductivity water the thermodynamic dissociation constant ($pK = 1.56 \pm 0.03$), the limiting ionic mobility, the diffusion coefficient at infinite dilution ($D_0 = 1.03 \cdot 10^{-5}\,cm^2 \cdot sec^{-1}$) and the radius (3.88 Å) have been determined. [H.W.Nür.]

See also abstracts nos. 1287, 1304, 1305, 1316, 1428, 1457, 1473, 1475.

6. Electrolysis

1501 – Determination of cadmium and bismuth by a diaphragm method of inner electrolysis (in Russian). A. K. Zhdanov and U. Kh. Khodžaeva (V. I. Lenin State University, Tashkent, U.S.S.R.). *Uzbek. Khim. Zhur.*, [5] (1960) 46–51.
The apparatus used is described in an earlier paper (A. K. Zhdanov, *Zhur. Anal. Khim.*, 13 (1958) 661). Anolytes were, in the case of Cd, a 20% KCl solution and for Bi a 5% solution of Mohr's salt. Electrolysis was carried out at 50–80°, agitating by a stream of carbon dioxide or by an electromagnetic stirrer. Cadmium is best determined in a solution containing about 225 mg Cd, 10 g ammonium oxalate and 2.5 g oxalic acid in 250 ml. The relative error is 1%. For the determination of Bi, 250 ml of the solution should contain about 100 mg Bi, 1 g boric acid and 5 ml conc. acetic acid. The relative error is 0.8%. The cathode is a platinum net, the anode is of pure zinc or iron, time of electrolysis about one hour. The advantage of the method is its simplicity, since no external source of current is required. [Ot.So.]

1502 – Separation of Eu radioisotopes on a mercury cathode. I. Electrochemical behaviour of Eu (in Russian). V. P. Shvedov and I-pei-Fu. *Radiokhimiya*, 2 (1960) 57–64.
In order to prove whether free rare-earth ions appear during the dissociation of an amalgam complex by replacing the alkali metal in the amalgam, different factors which take part in the separation of a Eu isotope on mercury cathodes have been analyzed. Eu yield is related to the concentration of complexing agent used. Citric acid can be substituted by succinic or tartaric acid or by Trilon B in the separation. Rise of pH values from 4.23–10.0 increases the Eu yield, which does not vary with concentrations of Eu up to $3 \cdot 10^{-3}$ *M*. [Su.Mo.Ce.]

1503 – Isolation and analysis of carbides from austenitic steel alloyed with niobium and molybdenum. O. Opravil, O. Káčerová, J. Pažitný and I. Svatik (Výzk. Ustav Zváračský, Bratislava, Czechoslovakia). *Hutnické listy*, 15 (1960) 628–631.
Using a 10% solution of HCl in ethanol as electrolyte, the carbides can be separated from steel by electrolysis. The electrolysis is conducted at a current intensity < 0.1 A/sq. cm and at a temperature $< 5°$ for 8 h. The Nb can be determined by precipitation with H_2SO_3 or with tannin. The latter method is suitable for tungsten containing steels. [Gio.Ser.]

See also abstract no. 1276.

7. Coulometry

1504 – Coulometric titrations (in Russian). V. A. Mirkin. *Zavodskaya Lab.*, 27 (1961) 1063–1068.
This paper is a review, based on 89 references to the literature. Automation of coulometric analysis is described as being possible because of the precision and sensitivity of this method. Some papers on fully automated coulometric instruments are mentioned (*e.g.* A. Takahashi, *Japan Analyst*, 8 (1959) 661; 9 (1960) 220, 224). A review of various coulometric titrations of organic and inorganic substances is given. [Ot.So.]

1505 – Coulometric methods in analysis. D. T. Lewis (D.S.I.R., Laboratory of the Government Chemist, Clement's Inn Passage, London W.C. 2, Great Britain). *Analyst*, 86 (1961) 494–506.
This is a review article with 49 references. After summarising the values of relevant physical constants and of methods of measurement of quantities of electricity, the author describes the principle and experimental arrangements for coulometric titrations using constant current, controlled-tension methods and absorption coulometry. The article is concluded by a section on applications of particular interest. These are: (a), residue analysis of pesticides in foodstuffs; (b), titration of mg quantities of Ca, Pb, Zn and Mn with electrogenerated complex ion of the soluble Hg(II) salt of EDTA; (c), an electronic method for titration of 10^{-4} g or less; (d), determination of the number of electrons involved in reduction processes; (e), determination of Sn in tin plate by anodic dissolution; (f), measurement of the thickness of oxide tarnish; (g), a very rapid method based on a combination of coulometry and diffusion, and (h), the possibility of using "fuel cells" as coulometric indicators for gas–liquid chromatography. [P.O.Ka.]

1506 – Differential electrolytic potentiometry. IV. Application to micro coulometric titrimetry. E. Bishop (Washington Singer Laboratories, The University, Exeter, Devon, Great Britain). *Mikrochim. Acta*, (1960) 803–815.
In this article a description is given of two micro-titration cells, one with a content of 500 μl, the other with a content of 50 μl, each having 3 electrodes. The fourth auxiliary electrode has contact with the solution *via* a capillary. The solution is mixed by a stream of fine gas bubbles, taking preventions against evaporation. A procedure is given for the determination of hydrazine. The supporting electrolyte was a solution 1 *N* in HCl and 0.1 *M* in KBr. The lower limit for the generating current is about 10 μA. The differential electrolytic potentiometry is used for establishing the end-point. In the mmolar range it is possible to determine 10^{-6} mole with an accuracy of 0.1% and in the micromolar range 5.10^{-10} mole with an accuracy of 5%. [H. L. Ki.]

1507 – Electrochemical methods of analysis in the atomic energy field G. W. C. Milner (Analytical Chemical Group, A.E.R.E., Harwell, Berks., Great Britain). *Trans. Soc. Instrument Technol.*, 11 (1959) 72–76.
A review on instruments and methods for coulometric titrations and polarographic analysis, the advantages of using square-waves and impulses at a pre-determined point during the life-time of falling Hg-drops being discussed. [Ca.Cas.]

1508 – Coulometric determination of thallium(I) by electrogenerated Cl_2 (in Russian). V. K. Khakimova and P. K. Agasyan (M. V. Lomonosov University, and Institute of Chemistry of the Academy of Sciences of the Uzbekian S.S.R.). *Uzbekh. Khim. Zhur.*, [5] (1960) 31–37.
The sample of thallium is placed in the anodic chamber (a beaker of 50 ml volume) with addition of HCl to make a 4 *N* solution. HCl of the same concentration is placed in the cathodic chamber, its level being higher than in the anodic chamber. Both chambers are connected by a salt bridge. End-point indication is potentiometrical, using a platinum foil and a saturated calomel electrode. Generating electrodes are platinum foils of 0.7×0.7 cm² area. The sensitivity of the method was found to be $2.5 \cdot 10^{-5}$ mequiv/ml. [Ot.So.]

1509 – Coulometric titrations with electro-generated cyanide ion. Fred C. Anson, Karl H. Pool and John M. Wright (California Institute of Technology, Pasadena, Calif., U.S.A.). *J. Electroanal. Chem.*, 2 (1961) 234–241.
A procedure for generating cyanide ion electrolytically is studied. It is possible to generate ions with 100% current efficiency in a solution of potassium dicyano-argentate according to the electrode reaction: $Ag(CN)_2^- + e^- \rightarrow Ag + 2\ CN^-$. The liberated cyanide ion formed can be used to titrate metal cations. Titration of silver, nickel and gold by this procedure are described. [Fra.Cla.]

1510 – Coulometric determination of uranium(IV) by oxidation at controlled potentials. C. M. Boyd and Oscar Menis (Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn., U.S.A.). *Anal. Chem.*, 33 (1961) 1016–1018.
As a result of a study on the non anodic oxidation of uranium(IV) in 3 *M* H_3PO_4 a controlled-electric tension coulometric technique, using a Pt gauze anode, is described for the titration of uranium(IV) in that medium. As the couple U(IV)/U(VI) is non-reversible, the selected practical electric tension (+1.4 V *vs.* S.C.E.) is far more positive than the formal electric tension (+0.305 *vs.* S.C.E.). The coefficient of variation for the titration of 1–10 mg of U(IV) is ±0.3% with pure solutions. The interference of several ions is discussed. The method has been applied to the determination of U(IV) in samples of UO_2 and in ThO_2–UO_2 mixtures. For amounts of uranium of only 1–2 mg the agreement with the chemical method was 5% or better. [Su.Mo.Ce.]

1511 – Voltage scanning coulometry for the determination of traces of iron. F. A. Scott, R. M. Peekema and R. E. Connally (Hanford Laboratories Operation, General Electric Company, Richland, Washington, U.S.A.). *Anal. Chem.*, 33 (1961) 1024–1027.
A new electro-analytical technique, called voltage scanning coulometry, has been developed. The new method has greater inherent specificity and greater sensitivity than conventional coulometry at controlled electric tension, shifting the lower limit of detection to 10^{-3} μequiv. Its application to the determination of traces of iron has been extensively studied: amounts of iron up to 5 μg have been determined with a standard deviation of ± 0.02 μg. The procedure is based on the measurement of the electrolysis current passed while the electric tension between the sample solution and the titrating electrode is changed at a constant rate. Theoretical discussion and practical details about the technique, including a diagram of the titration cell and circuit diagram of voltage scanning coulometer, are given. [Su.Mo.Ce]

See also abstract no. 1449.

8. Electrophoresis

1512 – Electrophoresis. P. F. S. Cartwright and D. W. Wilson. *Ann. Repts. on Progr. Chem., for 1960*, 57 (1961) 432–433.
A review concerning separation of both organic and inorganic ions for 1960, with 19 references. [Red.]

1513 – The electrophoretic migration velocity of complexes and weak electrolytes (in German). K. Wetzel and G. Voigt (Institut für physikalische Stofftrennung, Leipzig, Deutschland). *Z. physik. Chem. (Leipzig)*, 216 (1961) 7–12.
Die Wanderungsgeschwindigkeit der Komponenten A bzw. A' ist eine Funktion der Wanderungsgeschwindigkeit der komplexen Teilchen AB_i bzw. $A'B_i$, der Instabilitätskonstanten K_i bzw. K'_i und der Komplexbildnerkonzentration C_B. Schnelle Einstellung der Komplexgleichgewichte, überschüssige Komplexbildnerkonzentration C_B, so dass C_B räumlich und zeitlich konstant ist, und Vernachlässigbarkeit elektro-osmotischer Effekte werden vorausgesetzt. Auf dieser Grundlage werden mathematische Beziehungen abgeleitet, um die für die Trennung eines Stoffpaares A/A' optimale Komplexbildnerkonzentration C_B zu ermitteln. [H.W.Nür.]

1514 – A simple method for isolation of thin non-metallic surface layers (in German). G. König (Mineralogical Institute, University of Erlangen-Nürnberg, Germany). *Arch. Eisenhüttenw.*, 32 (1961) 729–731.
Die Beläge werden mit einem wasserunlöslichen Kunststoff-film abgedeckt und das Metall von der Rückseite her elektrolytisch abgelöst. Der zurückbleibende nichtmetallische Oberflächenbelag wird danach mit organischen Lösungsmitteln vom Kunststoff befreit und kann nun analysiert werden. [H.W.Nür.]

1515 – Movement of inorganic anions in paper electrophoresis (in English). M. Lederer (Institut du Radium, Laboratoire Curie, Paris, France). *J. Electroanal. Chem.*, 2 (1961) 174–176.
The author points out the different factors which influence paper electrophoresis. An empirical relation between the movement of monovalent inorganic anions and their mobility is described. It is possible to measure the mobility of some monovalent anions by electrophoretic data. [Fra.Cla.]

1516 – Paper electrophoresis of metal ions in bivalent acids and their salts.II (in English). H. C. Chakrabortty (Radium Institute, Paris, France, and Bose Institute, Calcutta, India). *J. Electroanal. Chem.*, 2 (1961) 261–262.
The iso-electric point of Fe(III) is determined in mixtures of N H_2SO_4 and 0.5 M Na_2SO_4. Electromigration of numerous metal ions in oxalic acid and sodium oxalate is also investigated, several analytical separations being possible in these media, which are known to have serious limitations in analytical separations, since so many oxalates are insoluble. [Fra.Cla.]

1517 – Chromatographic and electrophoretic analysis of commercial triphosphates and hexametaphosphates (in Italian). M. Lenzi and E. Mariana (University of Rome, Rome, Italy). *Rass. chim.*, 11 (1959) 11–15.
A number of methods have been reviewed for the analysis of commercial triphosphates and metaphosphates. Chromatographic methods allow the separation of ortho-, pyro-, tri-, trimeta-, tetra- and tetrametaphosphates. By electrophoresis on Whatman No. 3 paper at 1000 V for 1 h in a borax–HBO_3–NaCl buffer, pH 8.5, the following displacements (in cm) were found: trimeta-, 0.55; tetrameta-, 0.39; ortho-, 0.43; tri- and tetra-, 0.33; and pyro-phosphate, 0.26.
For commercial triphosphates the lack of separation between higher polyphosphates is not important. [Gio.Ser.]

1518 – Determination of ε-aminocaproic acid in urine by means of high voltage paper electrophoresis (in English). Albert Sjoerdsma (Visiting scientist, National Heart Institute, Bethesda 14, Maryland, U.S.A.) and Arne Hanson (Medical Clinic and Department of Clinical Chemistry, General Hospital, Malmö, Sweden). *Acta Chem. Scand.*, 13 (1950) 2150–2151.
A quick and simple method was developed for the determination of ε-aminocaproic acid (ε-ACA). The method consists of isolation of ε-ACA by high-voltage paper electrophoresis, development of colour with a ninhydrin and copper spray, elution of the spots from paper and measurement of the color in a spectrophotometer. [G.Ekl.]

1519 – Zone-electrophoresis of aminopeptidases in starch gel (in German). E. Wintersberger

and H. Tuppy (Institute of Biochemistry, University of Vienna, Vienna, Austria). *Monatsh. Chem.*, 91 (1960) 406–411.
On a suitable gel layer (25 × 2, 5 × 1.0 cm) of partly hydrolyzed starch (separate experiments are needed in order to establish the necessary hydrolysis time) the sample of serum from normal subjects, from pregnant women or from patients suffering from hepatic diseases, is submitted to electrophoresis (2–3 V/cm for 12–14 h) in 0.025 *M*, pH 8.7 (for sera) or pH 8.0 (for erythrocytes lysate) borate buffer, or in 0.02 *M* pH 8.0 tris buffer (for leucinaminopeptidase). The gel is then cut in halves horizontally. One half is developed with a saturated Amidoschwarz 10 B in methanol–acetic acid–water (5 : 1 : 5) solution, and the other is incubated (37°, 1 h) with a mixture of 10 ml of substrate (26 mg of L-leucyl-β-naphthylamide in 0.2 ml boiling methanol and diluted to 10 ml with water) and 5 ml of diazonium solution (10 mg of Fast Garnet Salt GBC and 40 mg Nupercaine in 5 ml of 0.2 *M*, pH 7.0 triethanolamine). The portions are then water-washed (owing to conspicuous shrinking, marks are cut in the gel prior to this treatment): the peptidase bands appearing are compared to the protein bands. Different kinds of aminopeptidases are revealed by this means in the different cases investigated. [Ca.Cas.]

1520 – Separation of plasma glucoproteins by paper electrophoresis. I. Technique and results in normal plasmas (in French). F. Infante, S. Juillard, D. Schwartz and M. Sanz (Hôpital Cantonal, Genève, Suisse). *Clin. Chim. Acta*, 5 (1960) 672–679.
A new method is proposed for staining electrophoresis paper. The HIO_4–Schiff reaction is obtained with the dimethyl derivative of fuchsin and the reduction is effected with K-metabisulphite. Results obtained in normal plasma are reported. [Gio.Ser.]

1521 – Detection of prolamine in rice proteins by paper electrophoresis (in German). M. Padmoyo and O. Högl (Université de Berne, Institut de chimie alimentaire, Suisse). *Trav. chim. aliment. et hyg.*, 52 (1961) 29.
Les auteurs ont fait une étude approfondie des protéines du riz. Ils ont effectué l'analyse de l'azote dans les fractions solubles dans l'eau et dans l'alcool pour quatre riz différents. Ils ont établi des techniques d'extraction et effectué de nombreux électroférogrammes, sur lesquels ils ont déterminés les vitesses de migration et divers autres facteurs. Les diagrammes d'extinction ont aussi été établis. Des courbes sont données.
Grâce à ce travail, les auteurs ont pu identifier de façon certaine la prolamine dans les protéines du riz et ceci sur quatre riz de provenance différente. La fraction de protéine qui renferme la prolamine est soluble dans l'alcool. [De.Mo.]

1522 – Technical problems concerning the electrophoresis of haemoglobin on a starch block (in German). H. R. Marti (Polyclinique médicale Universitaire, Bâle, Suisse). *Experientia*, 17 (1961) 235.
L'auteur effectue l'électrophorèse sur amidon et donne tous les détails techniques de cette opération. Le bloc est refroidi à + 4° par un système ingénieux. Lorsqu'on utilise l'oxyhémoglobine, on commet une erreur qui est due, essentiellement, à l'instabilité des solutions d'hémoglobine. Une courbe de stabilité en fonction du temps est donnée. L'auteur s'est efforcé d'éliminer ce phénomène et il y est parvenu, partiellement du moins, en introduisant du KCN dans la solution initiale et dans les fractions d'hémoglobine éluées. [De.Mo.]

1523 – Improved technique for the quantitative estimation of serum haptoglobin. J. Javid and H. Horowitz (Department of Haematology, Montefiore Hospital, New York, U.S.A.). *Am. J. Clin. Pathol.*, 34 (1960) 35–39.
The serum was mixed with a standard solution of haemoglobin and subjected to electrophoresis on paper. Phosphate buffer, 0.05 *M*, pH 7 was used, and the ionophoresis was conducted for 14 h at 135 V. The electropherogram was stained with 3,3′-dimethoxybenzidine. The results obtained by densitometry were compared with those obtained by Nyman's method. The results agree within 2% over a range from 0–500 mg/100 ml. [Gio.Ser.]

1524 – Estimation of thyroxine in human plasma by an electrophoretic technique. R. P. Ekins (Middlesex Hospital Medical School, London, England). *Clin. Chim. Acta*, 5 (1960) 453–459.
A method is proposed for the determination of thyroxine. After addition of ^{131}I-labelled thyroxine the distribution of thyroxine between albumin and thyroxine-binding protein is measured by electrophoresis. [Gio.Ser.]

1525 – Densitometric evaluation of microelectrophoretic serum. Protein patterns on cellulose acetate membranes. B. W. Grunbaum, W. J. Fessel and C. F. Piel (Department of Pediatrics, University of California Medical Center, San Francisco, Calif., (first author); The Langley Porter Neuro-psychiatric Institute, California Department of Mental Hygiene, San Francisco, Calif., (second author); Department of Pediatrics, University of California

Medical Center, San Francisco, Calif., U.S.A., (third author)). *Anal. Chem.*, 33 (1961) 860–861.
A densitometric method is described to determine protein fractions separated by micro-electrophoresis on cellulose acetate membranes, using the technique described by Grunbaum and Kirk (*Anal. Chem.*, 32 (1960) 564). With this quantitative basis, the micro-electrophoretic technique is, in the authors' opinion, the most rapid, discriminating and versatile method available for this type of analysis. Results for 50 normal sera are given. [Su.Mo.Ce.]

1526 – Preliminary notes on the separation of nucleic acids and proteins by counter flow electrophoresis (in English). R. Eliasson, E. Hammarsten, T. Lindahl and H. Palmstierna (Department of Bacteriology, Karolinska Institute, Stockholm, Sweden). *Acta Chem. Scand.*, 15 (1961) 570–574.
A preliminary account is given of an electrophoretic method using the difference in the migration velocities between the nucleic acids and the most rapid acid proteins and *vice versa* from cell extracts. It is based on a counter-flow of buffer against the direction of the electric migration of the nucleic acids and the acid proteins. Technical details and some results, including finding depolymerase activity in the nucleic acid fraction, are reported. [G. Ekl.]

1527 – Detection of sucrose in dessert wines by paper electrophoresis (in German). H. Konrad (Institut für Lebensmittelchemie beim Magistrat v. Gross-Berlin, Deutschland). *Nahrung*, 4 (1960) 528–532.
After paper electrophoresis in 0.2 N borate buffer, pH 7.7 for 4 h at 10–12 V/cm and spraying with a mixture of 2% 1,3-dihydroxynaphthalene in acetone (10 ml) and 3 N phosphoric acid (1 ml), the sucrose appears as a red-brown spot, glucose as a pale blue spot, and fructose as a brown one. The method is particularly suitable for routine control of wine. [Gio.Ser.]

See also abstracts nos. 1306, 1313, 1314.

9. Other methods

1528 – Theory and applications of the chronopotentiometric method with an imposed current growing proportionally with square root of time. I. General introduction and direct discharge processes (in French). H. Hurwitz and L. Gierst (Laboratoire de chimie analytique, Faculté des Sciences, Université Libre de Bruxelles, Belgique). *J. Electroanal. Chem.*, 2 (1961) 128–141.
The circuit of the polarization unit is described and discussed. The equation for the potential–time curves is established for various types of reactions. [Fra.Cla.]

1529 – Theory and applications of chronopotentiometric method with an imposed current growing proportionally with square root of time. II. Direct discharge processes with spherical and cylindrical diffusion (in French). H. Hurwitz (Laboratoire de chimie analytique, Faculté des Sciences, Université Libre de Bruxelles, Belgique). *J. Electroanal. Chem.*, 2 (1961) 142–151.
The mass transfer equations are established for an imposed current of the form $i = \varrho\sqrt{t}$. The final expressions are compared with those obtained for linear diffusion and with the corresponding relations for the constant current method. [Fra.Cla.]

1530 – Distortion of chronopotentiograms from double layer and surface roughness effects. W. H. Reinmuth (Department of Chemistry, Columbia University, New York 27, N.Y., U.S.A.). *Anal. Chem.*, 33 (1961) 485–487.
The theory of the deviations of the experimental chronopotentiometric curves from the predictions of simple theory is discussed, for the cases where two major causes of distortion are involved: electrode surface roughness and double layer capacitance. [Su.Mo.Ce.]

1531 – Chronopotentiometric transition times and their interpretation. W. H. Reinmuth (Department of Chemistry, Columbia University, New York 27, N.Y., U.S.A.). *Anal. Chem.*, 33 (1961) 322–325.
Chronopotentiometric processes in which chemical kinetic or adsorption complications precede the electrode reaction are discussed. Mathematical treatment is given for transition time measurements. Unambiguous distinction between various reaction mechanisms can be made chronopotentiometrically: criteria to be applied and expected results are tabulated. [Su.Mo.Ce.]

1532 – A method for the determination of dielectric constants of single crystals at V.H.F. R. A. Padmanabam (National Physical Laboratory, New Delhi, India). *J. Sci. Ind. Research*, 20 B (1961) 303.
A technique for measuring dielectric constants of single crystals at very high frequencies (50–300 Mc/s) using a micrometer electrode system has been described. A suitable dielectric sample holder has been designed to minimise the errors due to edge effects. The electrical measurements have been carried out with the help of an Admittance Meter of the General Radio Co. (Type 1602-B). The experimental arrangement gives an accuracy of about 5% for values of the dielectric constant, depending upon the size and nature of the dielectric used. [R.S.Sa.]

1533 – Redoxokinetic and impedance titrations: new analytical techniques (in English). K. S. Narayanan and H. C. Gaur (Central Electrochemical Research Institute, Karaikudi, India). *J. Electroanal. Chem.*, 2 (1961) 161–165.
This paper describes the application of a redoxo-kinetic titration method developed by Doss *et al.*, for the system ferrous ammonium sulphate *vs.* ammonium meta-vanadate, and lead nitrate *vs.* potassium ferrocyanide. This method of titration is a slight modification of Franck's method and as a more appropriate name, impedance titration is suggested. [Fra.Cla.]

1534 – Determination of soil water by dielectric measurement of dioxane extract. (in English) H. W. van der Marel. *Soil Sci.*, 87 (1959) 105–119.
After shaking the sample with dioxane, it is filtered and its dielectric constant is measured. A calibration curve is made measuring the dielectric constant of known dioxane–water mixtures. Salinity of the soil has no effect on the results. [Gio.Ser.]

1535 – Tension-time measurements on oxide-covered aluminium surfaces (in German). S. Bloeck, *Metall*, 13 (1959) 196–198.
By means of tension–time measurements, it can easily be established whether a layer of oxide (resp. Böhmite) is present on the surface of Al, the media in which this layer is stable, and/or corrosion resistance. [Ca.Cas.]

1536 – Anodic chronopotentiometry at a liquid bismuth electrode in fused lithium chloride–potassium chloride. John D. Van Norman (Brookhaven National Laboratory, Upton, N.Y., U.S.A.). *Anal. Chem.*, 33 (1961) 946–948.
Chronopotentiometric studies of anodic processes are reported for zinc and lithium, dissolved in a liquid bismuth electrode, and in contact with a lithium chloride–potassium chloride eutectic at 450°. The chronopotentiometric technique has been shown to be useful for the determination of small amounts of zinc and lithium in liquid bismuth. Diffusion coefficients observed are 6.5 and $2.2 \cdot 10^{-5}$ cm^2 per sec for Zn and Li respectively. The accuracy obtained was ± 4%. [Su.Mo.Ce.]

1537 – Trace monitoring in gases using galvanic systems. Paul A. Hersch (Arthur D. Little Research Institute, Inveresk, Midlothian, Scotland). *Anal. Chem.*, 32 (1960) 1030–1034.
The principle and the theory of the galvanic method for the determination of O_2 in a gas stream are discussed. A simple robust laboratory cell for the measurement of parts per million of O_2 is described; the relation between flow rate, coulombic yield and sensitivity is considered, and equations correlating sensitivity and response time with the resistance of the indicating system are given. Present applications of the method and its possibilities are fully discussed. [Su.Mo.Ce.]

1538 – Exchange current densities for Fe(II)–Fe(III) solutions in sulfuric acid and perchloric acid. Fred. C. Anson (California Institute of Technology, Pasadena, Calif., U.S.A.). *Anal. Chem.*, 33 (1961) 939–942.
Heterogeneous rate constants (k_s) are calculated from measurements of exchange current densities (ECD) for the couple Fe(II)–Fe(III), in solutions of sulfuric and perchloric acids. The ECD are evaluated by observing, with a cathode ray oscilloscope, the electric tension–time curve obtained

when a current step is passed through the Pt electrode, in a solution with equal concentrations of Fe(II) and Fe(III). A decrease of k_s values, with the increase of pH in sulfuric acid medium, is observed and it is suggested that this phenomenon is chiefly due to sulfate complex formation with lower ECD. Perchloric acid solutions of Fe(II)–Fe(III) show a non-linear, anomalous dependence of ECD *vs.* concentration. The anomaly may be due to a contribution to the EC from adsorbed Fe(II) and Fe(III) on the electrode. [Su.Mo.Ce.]

1539 – **Effect of surface oxidation on the behaviour of platinum electrodes. The Fe(III)–Fe(II) couple in sulfuric and perchloric acids**. Fred. C. Anson (California Institute of Technology, Pasadena, Calif., U.S.A.). *Anal. Chem.*, 33 (1961) 934–939.

The effects of electrode oxidation on the voltammetric behaviour of the couple Fe(III)–Fe(II) have been studied using a chronopotentiometric technique and Pt electrodes. Chronopotentiograms for the reduction of Fe(III) and oxidation of Fe(II), both in perchloric and sulfuric acids, are given. Results indicate that the presence of a film of oxide has a marked effect on the behaviour of the electrode (the Fe(III)–Fe(II) reaction is rendered less reversible); in fact, when an electrode has been previously oxidized and reduced, a layer of freshly formed, finely divided platinum metal is formed on the surface and the presence of this platinized surface markedly affects the electrode behaviour. [Su.Mo.Ce.]

1540 – **The rotating, mercury-coated platinum electrode. Preparation and behaviour of continuously deposited mercury coatings and application to stripping analysis**. Stanley Bruckenstein and Toyoshi Nagai (School of Chemistry, University of Minnesota, Minneapolis, Minn., U.S.A.). *Anal. Chem.*, 33 (1961) 1201–1209.

Application and limitations of a rotating, mercury coated platinum electrode in the stripping analysis of thallium ($2 \cdot 10^{-7}$–$8 \cdot 10^{-5}$ *M*) and lead ($2 \cdot 10^{-7}$–$1 \cdot 10^{-6}$ *M*) are reported. Thallium and lead, simultaneously deposited with mercury, are stripped by oxidation of the amalgam with Hg(II); during this chemical oxidation a chronopotentiogram is obtained, which serves to determine the concentration of both metals from their mixtures. The oxidation reaction for Pb is complicated by a slow chemical step; the rate of reaction is comparatively fast, considering the velocity of the Hg(II) supply, in the case of thallium.

Technical details of the preparation of the electrode are given *i.e.* continuous plating of a rotating platinum electrode, with a large constant current, in a 0.1 *M* nitric acid solution of Hg(II). [Su.Mo.Ce.]

1541 – **Sur une anomalie polarographique de certains aldéhydes mononitrés. Etude chronopotentiométrique** (en français). E. Laviron et H. Troncin (Laboratoire de chimie générale, Faculté des Sciences, Dijon, France). *Compt. rend.*, 253 (1961) 1339–1346.

Le comportement polarographique anormal de l'*o*-nitrobenzaldéhyde, du nitro-5 furfural et du nitro-5 thiophénaldéhyde-2, a été précisé par polarographie (influence du pH) et par chronopotentiométrie. Pour ces trois composés on observe un dédoublement inégal (55–80%) de la vague à 4 électrons correspondant à la réduction du groupement NO_2. L'hypothèse d'une hydratation partielle du carbonyle selon

$$\underset{\text{(I)}}{\mathrm{NO_2{-}R{-}CHO}} + \mathrm{H_2O} \underset{k_f}{\overset{k_b}{\rightleftharpoons}} \underset{\text{(II)}}{\mathrm{NO_2{-}R{-}CH(OH)_2}}$$

avec

$$\frac{K}{(\mathrm{H_2O})} = \frac{\text{(I)}}{\text{(II)}}$$

rend compte des résultats expérimentaux. L'étude chronopotentiométrique permet de calculer la constante $K/(\mathrm{H_2O})$, soit 2.3, 1, et 2.3, respectivement pour l'*o*-nitrobenzaldéhyde, le nitro-5 furfural et le nitro-5 thiophénaldéhyde-2. Les grandeurs k_f et k_b dépendent du pH; les valeurs numériques sont rassemblées dans un tableau et mettent en évidence la catalyse de l'hydratation en milieu alcalin (ions borates). [Bad.Lam.]

1542 – **Dielectric properties of bromobenzene in carbon tetrachloride and dioxane** (in English). A. R. Tourky, H. A. Rizk and Y. M. Girgis (National Research Centre, Cairo, Egypt). *Z. physik. Chem. (Leipzig)*, 216 (1961) 176–183.

The apparent solution moment of bromobenzene has the same value in CCl_4 as in dioxane. (1.64 ± 0.03 Debye). In both solvents the association factor is 2. The time of relaxation is shorter in CCl_4 and longer in dioxane than in the pure state. The activation enthalpy of dipole orientation has the highest value in the pure state and the lowest in dioxane. [H.W.Nür.]

1543 – Measurements of dipole moments of associated halogenated benzoic acids and benzoic acid in benzene (in German). K. Palm and H. Dunken (Institut für physikalische Chemie, Universität Jena, Deutschland). *Z. physik. Chem. (Leipzig)*, 217 (1961) 248–262.
Von Benzoesäure und D-Halogenbenzoesäuren in Benzol wurden bei T = 15, 25, 35, und 45° im Konzentrationsbereich 0.002–0.2 Mol/Kg mit einer Präzisionsmessbrücke die Dielektrizitätskonstanten bestimmt. Messkondensator (quarzisolieter Plattenkondensator, Luftkapazität 227 pF; Füllvolmen 170 ml), Lösungsbereitungsanlage und Umlaufapparatur bildeten ein abgeschlossenes Umdrucksystem. Die Auswertung nach Clausius–Mosotti sowie Onsager ergibt Konzentrations- und temperaturabhängige Dipolmomente. Unter Voraussetzung eines thermodynamischen Gleichgewichtes zwischen Einfach- und Doppelmolekeln ergaben sich mit Hilfe unabhängig bestimmter Reaktionsisobaren die Dipolmomente der monomeren und dimeren Säuremolekeln. [H.W.Nür.]

1544 – Mechanism of *o*-nitrophenol reduction by chronopotentiometry. A. C. Testa and W. H. Reinmuth (Department of Chemistry, Columbia University, New York 27, N.Y., U.S.A.). *J. Am. Chem. Soc.*, 83 (1961) 784–786.
The authors have elucidated the mechanism of *o*-nitrophenol(ONP) reduction at a mercury electrode, for which conflicting postulates have previously been made, in 50% ethanol–water pH 6.2 buffer, by means of chronopotentiometric measurements. The variation of $i\tau^{1/2}$ with current density, i, indicated a diffusion-controlled six electron reduction at low i; a four electron reduction occurred at high i. The limiting value of $i\tau^{1/2}/C$ for both high and low i was independent of C. These data indicate a mechanism of the form: $\mathrm{ONP} \xrightarrow{4e} x \xrightarrow{k} x \xrightarrow{2e} \mathrm{Z}$. Curve-fitting of experimental data to a theoretical relation for this case leads to a value of $k = 0.2\ \mathrm{sec}^{-1}$. [R.Mur.]

1545 – Electrolyte–solvent interactions. Polar properties of electroyltes in low dielectric solvents. Edwin A. Richardson and Kurt H. Stern (Department of Chemistry, University of Arkansas, Fayetteville, Ark., U.S.A.). *J. Am. Chem. Soc.*, 82 (1960) 1296–1302.
The ion pair contact distances (*a*) of tetrabutylammonium picrate and tetrabutylammonium bromide have been determined in several solvents from dielectric constant measurements. Different methods of calculation of *a* from the experimental data are examined; the agreement between values of *a* for tetrabutylammonium picrate obtained by four different calculation methods (Debye, Allen, Oster, and Oster–Allen) is superior to that obtained when using conductance data. Tetrabutylammonium picrate was studied in three low dielectric constant solvents (benzene, dioxane, and toluene); the value of *a* obtained varied with the solvent and did not correlate with the dielectric constant of the solvent. No perceptible dependence on temperature was noted. It was observed in studies of tetrabutylammonium bromide in benzene that the addition of small amounts of polar solvents (methanol or nitrobenzene) markedly reduces the formation of higher ionic aggregates and favors the formation of ion pairs. This effect is dependent on the concentration of polar solvent and not on the dielectric constant of the solvent mixture. [R.Mur.]

1546 – The influence of antioxidants on the autoxidation of terpenic hydrocarbons, studied by means of dielectric constant measurements. F. Oehme (Institute for the Development of Physico-chemical Methods of Analysis, Weilheim/Obb., Germany). *Fette u. Seifen*, 61 (1959) 363–367.
The author describes a method, based on dielectric constant measurements, by which the autoxidation of terpenic hydrocarbons can be followed. Formation of oxidized products, owing to their highly polar character, enhances the dielectric constant of the starting material; the influence of antioxidant additives can be thus followed. [Ca.Cas.]

1547 – The possibility of separating basic narcotic drugs by electrophoresis (in English). K. Willner (Institute of Forensic and Social Medicine, The University, Würzburg, Germany). *Arch. Toxicol.*, 17 (1959) 347–356.
The author tried to separate electrophoretically the following compounds for which paper chromatography shows poor resolution: morphine(I)–dilaudid(II); dicodid(III)–acedicon(IV); codeine(V)–eucodal(VI); atropine(VII)–1-*n*-cocaine(VIII); dolantin(IX)–cliradon(X).
(V)–(VI), (VII)–(VIII) and (IX)–(X) have been separated at pH 11. Attempts to separate (I) from (II) and (III) from (IV) were unsuccessful, but separations are possible with mixtures of (I), (V), (VI), (VII), (VIII) and (X). (I) can be confused with (II), (VI) with polamidon and ticarda, (V) with (III), (IV) and (IX). [Ca.Cas.]

See also abstracts nos. 1279, 1294, 1295, 1296, 1299, 1307, 1312, 1557, 1558, 1559, 1561.

10. Related topics

1548 – Dissolution of copper in acidified ferric sulphate solutions (in English). Tor Hurlen (Central Institute for Industrial Research, Blindern, Oslo, Norway). *Acta Chem. Scand.*, 15 (1961) 615–620.
Measurements have been made on the dissolution rate (i_c) and combined electric tension (E_c) of copper in unstirred sulphuric acid solutions of ferric sulphate at 21°. These quantities have been found to be very nearly independent of time and to obey the following relationships: $i_c = 0.011\ c$ A/cm^2; $dE_c/d \log i_c = 2.303RT/2F$ where c is the ferric sulphate molarity. The mixed electric tension has moreover been found to be very nearly equal to the pure anodic dissolution electric tension of copper at equal dissolution rates. [G.Ekl.]

1549 – Heats of activation of the Cu/Cu_{aq}^{2+} electrode (in English). Tor Hurlen (Central Institute for Industrial Research, Blindern, Oslo, Norway). *Acta Chem. Scand.*, 15 (1961) 621–629.
From measurements of the effect of temperature (0–45°) on the anodic polarization of copper in 0.1 N sulphuric acid, and from known data on the temperature coefficient of the standard electric tension of this metal, a mean standard heat of activation of ΔH^* (mean) = 15.2 kcal has been found for the Cu/Cu_{aq}^{2+} electrode. On the basis of the kinetic stoichiometry and the heat of reaction of this electrode, this has been shown to indicate ΔH_0^*(anodic) = 30.6 kcal (H scale); ΔH_0^* (cathodic) = —0.2 kcal (H scale). The results further give an apparent Arrhenius factor of approximately $A = 35\ nFT/v$ A/cm^2. These values are compared with corresponding values for the Fe/Fe_{aq}^{2+} electrode and their accuracy and meaning are discussed.
The measurements support previous results in showing a Tafel slope of 2.303 $RT/2F$ for the anodic copper dissolution reaction under stationary conditions. [G.Ekl.]

1550 – The kinetics of the Cu/Cu_{aq}^{2+} electrode (in English). Tor Hurlen (Central Institute for Industrial Research, Blindern, Oslo, Norway). *Acta Chem. Scand.*, 15 (1961) 630–644.
Investigations have been made on the anodic dissolution and cathodic deposition of copper in acid sulphate solution at 20° and 25° by means of a slow amperostatic technique. The reactions have been found to obey the Tafel relationship, except for the occurrence of a cathodic limiting current, to have mutually symmetric Tafel lines with slopes of numerically 2.303 $RT/2F$, and to be little dependent on the pH and the sulphate concentration. The rate of deposition (in the Tafel region) is moreover found to be proportional to the square of the cupric ion activity, and the rate of dissolution to be independent of this activity. This indicates a mechanism covered by the equation $2\ Cu = 2\ Cu_{aq}^{2+} + 4e^-$. For the exchange current (i_0) of the Cu/Cu_{aq}^{2+} electrode in 0.1 N sulphuric acid solutions of cupric sulphate at 20° and 25° respectively, it is found: $i_0 = 2.4\ a \cdot 10^{-2}$ A/cm^2; $i_0 = 3.4\ a \cdot 10^{-2}$ A/cm^2; where a is the cupric sulphate activity. The standard exchange current is by definition $J_0 = i_0/a$. [G.Ekl.]

1551 – Deposition of ^{65}Zn and ^{32}P-phosphate on various metallic and non-metallic surfaces (in English). E. Herczýnska (Department of Radiochemistry, Institute of Nuclear Research, Zéran, Warsaw, Poland). *Z. physik. Chem. (Leipzig)*, 217 (1961) 139–158.
The deposition of these isotopes, and of previously investigated ones, ($^{131}I^-$ on Au, Pt; $^{35}S-SO_4^{2-}$, $^{60}Co^{2+}$ on Au, Pt and on a resin; $^{32}P-PO_4^{3-}$, $^{137}Cs^+$ on Au, Pt, resin and stainless steel) as a function of pH is explained on the general concept of ion exchange. In acid media, the deposition of anions is favoured and exchange takes place between the tracer anions and the anions of the pH adjusting acid, while in alkaline media, cations of the base are exchanged with tracer cations. It is shown that on metal foils the adsorption is favoured by surface oxide layers which act as an ion-exchanger. This theoretical concept is generally corroborated by the experiments. [H.W.Nür.]

1552 – Kinetics of the electrochemical oxidation and reduction of H_2, O_2 and oxy-hydrogen gas on a platinum electrode in electrolyte solutions (in Russian). K. I. Rosental and V. I. Veselovskii (L. Ya. Karpov Institute of Physical Chemistry, Moscow, U.S.S.R.). *Zhur. Fiz. Khim.*, 35 (1961) 2258–2264.
A relation has been found between the electric tension of a Pt electrode in 1 N H_2SO_4, 1 N $HClO_4$ and 1 N KOH solutions and the rate of oxidation of H_2, reduction of O_2 and the reaction between H_2 and O_2 on the electrode. Rate measurements were made from consumption of the gases for a given time, account being taken of the amount of electrical energy spent in the process. In contrast to polarographic data, there may be a rather high rate of oxidation of H_2 on a passivated electrode (0.9–1.4). It is suggested that H_2 oxidation on such an electrode takes place *via* reaction with chemisorbed oxygen, evolved both electrolytically or supplied from the gaseous phase. [Ot.So.]

1553 – Studies on the stability and electrokinetic potential of a sulphur hydrosol. B. N. Gosh and A. K. Gangopadhyay (University College of Science, Calcutta, India). *J. Indian Chem. Soc.*, 38 (1961) 69.

A pure and stable sol of sulphur has been prepared, with a view to ascertaining the existence of any relation between stability and electrokinetic potential. The true zeta-potential of the sol found for rapid coagulation from electrophoretic and electro-osmotic data is 31.3 mV, while that found for slow coagulation both by electrophoretic and electro-osmotic methods is 38.4 mV. The effect of surface conductance has been found to be appreciable. A given rate of coagulation of the sol is characterised by a definite value of the true zeta-potential independent of the valency of the counter ions used. [R.S.Sa.]

1554 – Research on the anodic process on indium amalgam by means of radioactive tracers (in Russian). G. M. Budow and W. W. Lossew (Institute of Electrochemistry, The Academy of Sciences, S.S.S.R. and Karpov Institute for Physico-chemical Research, U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.*, 129 (1959) 1321–1324.

By means of ^{114}In a linear relationship was found between the anodic log of the process rate (i_a) and anodic electric tension, the anodic amagalm containing In at 0.002–0.9 M concentration, and the electrolyte being 0.004–0.03 M $In(ClO_4)_3$ + 0.01 M $HClO_4$, the ionic strength being kept constant by means of $NaClO_4$ ($T = 210.0 \pm 0.1°$). If the amalgam concentration is kept constant (0.1 M) it is possible, from a study of the dependence of the exchange current (at the equilibrium electric tension) on the $In(ClO_4)_3$ concentration to show that the anodic process rate is regulated by the rate of reaction: $In^{2+} \rightarrow In^{3+} + e^-$. At higher In–amalgam concentrations a displacement of the anodic curve *vs.* more negative values occurs (the slope remaining constant at the value $b_a = 0.0265$, which corresponds to a transfer coefficient $B = 2.3\ RT/b_aF = 2.20 \pm 0.07$). The anodic process rate shows a linear dependence on the amalgam concentration, and its activation energy is 13.4 kcal. [Ca.Cas.]

1555 – Electrochemistry of fluoride solutions. VI. Electrodeposition of nickel from fluoride solutions. A. N. Kapanna and E. R. Talaty (Salt Research Institute, Bhavnagar, India). *J. Indian Chem. Soc.*, 38 (1961) 663.

The electrodeposition of nickel from acid fluoride solutions has been studied. The decomposition discharge and anodic dissolution tensions of Ni in acid baths have been determined. Nickel dissolves continuously at the anode without any sign of passivity. The nature of the deposits from different solutions, and the effect of added agents on deposits, have been studied, glucose, gelatin and H_2O_2 being most effective agents. The operating conditions for the acid fluoride bath, with H_2O_2 as the added agent, have been specified. This bath, which yields much better deposits than any other acid bath, deserves a high place in the list of nickel plating baths. [R.S.Sa.]

1556 – On the differential capacities of iron and nickel electrodes observed by Past and Jofa (in English). A. Matsuda (Research Institute for Catalysis, Hokkaido University, Sapporo, Japan). *J. Research Inst. Catalysis, Hokkaido Univ.*, 8 (1960) 151–156.

On the basis of the catalytic theory of Horiuti (*J. Research Inst. Catalysis, Hokkaido Univ.*, 4 (1956) 55), the changes of differential capacities of nickel and iron electrodes with the overvoltage, in the cathodic polarization region, observed by Past and Jofa (*J. Phys. Chem., U.S.S.R.*, 33 (1959) 913, 1320) can be explained, provided that the electrode surface is more than 50% covered by adsorbed hydrogen atoms. A method for calculating differential capacity from charging and decay curves is given in an appendix. [Ca.Cas.]

1557 – Dielectric constant and dipole moment: ethers, aldehydes and chloro-compounds. S. K. K. Jatkar and C. M. Deshpande (University of Poona, Poona, India). *J. Indian Chem. Soc.*, 37 (1960) 1.

The dielectric constants and densities of a number of ethers, pentachloroethane and vanillin have been measured in a liquid state and in solution. By applying the D.C.M., the Onsager, the Kirkwood and the new equation, the moments of different compounds have been calculated and compared with theoretical values. The values of moments are: phenetole, 1.14; β-napthylmethyl ether, 1.12; furan, 0.74; tetrahydrofuran, 1.63; *o*-dimethoxybenzene, 1.15; *m*-dimethoxybenzene, 1.40; *p*-dimethoxybenzene, 1.60; pentachloroethane, 0.94; vanillin, 2.45.

The new moments of compounds in a liquid state and in solution compare well with the vapour values, and also with those calculated theoretically. The moments in the liquid state, as given by the Onsager and Kirkwood equations, are consistently higher. [R.S.Sa.]

1558 – Dielectric constant and dipole moment: pyridine and 2,4,6-trimethylpyridine. S. K. K. Jatkar and C. M. Deshpande (University of Poona, Poona, India). *J. Indian Chem. Soc.*, 37 (1960) 11.

The dielectric constants and densities of pyridine and 2,4,6-trimethylpyridine have been measured in the pure liquid state and also in benzene over a range of temperature and at various concentrations, by applying the Onsager, the Kirkwood and the new equations. The new moment of pyridine in a pure form is 2.23, which is independent of temperature; in benzene and dioxane its value is 1.84. The moment for 2,4,6-trimethylpyridine is 1.96, independent of temperature. [R.S.Sa.]

1559 – Dielectric constant and dipole moment of camphor. S. K. K. Jatkar and C. M. Deshpande (University of Poona, Poona, India). *J. Indian Chem. Soc.*, 37 (1960) 15.
The dielectric constant and density of concentrated solutions of camphor in benzene have been measured over a range of temperature and at various concentrations, and the dipole moment of liquid and solid camphor calculated by applying the new equation. The moment of solid camphor at low temperatures is 2.80, which decreases with rise of temperature and finally reaches a value of 2.25 in the liquid state. [R.S.Sa.]

1560 – Dielectric constant and dipole moment of coumarin. S. K. K. Jatkar and C. M. Deshpande (University of Poona, Poona, India). *J. Indian Chem. Soc.*, 37 (1960) 19.
The dipole moment of coumarin in dioxane is 3.85, and in the molten state 4.89. Its value in benzene solution is 3.82. The moments of 4-methyl, 6-ethyl, 8-acetyl and 4-methyl, 8-acetylumbelliferones have also been calculated, by applying the new equation for the first time, and have been found to be 3.33 and 3.33–3.58 respectively. The structures of these compounds have been explained on the basis of dipole moments. [R.S.Sa.]

1561 – Dielectric constant and dipole moment: chromones, flavones and benzylidene coumaranones. S. K. K. Jatkar and C. M. Deshpande (University of Poona, Poona, India). *J. Indian Chem. Soc.*, 37 (1960) 69.
The dielectric constant and densities of 2,6-dimethyl-*γ*-pyrone, 2-methyl, 5-hydroxychromone and 2-methyl, 7-methoxychromone, four flavones and two benzylidene-coumaranones have been measured at various concentrations and temperatures. The dipole moments have been calculated by applying the new equation, and the values obtained have been compared with theoretical values. The values of moments for compounds are: 2,6-dimethyl-*γ*-pyrone, 3.61; 2-methyl, 5-hydroxychromone, 3.32–3.60; 2-methyl, 7-methoxychromone, 3.61; 4-methoxyflavone, 2.83; 6-methyl, 4-methoxyflavone, 2.76; 6-benzoyl, 4-methoxyflavone, 3.55; 4-benzyloxyflavone, 4.23; 4-methoxybenzylidene-coumaranone, 2.76; 4-methoxy, 5-methylbenzylidene-coumaranone, 2.75. [R.S.Sa.]

1562 – ESR of polarographically generated phenazine-radical-ions (in German). K. Hausser, A. Häbich and V. Franzen (Max-Planck Institute of Medical Research, Heidelberg, Germany). *Z. Naturforsch.*, 16A (1961) 836–838.
Zur elektrolytischen Generierung von Radikalen an einem Platindraht wurde die trichterförmige Elektrolysenzelle von oben in den Resonanzhohlraum eingesetzt. Das Phenazin ist in Acetonitril (Tetrapropylammoniumperchlorat als Leitsalz) gelöst und wird zum Phenazin-Radikal-Anion reduziert. Sein ESR-Spektrum besteht aus 17 Gruppen zu je 5 Linien mit den Kopplungskonstanten $J_N = 4.8$ Gauss, $J_{P_1} = 1.6$ Gauss, $J_{P_2} = 0.16$ Gauss. Das Phenazylium-Kation hingegen erhält man durch Reduktion des doppelt geladenen Phenazinium-diperchlorats. Es ergibt insgesamt 127 Komponenten in 7 Hauptgruppen. Messung und Berechnung stimmen gut überein. [He.Be.]

See also abstracts nos. 1283, 1284, 1285.

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