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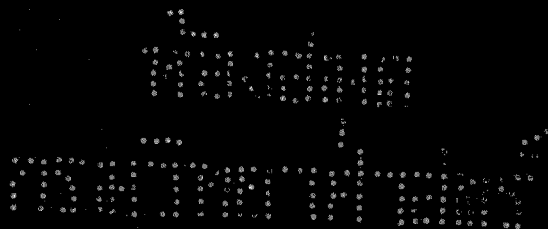
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## SUMMARIES OF CARD INDEXES

**Determination of the hydrogen content of palladium and palladium alloys from measurements of electrode potential and electrical resistance: A review:** J. C. BARTON and F. A. LEWIS, *Talanta*, 1963, 10, 237.

**Summary**—This paper is primarily concerned with a review of the methods which have been used to establish relationships between the hydrogen content, electrical resistance and electrode potential of hydrided palladium and palladium alloys at close to room temperatures. Problems concerning the utility of these relationships are discussed with special regard to hysteresis effects and to the limitations imposed on the measurement of the electrical resistance in solutions by the parallel conduction of the bridge (or measuring) current through the electrolyte.

**An investigation of the chelatometry of  $\text{Cu}^{II}$  with ethylenediamine-*N,N,N',N'*-tetra-*n*-propionic acid:** I. P. SANDERSON and T. S. WEST. *Talanta*, 1963, 10, 247.

**Summary**—A selective new polyaminocarboxylic acid-metallochromic indicator system is proposed for the accurate and interference-free titration of copper in aqueous solution in the presence of other metals such as Pb, Zn, Cd, Al, Mg, Ca, Ba, Sr, *etc.* No separations or addition of masking agents are necessary in this procedure. Nickel interferes only slightly.

**Voltammetry of silver in molten sodium nitrate-potassium nitrate: Use of a controlled-potential polarograph and a platinum quasi-reference electrode:** D. L. MANNING, *Talanta*, 1963, 10, 255.

**Summary**—The voltammetry of silver in molten sodium nitrate-potassium nitrate has been investigated over the temperature range 246°-326°. The polarograms were recorded by means of a controlled-potential polarograph and a stationary platinum microelectrode coupled with a platinum quasi-reference electrode. A third platinum electrode, which was isolated, was the counter electrode. The reduction of  $\text{Ag}^+$  to  $\text{Ag}^0$  proceeds reversibly, and the limiting current is proportional to the concentration of silver. The activation energy for the current-limiting process has been determined to be approximately 6.4 kcal/mole.

**The chronopotentiometric behaviour of antioxidants and antiozonants at the graphite electrode:** G. A. WARD, *Talanta*, 1963, 10, 261.

**Summary**—The chronopotentiometric behaviour of the phenylenediamines, dihydroxybenzenes, and several commercial antioxidants and antiozonants, has been studied using a graphite indicating electrode. The advantages of using non-aqueous solvents such as ethanol and acetonitrile in such work are pointed out—in particular, a significant increase in the precision of the technique arising from the ability of the solvent to wet the electrode efficiently.

**Comparison of solvents for the differentiating titration of phenols:** N. T. CRABB and F. E. CRITCHFIELD, *Talanta*, 1963, 10, 271.

**Summary**—Nine of the more commonly used solvents for the differentiating titration of acids have been compared for their ability to resolve phenols. Two methods of defining the differentiating quality of a solvent were used for this investigation. The first technique utilises the  $\Delta\text{HNP}(\text{solvent})$  vs.  $\text{pK}_a(\text{H}_2\text{O})$  curves described by Streuli. The magnitude of the slope of such curves determines the resolving power of the solvent. The other method used is based upon the practical observation that the extent of the first "break",  $\Delta E$  e. pt., for the potentiometric titration of a mixture of two phenols of similar  $\text{pK}_a(\text{H}_2\text{O})$  will define the differentiating quality of the solvent. A nearly linear relationship exists between these two methods of defining the differentiating quality of the solvent. A good correlation has been observed between  $\Delta E$  e. pt. and the dielectric constant of the solvent, and, in general, solvents with the lower dielectric constants have greater resolving powers. On the basis of this study *t*-butanol, the solvent recommended by Fritz and Marple, is superior to the other solvents investigated.

**The determination of traces of selenium and tellurium in samples of platinum by neutron-activation analysis:** D. F. C. MORRIS and R. A. KILLICK, *Talanta*, 1963, 10, 279.

**Summary**—A method is described for the determination of submicrogram amounts of selenium and tellurium in platinum by neutron-activation analysis. After a sample has been irradiated in a nuclear reactor, known amounts of tellurium and selenium carriers are added and a chemical separation of the elements is made. The activities of  $^{127}\text{Te}$  and  $^{76}\text{Se}$  isolated from the samples are then compared with corresponding activities separated from comparators irradiated simultaneously with the samples. The results obtained on 7 batches of pure platinum are reported.

**A new principle of activation-analysis separations—I: Theory of substoichiometric determinations:** JAROMÍR RŮŽIČKA and Jiří STARÝ, *Talanta*, 1963, 10, 287.

**Summary**—Separation procedures in the activation analysis of elements mainly consist of many steps which are usually derived from classical analysis schemes. In all cases an excess of reagent (precipitating, complexing, etc.) is used for separation of the element to be determined. In the present paper separations by means of a smaller amount of reagent than corresponds to the stoichiometric ratio of element to be determined are discussed. The use of an insufficient amount of the reagent has two advantages: greater selectivity (possibility of eliminating many steps) and elimination of the necessity for determining the chemical yield of the element in question. As a result the analysis is more rapid.

## Summaries for card indexes

**A new reductimetric reagent: iron<sup>II</sup> in a strong phosphoric acid medium—III: Titration of vanadium<sup>IV</sup> or vanadium<sup>V</sup> with iron<sup>II</sup> at room temperature: Determination of chromium<sup>VI</sup> and vanadium<sup>V</sup> in the same solution:** G. GOPALA RAO and L. S. A. DIKSHITULU *Talanta*, 1963, 10, 295.

**Summary**—The formal redox potential of the V<sup>IV</sup>/V<sup>III</sup> couple has been determined in a medium of varying phosphoric acid concentration. From these results and those previously reported for the Fe<sup>III</sup>/Fe<sup>II</sup> couple, the formal redox potential of the V<sup>IV</sup>/V<sup>III</sup> couple is higher than that of the Fe<sup>III</sup>/Fe<sup>II</sup> couple for a concentration of phosphoric acid above 4.0M, the difference between the formal redox potentials increasing with increasing concentration of phosphoric acid. At a concentration of 10.5M phosphoric acid the V<sup>IV</sup>/V<sup>III</sup> couple has a potential which is about 0.27 V higher than that of the Fe<sup>III</sup>/Fe<sup>II</sup> couple, so that iron<sup>II</sup> then rapidly reduces vanadium<sup>IV</sup> to vanadium<sup>III</sup> even at room temperature. Using this reaction a titrimetric procedure has been developed for determination of vanadium<sup>IV</sup> either with a potentiometric end-point or with a visual end-point using methylene blue or thionine as redox indicators. Titrations using these indicators must be carried out in an inert atmosphere. The new reagent is more advantageous than titanium<sup>III</sup> or chromium<sup>II</sup> which require special storage conditions. Moreover, iron<sup>III</sup> and tungsten<sup>VI</sup> do not interfere with the use of this reagent as they do with titanium<sup>III</sup> or chromium<sup>II</sup>. Further, the new reagent enables the determination of chromium<sup>VI</sup> and vanadium<sup>V</sup> in a single solution to be carried out with a potentiometric end-point. The first break in the potential curve corresponds to the reduction of chromium<sup>VI</sup> to chromium<sup>III</sup> and of vanadium<sup>V</sup> to vanadium<sup>IV</sup>, and the second break corresponds to the further reduction of vanadium<sup>IV</sup> to vanadium<sup>III</sup>. Iron<sup>III</sup>, manganese<sup>II</sup>, cobalt<sup>II</sup> and tungsten<sup>VI</sup> do not interfere. This procedure is likely to be of considerable value in the analysis of special steels.

**Indirect spectrophotometric determination of sulphate ion:** VLADIMÍR PALATÝ, *Talanta*, 1963, 10, 307

**Summary**—A method for the indirect spectrophotometric determination of sulphate ion has been developed, based on its decomposition of the thorium-Xylenol Orange complex. The amount of decomposed complex is proportional to the concentration of sulphate ion. Optimum conditions for this method are given.

**Use of the argon chromatograph in the determination of carbon in steel:** A. K. GALWEY, *Talanta*, 1963, 10, 310.

**Summary**—A method is described in which carbon dioxide, formed by the combustion of steel, can be determined in the argon gas chromatograph. Results indicate that 0.03% carbon may be determined with an accuracy of about  $\pm 0.01\%$ , but the accuracy is rather less for higher carbon steels. The method may be useful in the determination of small concentrations of carbon and it may be possible to make it largely automatic. The possibility of determining both carbon and sulphur in a single sample of steel by gas chromatographic methods is also discussed.

**The determination of oxidising and reducing cations in transition-metal oxides using vanadium sulphate solutions:** D. G. WICKHÁM and E. R. WHIPPLE, *Talanta*, 1963, **10**, 314.

**Summary**—Because vanadium sulphate solutions are very stable, they make useful analytical reagents. A solution of quinquevalent vanadium sulphate in dilute sulphuric acid can be used for the determination of  $\text{Fe}^{\text{II}}$ ,  $\text{Ti}^{\text{III}}$  and  $\text{V}^{\text{III}}$  ions present in solid oxides. A similar solution of quadrivalent vanadium can be used for the determination of  $\text{Co}^{\text{III}}$ ,  $\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{IV}}$ . The importance of the method in studies of mixed transition-metal oxides is briefly discussed.

**The polarography of cerium<sup>IV</sup> in acetate buffer:** O. P. AGRAWAL and R. C. KAPOOR, *Talanta*, 1963, **10**, 316.

**Summary**—The polarographic behaviour of cerium<sup>IV</sup> has been studied in Walpole acetate buffers of different concentrations and pH values (4, 5 and 5.6). 1M Acetate media of pH 4 and 5 have been found useful for the polarographic determination of cerium<sup>IV</sup>. At pH 4, in 0.2M acetate medium, a second wave at  $-0.9$  v vs. S.C.E. was observed, which had anomalous characteristics.

**Spectrophotometric determination of the dissociation constant of the Woods reagent;** R. WILSON and G. W. LESTER. *Talanta*, 1963, **10**, 319.

**Summary**—The spectrophotometric determination of the dissociation constant for the Woods reagent, 2-hydroxymethyl-6-(2'-hydroxymethyl-5'-hydroxy-4'-pyrone-6')-pyranil[3,2-b]pyran-4,8-dione, which contains one weakly ionised phenolic hydroxyl group, is presented. The value  $9.7 \times 10^{-9}$  is the average of the values obtained for the dissociation constant at wavelengths 270 m $\mu$  and 315 m $\mu$ . The best recommended value of the dissociation constant for the Woods reagent is  $9.7 \times 10^{-9}$ , which is obtained from the plot of logR against the corresponding pH values according to equation (2) and extrapolating to pH 0

**Interference of silicon in determination of phosphorus by the vanadomolybdate method:** ROBERT B. LEW and FRED JAKOB, *Talanta* 1963, **10**, 322.

**Summary**—Silicon interferes with the determination of phosphorus by the vanadomolybdate method because it forms a yellow complex that shows strong absorbance at 400 m $\mu$ . Alkaline ammonium persulphate oxidation in polypropylene test tubes, instead of glass, eliminates the interference of silicon in the determination of organophosphorus compounds.

**Quantitative treatment of exchange equilibria involving complexans—III: Chelatometric determination of calcium in presence of magnesium with EGTA:** GENKICHI NAKAGAWA, HIROKO WADA and MOTOHARI TANAKA, *Talanta*, 1963, **10**, 325.

**Summary**—A method of selective chelatometry of calcium in the presence of magnesium is established using the Zn-EGTA-PAN system as indicator. Effects of pH and concentrations of Zn-EGTA, PAN and magnesium are studied by means of photometric titration curves. The method allows the visual titration of calcium in a sample of which the ratio Mg:Ca does not exceed 10.

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- <sup>2</sup> S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
- <sup>3</sup> A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
- <sup>4</sup> W. Jones, *Brit. Pat.* 654321, 1959.

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# DETERMINATION OF THE HYDROGEN CONTENT OF PALLADIUM AND PALLADIUM ALLOYS FROM MEASUREMENTS OF ELECTRODE POTENTIAL AND ELECTRICAL RESISTANCE

## A REVIEW

J. C. BARTON and F. A. LEWIS

Department of Chemistry, The Queen's University of Belfast, Northern Ireland

(Received 28 September 1962. Accepted 21 November 1962)

**Summary**—This paper is primarily concerned with a review of the methods which have been used to establish relationships between the hydrogen content, electrical resistance and electrode potential of hydrided palladium and palladium alloys at close to room temperatures. Problems concerning the utility of these relationships are discussed with special regard to hysteresis effects and to the limitations imposed on the measurement of the electrical resistance in solutions by the parallel conduction of the bridge (or measuring) current through the electrolyte.

At 25° palladium can form non-stoichiometric solid hydrides of compositions corresponding to atomic ratios of hydrogen to palladium (H/Pd) approaching 0.9.<sup>1-3</sup> Diffusion of hydrogen in the solids is relatively rapid, so that it is quickly dispersed homogeneously throughout the solids—apart from phase boundary considerations which apply when  $\alpha$ - and  $\beta$ -phase hydrides are in co-existence. However, specimens are not significantly disrupted by the absorption of hydrogen, and a workable degree of ductility is retained by the hydrides. This somewhat unique mechanical robustness is an important aid in allowing a maximum advantage to be taken of changes of physicochemical parameters when these are employed as analytical measures of hydrogen content. A further useful consideration is that the same specimen may often be utilised for several successive experiments, since its original dimensions are not altered to a large degree by a moderate number of cycles of absorption and desorption of hydrogen.

### *1. Review of studies of the relationship between hydrogen content and electrode potential and correlations with free energy of hydride formation and P-C-T data for the Pd/H system*

For the majority of experiments in which electrical resistance is one of the parameters under study, it is generally most convenient for the palladium specimen to be in the form of a wire. In such a "massive" or "fully fused" form, palladium is found to attain thermodynamic equilibrium fairly readily with gaseous hydrogen at temperatures  $>160^\circ$ ; and detailed isothermal data relating H/Pd to the vapour pressure of the hydride [pressure-composition-temperature (P-C-T) data] have been obtained<sup>4</sup> for temperatures as high as *ca.* 500°. Although by using more finely particulated palladium, P-C-T values have also been obtained<sup>5</sup> at temperatures as low as 0°, only limited

P-C-T studies have, however, so far been made at temperatures below  $160^\circ$  with specimens of a physical form suitable for electrical resistance measurements—with the exception of some recent results obtained with evaporated metal films<sup>6</sup>—despite the use of a variety of methods for surface activation.<sup>7</sup>

Compilation, by direct experimentation, of the relationships between hydrogen content and electrode potential has a later historical origin than the compilation of P-C-T data. Perhaps the first useful investigation was that carried out by Nylén<sup>8</sup> in 1937, and it is only recently that the essential interdependence of the P-C-T and electrode potential data has been more widely appreciated. This is perhaps surprising, because it has been widely known since Graham's pioneering studies<sup>9</sup> that palladium cathodes readily absorbed considerable amounts of hydrogen discharged during electrolysis. Nevertheless, the ease with which electrolytically discharged hydrogen can be absorbed by palladium at temperatures close to  $25^\circ$ , compared with the generally slow rate of equilibration between palladium and hydrogen molecules at these temperatures, has, even quite recently, encouraged suggestions that the hydrides formed during electrolysis may be of a slightly different type. It is now clear, however, that this is not the case,<sup>10,11</sup> and that very slow rates of absorption of hydrogen molecules are associated with surface films which inhibit molecular dissociation. Such disputes of general principle seem to have been adequately resolved, and the essential validity of the relationships (at  $25^\circ$ ) between H/Pd and electrode potential, illustrated in Fig. 1, is now generally recognised.

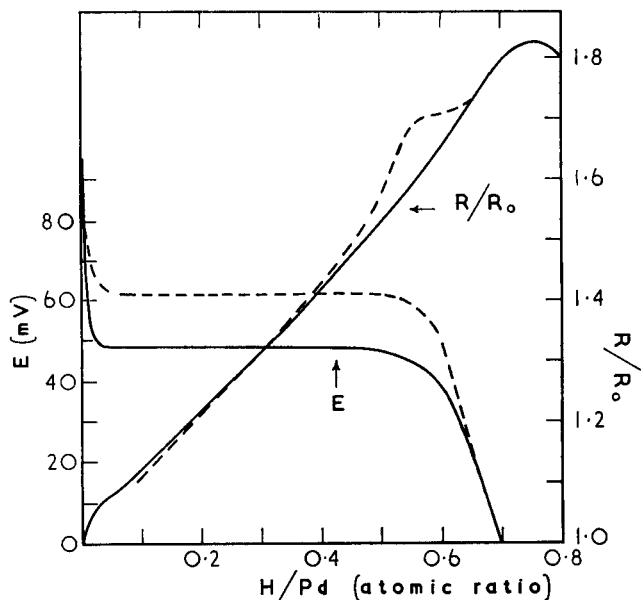
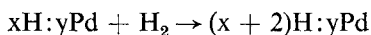


FIG. 1.—Absorption (—) and desorption (---) relationships between the hydrogen content of palladium and relative electrical resistance, and between hydrogen content and electrode potential ( $25^\circ$ ).

To relate electrode potential satisfactorily to other thermodynamic parameters it is found necessary to employ partial molar functions because of the non-stoichiometric composition of the hydrides. Such correlations have, however, an excellent experimental foundation, since it has been directly shown<sup>12</sup> that over the entire range of

H/Pd, the electrode potential  $E$  is related to the partial molar free energy change,  $\Delta\bar{G}$ , corresponding to the reaction



(where  $x$  and  $y$  represent total numbers of atoms in the solids) by the usual expression:

$$-\Delta\bar{G} = 2FE, \quad (1)$$

where  $F$  is the Faraday constant.

These findings are securely substantiated, since it is also possible to correlate  $\Delta\bar{G}$  with H/Pd from independently determined P-C-T data by means of the relationship:

$$\Delta\bar{G} = RT \ln p, \quad (2)$$

where  $p$  is the vapour pressure of the hydride.

The principle of the interrelationships having been established over ranges of H/Pd where both  $p$  and  $E$  are known independently, it is then possible as a consequence, to derive one set of values from the other over a wider range of values of H/Pd, depending on whether  $p$  or  $E$  is the more conveniently measurable.

It is shown in Fig. 1 that there is a marked hysteresis between the isothermal values recorded when H/Pd is steadily increased (absorption) and those recorded during the decrease of H/Pd (desorption). Although hysteresis is especially evident over ranges of H/Pd where  $\alpha$ - and  $\beta$ -phase hydrides co-exist, the effect extends some little way beyond the limits of electrode potential invariance to which such ranges correspond. Hysteresis phenomena represent a feature of the relationships concerning which the problems of interpretation have not as yet been fully resolved<sup>7</sup> but there is good evidence that Fig. 1 adequately represents the course of the relationships, provided that the experimental conditions are such that the electrode is neither absorbing nor desorbing hydrogen at an excessively fast rate.<sup>13</sup>

## 2. Preparation of electrodes

To obtain  $E$ -H/Pd relationships in sensible accord with those shown in Fig. 1, it is necessary to prevent platinum, and other metal electrical leads to the specimen, from contacting the electrolyte: methods of achieving this have been compared.<sup>14</sup> There is also much evidence to suggest that the electrode surface should be so catalytically active that the kinetics of equilibration with hydrogen molecules are governed, in vigorously stirred solutions, by the rate of diffusion of the molecules through the Brunner-Nernst layer, *i.e.*, by transport of the dissolved molecules up to, or away from, the surface of the electrode. Although the mechanism of activation is not fully understood, electrodes in the "bright" state which fulfil this latter condition have been prepared by preflaming<sup>15</sup> and/or by anodisation.<sup>12</sup> However, fairly rigid conditions of purity of both hydrogen gas and electrolyte must then apply throughout the experiments in order to maintain a high catalytic activity.

An electrode surface that is much less readily poisoned may be obtained<sup>15</sup> by "palladising", *i.e.*, by plating the palladium (or palladium alloy) with a layer of palladium black from a dilute solution of chloropalladous acid (*e.g.*, 2% PdCl<sub>2</sub> in 0.1*N* HCl). Moreover, hydrogen rapidly permeates through the interface between the "palladised" layer and the bulk palladium substrate—although, over ranges of hydrogen content where  $\alpha$ - and  $\beta$ -phase hydrides co-exist, the electrode potentials may be

ca. 4 mV lower (more noble) than is found for catalytically active "bright" electrodes. Palladised electrodes can often be employed in conjunction with hydrogen gas obtained from commercial cylinders without further purification. It may be mentioned that potentials measured with respect to a Pt/H<sub>2</sub> reference immersed in the same solution (where necessary in a compartment separated from the palladium by a sintered-glass disc) are conveniently exclusive of a hydrogen ion term. Fuller discussion of the assembly of electrodes and of other experimental arrangements may be found in ref. 14.

### 3. Comparison of methods employed for obtaining relationships between electrode potential and hydrogen content

It is inconvenient, in this brief outline, to discuss the methods in chronological sequence.

The discussions above and in Section 8 indicate that P-C-T data, when available, provide a source of *E*-H/Pd data which is particularly useful where *E* varies markedly with small changes of H/Pd. However, for a direct experimental derivation of relationships, H/Pd is probably most conveniently obtained by measuring, in conjunction with *E*, an additional parameter, such as the relative resistance, *R/R*<sub>0</sub>, which has already been independently related to H/Pd. (*R* is the actual resistance and *R*<sub>0</sub> is the "hydrogen-free" resistance.) In circumstances where the hydrogen content also has to be measured directly, even *controlled* addition and removal of hydrogen by electrolysis must be examined in relation to control of H/Pd by diffusion of molecules to and from the surface.

For a catalytically active electrode, immersed in a well stirred solution, and continuously saturated with either hydrogen or an inert gas (*e.g.*, argon or nitrogen) at a known pressure, the kinetics of absorption and desorption of hydrogen are given<sup>13</sup> by the equation

$$\frac{d(\text{H/Pd})}{dt} = k_0 k'_0 (P - p), \quad (3)$$

where *p* is again the hydride pressure [*cf.* eqn. (2)] and *P* is the pressure under which H<sub>2</sub> is dissolved in solution; the rate constant *k*<sub>0</sub> ~ 10<sup>16</sup> molecules.cm<sup>-2</sup>.sec<sup>-1</sup>.atm<sup>-1</sup> (when *P* and *p* are expressed in atmospheres) and *k*'<sub>0</sub> is a conversion constant which depends on the dimensions of the specimen.

Provided *k*<sub>0</sub> has been independently determined under the conditions of stirring subsequently employed (*R/R*<sub>0</sub>-time measurements prove valuable in this respect—see Section 5) H/Pd can be calculated at any time from the integrated form of equation (3).

In principle, when varied by electrolysis, H/Pd may be accurately calculated from differences between coulometric measurements and the volume of unreacted gas collected in a burette above the electrode. Although gas burettes have been employed in determining relationships between H/Pd and *R/R*<sub>0</sub> (see Section 1) this refinement appears never to have been employed in studies of *E*-H/Pd relationships. Provided, however, that surfaces are prepared in such a way that each discharged proton is absorbed by the palladium in absorption studies, and each discharged anion is stoichiometrically effective in removing hydrogen during desorption studies, changes of hydrogen content can again, in principle, be measured solely by accurate coulometry. By interrupting the current at intervals, *E* can be measured independently of overvoltage terms. Despite the rapid diffusion of hydrogen in the hydrides, very high

current densities should be avoided, since differences between hydrogen concentrations in the surface layers (which govern the measured value of  $E$ ) and in the interior may also give rise to misleading relationships.<sup>12</sup> It is still necessary, however, to assess the magnitude of concurrent diffusion of hydrogen molecules from the surface (which has often been overlooked when relationships have been obtained by electrolysis). In this article it is convenient to examine this problem with reference to the relationships illustrated in Fig. 1.

Assume that a low but convenient current density of *ca.* 3 mA.cm<sup>-2</sup> is chosen for electrolysis studies. This would result in hydrogen being absorbed (cathodisation) or desorbed (anodisation) at rates comparable to those calculated from equation (3) with either  $P$  or  $p = 760$  mm of Hg respectively. However, for the greater range of H/Pd in Fig. 1 the values of  $E(\geq 46$  mv) would correspond to  $p \leq 18$  mm [see equations (1) and (2)], so that the simultaneous loss of hydrogen by diffusion would be no more than  $\sim 2.5\%$  of that discharged or removed by electrolysis at this current density. It is, therefore, only over values of H/Pd ranging from *ca.* 0.57 to *ca.* 0.7 (where  $p$  rises steeply as  $E$  decreases through zero to negative values) that the simultaneous loss of hydrogen by diffusion shows a marked increase. It has therefore been possible to obtain "desorption" relationships in sensible accord with P-C-T data by anodisation<sup>16</sup> ("the method of charging curves") for the Pd + H electrode at 25°. Nevertheless, at higher temperatures (and<sup>17</sup> for many hydrided palladium alloy electrodes at 25°) where the value of  $p$  is higher over a wider range of hydrogen contents, the loss of hydrogen by diffusion could result in more serious general errors if measurement of electrolytic current were taken as the sole guide to changes in H/Pd.

#### 4. Advantages of concurrent measurement of $E$ and $R/R_0$

Changes of electrical resistance are conveniently plotted as relative resistance,  $R/R_0$  (see Section 3). Fig. 1 illustrates that the relationships between H/Pd and  $R/R_0$  are also dependent on whether hydrogen is being absorbed or desorbed.

Since  $R/R_0$  can also be measured potentiometrically, it is a most convenient parameter for conjoint measurement with  $E$ . The consequent advantages are clear from Fig. 1; because where  $E$  is relatively invariant ( $\alpha$ - and  $\beta$ -phase hydrides in co-existence<sup>9</sup>),  $R/R_0$  varies continuously with changes of H/Pd. On the other hand, in single phase regions  $E$  is markedly dependent on H/Pd, and particularly in  $\beta$ -phase (H/Pd > 0.57), is clearly the more sensitive parameter for most practical purposes. Covering the leads to the specimen in order to avoid gross errors<sup>14</sup> in the measurements of  $E$  usually also necessitates coating a short length of the specimen, but with reasonable care this need not greatly reduce the accuracy of the  $R/R_0$  measurements.

#### 5. Derivation of relationship between H/Pd and $R/R_0$

Near 25° only "absorption" relationships were available until recently; and these had mainly been derived under conditions where hydrogen was absorbed by palladium during electrolysis. The problems of measuring H/Pd during electrolysis experiments have already been discussed above, but  $R/R_0$  relationships so derived have been additionally criticised on the grounds that generally insufficient precautions were taken to exclude oxygen or other anodic products from the cathode compartment; and on the grounds that the possibility of co-conduction of the measuring current through the electrolyte had been insufficiently considered (see further below).

In order that, in the interpretation of kinetic experiments,  $H/Pd$  may at all times be sensibly derived without pleading an unconvincing allowance for experimental scatter, it is necessary that measurements of  $R/R_0$  should conform in magnitude, and should alter in a manner to be expected from the detailed form of the  $H/Pd-R/R_0$  relationships.

Results recorded during more recent kinetic studies could not be satisfactorily interpreted at higher values of  $H/Pd$  from  $H/Pd-R/R_0$  relationships previously obtained by the electrolytic method. Moreover, it was found not only necessary<sup>18,19</sup> to derive additional "absorption" values, but also<sup>20</sup> to derive the "desorption" relationships illustrated in Fig. 1. In obtaining these relationships,  $H/Pd$  was determined at each value of  $R/R_0$  either by quantitative reduction of standardised oxidants, or by measurement of the volume of gas evolved on heating the specimen in a previously evacuated container of known volume.

In principle, however, for specimens of high catalytic surface activity the relationships between  $H/Pd$  and  $R/R_0$  can also be derived, in gas-saturated solutions, by calculating  $H/Pd$  from the integrated form of equation (3). Reliable use of this method again requires that  $k_0$  be accurately known; so that carefully controlled conditions of stirring are required. Furthermore, unless the relationship between  $E$  and  $R/R_0$  has been previously determined in a separate experiment, continuous concurrent measurement of  $E$  is also necessary. Provided that an electrolyte of low conductance is employed (so that the problems associated with co-conduction, discussed below, are virtually eliminated) this method can prove useful for obtaining fine details of the  $H/Pd-R/R_0$  relationships, and also for convenient determination of equivalent relationships for palladium alloys.

#### 6. Convenient dimensions for specimens

For many measurements it is perhaps most satisfactory to use specimens which are freely suspended, *i.e.*, not wound on a former. However, free suspension generally imposes some restriction on length and diameter, since fine wires arranged in a compact way can be so buffeted in vigorously stirred solutions that adjacent portions touch, and cause short circuiting during an experiment.

On the other hand, by using wires of larger diameter the accuracy and sensitivity of changes in electrical resistance are, in general, somewhat decreased—unless a correspondingly longer specimen is employed. Moreover, the decreased ratio of surface to volume is generally complementary to a longer time for attainment of chemical equilibrium (as, *e.g.*, reflected by a slower rate of change of  $R/R_0$ ), and this may be inconvenient experimentally.

From somewhat empirical consideration of the factors discussed above, specimens of 40 s.w.g. (*ca.* 0.012 cm in diam.) and about 12 cm in length ( $R_0 \sim 1\Omega$ ) have been found convenient for use in a number of experimental studies<sup>13,15,20</sup>.

#### 7. The problem of co-conduction of the bridge current through solution

When a specimen is immersed in solution the electrolyte provides a parallel path for conduction of the bridge current.<sup>21</sup> Obviously, the relative importance of this path will be greater in strong electrolytes and for specimens of high electrical resistance (which are often to be preferred in other respects).

The total electrical impedance through the electrolyte is comprised of the resistance of the bulk of the solution together with the impedance at the interface between the



specimen and the electrolyte. Now, interfacial phenomena at electrodes are still imperfectly characterised, but it is clear<sup>22,23</sup> that the total effective surface impedance is relatively low at surfaces which are catalytically active (e.g., for dissociation of hydrogen molecules). Thus, co-conduction problems will be most serious for surface-active specimens which are generally most suitable for study on other grounds.

During d.c. measurements,<sup>22</sup> the co-conduction of current through the electrolyte is associated with a non-homogeneous<sup>21,22</sup> transfer of hydrogen from one "side" of the specimen to the other (related to the gradient of the potential drop along the wire). The resultant non-homogeneous distribution of hydrogen along the specimen gives rise to a potential difference (of opposite sign to that imposed by the measuring current) which gradually increases with time, until it is of sufficient magnitude virtually to polarise further current flow through the electrolyte [a small "residual" current will still flow, since the local differences of  $E$  along the wire are reflected in complementary differences in the loss and gain of hydrogen by diffusion—*cf.* equation (1)].

"Co-conduction" of the measuring current is reflected by a lower apparent value of the resistance of the immersed specimen, but, during the build-up of the polarising back-e.m.f., the apparent resistance "drifts-up" with time until it approaches the true value of the specimen resistance in the absence of co-conduction. However, when the average hydrogen content of the specimen corresponds to regions of co-existence of  $\alpha$ - and  $\beta$ -phase hydrides, the establishment of a polarising e.m.f. is especially difficult<sup>22</sup>; since here a non-homogeneous distribution of hydrogen throughout the specimen need not be reflected by local differences of  $E$ . Moreover, care must be taken that during measurements of resistance over regions of  $\alpha$ - and  $\beta$ -phase co-existence, co-conduction does not also alter significantly the "mean" value of  $E$  from a value characteristic of the average value of H/Pd—as given by the relationships illustrated in Fig. 1.

Furthermore, in solutions which are strongly oxidising<sup>13</sup>—in addition to being otherwise strongly conducting—erratic fluctuations of the apparent resistance can occur which seem likely to result from co-conduction in conjunction with rapid, local variations of  $E$ .

Although such co-conduction phenomena have initiated interesting experimental investigations<sup>22,23</sup> concerning their origin, there is no escaping the fact that they can be an experimental nuisance when utilising  $R/R_0$ , and, to a lesser extent,  $E$ , as analytical parameters. Obviously, they can be effectively avoided by carrying out experiments in dilute electrolytes of low conductance. Where this is not possible, use may still be made<sup>13</sup> of the H/Pd- $R/R_0$  relationships by temporarily transferring the specimen to distilled water; this allows a quite accurate estimate of the average reaction rate to be made at several stages of an experiment.<sup>13</sup>

Although d.c. measurement of  $R/R_0$  by potentiometry is generally very convenient, measurements obtained with an a.c. bridge have a particular advantage when studying changes of the hydrogen content of palladium cathodes.<sup>23,24</sup> Here, the simultaneous measurement of  $R/R_0$  during actual electrolysis can provide valuable experimental results. However, co-conduction of the bridge current through the electrolyte can constitute an even more serious problem in a.c. measurements since, unless the equivalent components of the interface impedance are exactly simulated in the balance arm of the bridge, the capacitive component may be equivalent to a short circuit at high frequencies.<sup>23</sup> In general, therefore, the use of low-conductance electrolytes in such studies is, in practice, almost obligatory.

### 8. The effect of temperature on the relationships

Although the majority of recent work has been primarily concerned with the relationships at 25°, quite useful estimates of relationships at other temperatures (expressed in °K) are not difficult to extrapolate or interpolate from available data.

With reference to the  $E$ -H/Pd relationships, attention has so far been most specifically centred on the temperature dependence of the relatively invariant or plateau values of  $E$ , *i.e.*,  $E_{\alpha,\beta}$ , corresponding to regions of co-existence of  $\alpha$ - and  $\beta$ -phase hydrides. A relationship has been reported,<sup>25</sup> *viz.*,

$$E(\text{volts})_{\alpha,\beta} (\text{during absorption}) = 0.063 - 0.0005(T - 273.16) \quad (4)$$

Comparison<sup>12,25</sup> of equation (4) with absorption results for  $E_{\alpha,\beta}$  reported from several sources, and obtained following different methods of surface activation, suggests that, at least over the range 0°–60°, it should be generally reliable to within *ca.*  $\pm 3$  mv.

Results also suggest<sup>13,20,25</sup> that the complementary equation, during desorption, is likely to be,

$$E(\text{volts})_{\beta,\alpha} (\text{during desorption}) = 0.073 - 0.005(T - 273.16) \quad (5)$$

Scarcely any numerical values have so far been published for low H/Pd in regions of  $\alpha$ -phase, where indeed  $E$  is a sensitive function of H/Pd. This is probably due, in part, to the lack of controversy concerning the general interpretation of such values and also due, in part, to the neglect of their general use as an analytical measure of H/Pd; since, in  $\alpha$ -phase fairly sensitive relationships also exist between H/Pd and  $R/R_0$ . Moreover, in obtaining such values, errors can arise; either from co-conduction effects; or from the occurrence<sup>12,25,26</sup> of supersaturation minima; or from insufficient care being taken in outgassing the solution before, *e.g.*, hydrogen absorption.<sup>13</sup> However, in principle, the values may also be calculated from relationships between hydride pressure  $p$  and H/Pd—for which temperature dependent equations have been derived.<sup>27</sup> Nonetheless—the possible sources of error having latterly been more fully appreciated—it may, in the future, yet prove useful to compile results in the  $\alpha$ -phase by careful direct experimentation.

It is for  $E \rightarrow 0$ , where  $R/R_0$  is no longer very sensitive to small changes of H/Pd, (furthermore, any errors in the measurement of  $R_0$  will enhance increasingly the error in  $R/R_0$  at higher values of this parameter) that the almost linear relationship between  $E(\text{volts})$  and H/Pd has proved of particular value.<sup>15,28</sup> This may be written,

$$\text{H/Pd} = A - \left( \frac{2F}{.18 RTb_1} \right) E \quad (6)$$

where  $A$  represents the ratio of H/Pd at  $E = 0$  ( $\sim 0.7$  at 25°) and  $b_1$  is a proportionality constant.

A more exact experimental agreement than has so far been obtained would be desirable between constants corresponding to  $b_1$ . However, it seems that this relationship is not markedly dependent on temperature over the range 0°–50°, since here it has been determined experimentally that  $A$  decreases from only 0.72 to 0.68 whilst (for a similar physical form of palladium)  $b_1$  decreases only from *ca.* 50 to *ca.* 40. The plot of the relationship in Fig. 1 from  $E \sim 20$  mv to  $E = 0$  was obtained by substituting  $A = 0.7$  and  $2F/4.18 RTb_1 = 2.18$  in equation (6).

Relationships between  $H/Pd$  and  $R/R_0$  have recently been re-determined<sup>19,20</sup> in fair detail at  $0^\circ$  and  $59^\circ$  during absorption; and at  $0^\circ$  and  $50^\circ$  during desorption. Plots of temperature coefficients of resistance permit satisfactory interpolation of these results; but, within this range, the relationships are almost independent of temperature for  $R/R_0 < ca. 1.4$ .

### 9. Utility of the relationships

During measurement of many properties of palladium hydrides (over a range of  $H/Pd$ ) it is often difficult to avoid entirely some risk of hydrogen loss by atmospheric oxidation:<sup>20</sup> concurrent measurement of  $R/R_0$  can be a convenient non-destructive guide as to whether this may have taken place. In general, however, a wider field of application for the relationships discussed here is provided in the study of the kinetics (including electrochemical kinetics) of reactions at the surface of hydrided palladium immersed in solution. It is in this general field that conjoint measurement of  $E$  and  $R/R_0$  proves most valuable. Examples of their utility in studies of hydrogen absorption and hydrogen over-voltage at palladium cathodes have already been specifically reviewed<sup>14</sup> and the more recently examined<sup>20</sup> desorption relationships provide further scope for application. In this general field of study, similar relationships, which have been derived for certain palladium rich alloys, have already proved to have certain advantages over those available for pure palladium.<sup>3,29</sup>

**Zusammenfassung**—Die Arbeit ist vorwiegend einer Zusammenfassung von Methoden gewidmet, die sich mit den Zusammenhängen zwischen Wasserstoffgehalt, elektrischem Widerstand und Elektrodenpotential von hydrogeniertem Palladium und Palladiumlegierungen bei etwa Raumtemperatur befassen. Probleme der Anwendbarkeit dieser Beziehungen werden diskutiert und zwar im besondern Hinblick auf Hystereeffekte und die Beschränkungen bei der Messung elektrischer Widerstände in Lösungen durch Paralleleitfähigkeit oder Messung des Stromdurchanges durch Elektrolyte.

**Résumé**—L'essentiel de cet article est consacré à une vue d'ensemble des méthodes utilisées pour l'établissement des relations générales entre la teneur en hydrogène, la résistance électrique et le potentiel de l'électrode du palladium hydrogéné et les alliages de palladium à température ambiante. Discussion de l'utilité de ces relations avec un paragraphe spécial concernant l'effet d'hystérésis et les restrictions imposées dans la mesure de la résistance électrique dans les solutions par la méthode du pont ou la mesure directe du courant dans l'électrolyte.

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## AN INVESTIGATION OF THE CHELATOMETRY OF Cu<sup>II</sup> WITH ETHYLENEDIAMINE-*N,N,N',N'*- TETRA-*n*-PROPIONIC ACID

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**Summary**—A selective new polyaminocarboxylic acid-metallochromic indicator system is proposed for the accurate and interference-free titration of copper in aqueous solution in the presence of other metals such as Pb, Zn, Cd, Al, Mg, Ca, Ba, Sr, *etc.* No separations or addition of masking agents are necessary in this procedure. Nickel interferes only slightly.

IN a preliminary communication to this journal we indicated the possibility of a highly selective titration of copper<sup>II</sup> in the presence of other heavy metals without the use of separation methods or masking agents.<sup>1</sup> At that time we were unable to pursue the examination further. The present communication reports more fully on this system.

It is generally accepted that one of the weaknesses of the compleximetric technique based on ethylenediaminetetra-acetic acid, EDTA, is the unselective nature of the reagents used. Both EDTA and the metallochromic indicators used are highly unselective, and consequently it is only by titrating some of the more strongly chelating cations in an acid medium, or by the judicious use of selective masking and demasking reactions that the technique has achieved its present status in inorganic analysis. Two outstanding methods have been described which illustrate the selectivity that may be obtained by the use of more selective reagents. The first, chronologically, consists of titrating calcium in the presence of magnesium with 1,2-bis[2-di(carboxymethyl)-aminoethoxy]ethane, EGTA, as titrant.<sup>2</sup> In the classical method of Schwarzenbach and Gysling,<sup>3</sup> where murexide is used as indicator and EDTA as the titrant, the magnesium must be precipitated as hydroxide (though not separated) by raising the pH to 12. In the EGTA method, the titrant is sufficiently unreactive towards magnesium to render precipitation of the latter unnecessary. The yet unresolved problem, however, is that the visual means of indicating the end-point, based on the use of a zinc-sensitised-Zincon system,<sup>4,5</sup> is only partly satisfactory. The conditions for applying this system are very restrictive and have not been improved despite considerable discussion.<sup>6</sup>

The second procedure uses 1,2-diaminocyclohexane-*N,N,N',N'*-tetra-acetic acid, CDTA, for the titration of calcium, in the presence of soluble barium up to 10- or 12-fold ratios of barium.<sup>7</sup> CDTA is so reactive towards calcium, relative to barium, that separation or masking is not necessary. In this case the availability of a specific indicator, Calcichrome,<sup>7</sup> for calcium provided a very satisfactory method for the determination of calcium in the presence of barium.

Chaberek and Martell<sup>8</sup> synthesised the reagent ethylenediamine-*N,N,N',N'*-tetrapropionic acid (EDTP) and showed that its copper<sup>II</sup> chelate is relatively strong and its calcium chelate weak. Subsequently<sup>9</sup> they showed that the replacement of

one *N*- and one *N'*-acetic acid group of EDTA by propionic acid groups produces a reagent which is still highly reactive towards  $\text{Cu}^{\text{II}}$  relative to other ions. In a later paper, Courtney, Chaberek and Martell<sup>10</sup> carried out further systematic studies and established the dissociation constants of some metal complexes of these and allied reagents. It is not possible to discuss these studies here, but the contrast between EDTA and EDTP is shown in Table I.

TABLE I. COMPARISON OF EDTA AND EDTP AS COMPLEXIMETRIC REAGENTS  
(Log Dissociation Constant Values)

	$\text{H}_{(1)}^+$ $\text{H}_{(2)}^+$ $\text{H}_{(3)}^+$ $\text{H}_{(4)}^+$									
	EDTP	3.0	3.43	6.77	9.60					
	EDTA	2.0	2.67	6.13	10.26					
	$\text{Cu}^{2+}$	$\text{Fe}^{3+}$	$\text{Ni}^{2+}$	$\text{Zn}^{2+}$	$\text{Co}^{2+}$	$\text{Fe}^{2+}$	$\text{Cd}^{2+}$	$\text{Mn}^{2+}$	$\text{Mg}^{2+}$	
EDTP	15.4	14.4	9.7	7.8	7.6	6.2	6.0	4.7	1.8	
EDTA	18.3	25.0	18.4	16.1	16.1	14.3	16.4	13.4	8.7	
$\Delta \log K$	2.9	10.6	8.7	8.3	8.5	8.1	10.4	8.7	6.9	

From this it will be observed that EDTP always forms weaker complexes with cations than does EDTA, and that only the copper<sup>II</sup>, iron<sup>III</sup> and nickel complexes are sufficiently stable to provide the basis for a reliable compleximetric method with this reagent. However, the most significant feature is that whereas the stability of the copper<sup>II</sup> complex has decreased by less than 3 orders of magnitude, that of most other ions has decreased by 8–10 orders. Only the iron<sup>III</sup> complex is comparable in strength with the copper<sup>II</sup> complex. On this basis, and on the availability of the nearly specific copper<sup>II</sup> metallochromic indicator, Fast Sulphon Black F,<sup>11</sup> it was first suggested that it might be possible to devise a highly selective compleximetric titration of copper with EDTP as the titrant.<sup>12</sup>

Our preliminary findings<sup>1</sup> were reported for the microscale because sufficient reagent was not available for larger-scale work. In that case the equally selective indicator, Ponceau 3R,<sup>13</sup> was used at pH 9. The titration was performed successfully to an end-point that was only slightly inferior to that obtained with the stronger EDTA. Interference studies were carried out with  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Al}^{3+}$ . When EDTA was used as titrant, all the cations except  $\text{Ni}^{2+}$  titrated additively with the  $\text{Cu}^{\text{II}}$ , despite their non-interaction with the indicator. With EDTP, however, no interference was found from 10-fold amounts of  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ , or from five-fold amounts of  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  or  $\text{Cd}^{2+}$ ; in no case was an upper limit sought. Manganese was tolerated up to a two-mole ratio. Difficulty was experienced in holding the  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Al}^{3+}$  in solution at pH 9. However, addition of fluoride held the aluminium harmlessly in solution; and raising the pH to 10 allowed the titration of copper in the presence of a one-fold amount of zinc with a considerably impaired end-point, because the functioning of the indicator is less satisfactory at pH 10. Nickel interfered, as expected, because it reacts with both titrant and indicator.

The originally suggested indicator, Fast Sulphon Black F,<sup>11</sup> may not be used successfully because the indicator action is sluggish even with EDTA, and markedly more so with the weaker EDTP. Working with 0.02M solutions of  $\text{Cu}^{\text{II}}$ , and EDTP on a normal scale of working it was found possible to hold zinc and lead in solution at pH 9, by substituting the formerly used ammonia-ammonium chloride

buffer with an ammonia-ammonium acetate buffer at pH 9. The acetate ion is effective in holding these ions in solution as their more soluble acetate complexes. In all titrations with Ponceau 3R as indicator, it is recommended that only the minimum amount of buffer necessary to obtain a clear solution free from any trace of precipitate should be used. The indicator action falls off in buffer solutions of high concentration—a factor particularly noted elsewhere.<sup>13</sup>

Although the Ponceau 3R indicator works reliably when used under the correctly controlled conditions, it seemed desirable to try and devise a considerably more flexible experimental procedure with an alternative indicator system. The choice was limited to indicators which react only with copper or with very few other ions. With this in mind, 1,3-dimethyl-4-imino-5-oximino-alloxan, recently described by Burger<sup>14</sup> as a selective spectrophotometric reagent for  $\text{Cu}^{\text{II}}$ , was examined; but the extinction coefficient of the copper complex ( $\epsilon_{382\text{m}\mu} = 5050$ ) was much too low for indicator purposes; and though the free reagent fluoresces appreciably,  $\text{Cu}^{\text{II}}$  does not quench the fluorescence completely, so that the compound may not be used here as a metallo-fluorescent indicator. Because of the observations by Wilkins<sup>15</sup> concerning the pH ranges of fluorescence-quenching by  $\text{Cu}^{\text{II}}$  and other ions of the indicator Calcein Blue, this compound was examined, but the action relative to Ponceau 3R was too sluggish even with EDTA to warrant adoption. The *o*-dianisidine-*N,N,N',N'*-tetra-acetate indicator of Belcher, Rees and Stephen<sup>16</sup> functioned much better, but lacked selectivity. Several other indicators examined were equally unsatisfactory relative to Ponceau 3R, but finally Glycine Thymol Blue, first proposed as a metallochromic indicator by Körbl, Kraus and Přibil,<sup>17</sup> proved to be suitable. In solutions of  $\text{pH} \leq 5.8$  this indicator is yellow and its copper complex is blue. At  $\text{pH} > 8$  the indicator itself is blue. It is therefore used over the range  $\text{pH} 6-8$ , *i.e.*, in nearly neutral solution. The colour change when using this indicator is from blue to yellow-green or green depending on the amount of copper present. Less difficulty was experienced in holding various ions such as  $\text{Pb}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ , *etc.*, in solution with this indicator because its buffer region was lower and the end-points were not impaired by the presence of varying amounts of buffer. Consequently, on the whole, this indicator is preferable to Ponceau 3R, though many operators may prefer the colour contrast of the latter indicator, particularly when dealing with large amounts of copper in the absence of foreign ions. One unquestioned advantage of the Glycine Thymol Blue indicator, however, is that nickel no longer interferes very seriously, as it does with Ponceau 3R, because it does not react with the indicator. Because of its relatively stable complex with EDTP it does, however, tend to give slightly high results. At the 0.5:1 (Ni:Cu) level results are high by *ca.* 1% whilst at 1:1, 2:1 and 4:1 results are high by 2.4, 3 and 5%, respectively.

Table II summarises a series of results obtained in the analysis of a series of unknowns which contained foreign ions which interfere seriously when EDTA is used as titrant. Both indicator systems were used. These results indicate clearly the selectivity of the titrant-indicator systems in both cases. In particular the freedom from *additive* interference, except in the case of nickel, amply demonstrates this. The average error (ignoring sign and excluding nickel) in these determinations is 0.44%. These titrations were carried out with 0.02M titrant with not more than 5 ml of 0.02M  $\text{Cu}^{\text{II}}$ , diluted to 100 ml, before titration. Consequently, the accuracy and precision of the method are entirely satisfactory. No attempt was made to use

titrant and copper<sup>II</sup> solutions stronger than 0.02M, because the intense absorption of the Cu-EDTP chelate would screen the end-point. In this respect the EDTP titrant is only slightly less tolerant than EDTA. The effect of Fe<sup>III</sup> was not examined, but it would obviously interfere by precipitation and additive reaction with the titrant. Both eventualities should be eliminated by the addition of triethanolamine or possibly of fluoride ion. Similar experiments with EDTA give nearly quantitative recovery of both ions, thus indicating 100% interference by these ions in a Cu<sup>II</sup>-EDTA determination.

TABLE II. SERIES OF "UNKNOWN'S"  
Determination of copper<sup>II</sup> with EDTP in presence of heavy metals, Ponceau 3R (P.R.) and Glycine Thymol Blue (G.T.B.) as indicators. Results reported in milliequivalents  $\times 10^2$

Titration system (pH in brackets)	Foreign ion, <i>meq</i> $\times 10^2$	Copper taken, <i>meq</i> $\times 10^2$	Copper found, <i>meq</i> $\times 10^2$	Error, %
G.T.B (5.8)	—	4.40	4.38	0.45
	—	8.00	7.94	0.75
	—	2.60	2.58	0.77
P.R. (9)	Mn <sup>2+</sup> 10.00	10.00	9.92	0.80
	Pb <sup>2+</sup> 1.70	15.00	14.98	0.13
P.R. (9) + F <sup>-</sup>	Al <sup>3+</sup> 4.00	10.00	10.00	0.00
P.R. (9)	Mg <sup>2+</sup> 20.00	10.00	10.00	0.00
	Cd <sup>2+</sup> 10.00	9.00	8.98	0.22
	Zn <sup>2+</sup> 10.00	9.44	9.38	0.64
G.T.B (5.8)	Zn <sup>2+</sup> 4.00	6.00	6.04	0.66
	Al <sup>3+</sup> 4.00	9.40	9.40	0.00
	Pb <sup>2+</sup> 10.00	5.00	4.98	0.40
	Al <sup>3+</sup> 2.0 +			
	Cd <sup>2+</sup> 10.0	5.40	5.37	0.55
	Al <sup>3+</sup> 1.0 +			
	Zn <sup>2+</sup> 2.0	7.00	7.00	0.00
	Pb <sup>2+</sup> 4.0 +			
	Cd <sup>2+</sup> 5.0	2.20	2.18	0.90
	Zn <sup>2+</sup> 2.0 +			
	Cd <sup>2+</sup> 4.0	2.80	2.28	0.76
	Ni <sup>2+</sup> 2.5	5.00	5.06	1.2
	Ni <sup>2+</sup> 5.0	5.00	5.12	2.4
	Ni <sup>2+</sup> 10.00	5.00	5.16	3.2
Ni <sup>2+</sup> 20.00	5.00	5.26	5.2	

#### Colour changes at equivalence

A considerable difference is observed in the colour change of both indicators at the end-point of EDTA and EDTP titrations. With EDTA-Ponceau 3R the end-point is from yellow-green to bright light red, but with EDTP it is from blue to red-violet, irrespective of whether the buffer is based on ammonium chloride or ammonium acetate. Similarly with Glycine Thymol Blue, the EDTA end-point is from blue to yellow-green, whilst with EDTP the change is from a deeper blue to green or green-yellow in more dilute solutions.

Fig. 1a shows the absorption curves of (i) Ponceau 3R, (ii) its copper complex, (iii) Cu-EDTA, and (iv) Cu-EDTP at pH 9. In Fig. 1b the appropriate curves have been added algebraically to illustrate the colours to be obtained a few drops before,



and a few drops beyond the equivalence point in both systems, with Ponceau 3R as indicator. Curve *A* represents the absorption spectrum of the solution of a few drops of titrant before the end-point. There is a sharply defined band at  $455\text{ m}\mu$  arising from the Ponceau- $\text{Cu}^{\text{II}}$  complex, and a broad band of low intensity *ca.*  $700\text{--}760\text{ m}\mu$  from

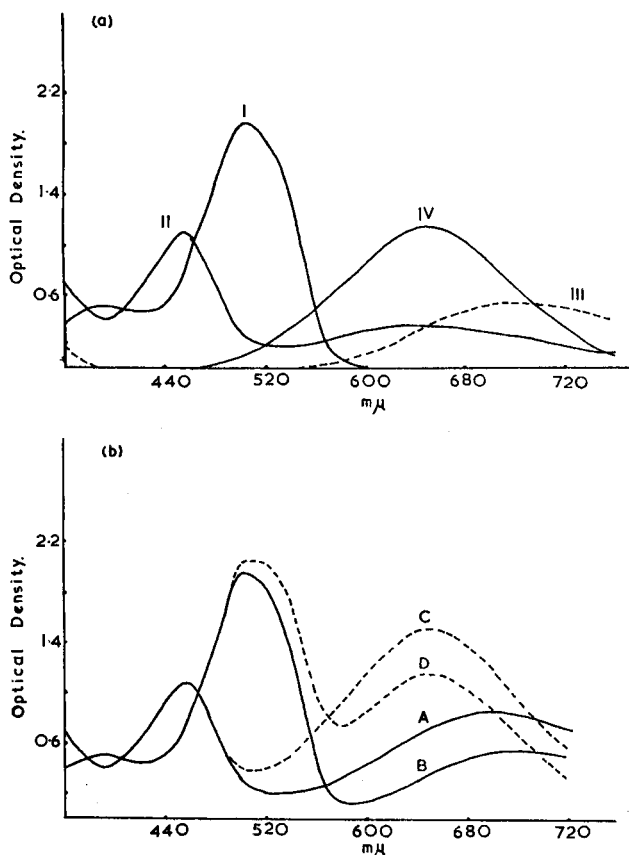


FIG. 1.—Absorption spectra of end-point species in Cu-EDTP-Ponceau 3R system.  
 (a) (i) Free Ponceau 3R at pH 9. (ii)  $\text{Cu}^{\text{II}}$ -Ponceau 3R at pH 9. (iii)  $\text{Cu}^{\text{II}}$ -EDTA at pH 9.  
 (iv)  $\text{Cu}^{\text{II}}$ -EDTP at pH 9.

(b) *A*: Spectrum before EDTA end-point. *B*: Spectrum after EDTA end-point.  
*C*: Spectrum before EDTP end-point. *D*: Spectrum after EDTP end-point.

$\text{Cu}^{\text{II}}$ -EDTA. Beyond the end-point (Curve *B*) the band at  $455\text{ m}\mu$  disappears suddenly, and a new band from free Ponceau 3R appears *ca.*  $500\text{ m}\mu$ , whilst the background at  $700\text{--}760\text{ m}\mu$  decreases slightly, but is still of lower intensity than the indicator band at  $455\text{ m}\mu$ . Curve *C* represents the situation a few drops before equivalence in the EDTP titration. A very similar Ponceau- $\text{Cu}^{\text{II}}$  band exists at  $500\text{ m}\mu$ , but the background band of  $\text{Cu}^{\text{II}}$ -EDTP at  $650\text{ m}\mu$  is of higher intensity, and is close enough to the indicator band to merge with it. Beyond the EDTP end-point (Curve *D*) the band at  $455\text{ m}\mu$  disappears less suddenly, and the band at  $500\text{ m}\mu$  from free Ponceau 3R appears, but is now merged with the broad band of the Cu-EDTP background at  $650\text{ m}\mu$ . Consequently there is a much shallower and narrower “hole” produced in the absorption spectrum at the end-point of an EDTP titration (curve

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C → D) than in an EDTA titration (curve A → B) where the indicator bands are always the more intense.

### Selectivity of the EDTP titrant

It is problematical whether EDTA can react more than tetradentately with  $\text{Cu}^{\text{II}}$  because of the normal square coplanar habit of the cupric ion. Consequently, the removal of two acetic acid groups, one from each nitrogen atom, as in ethylenediamine-*N,N'*-diacetic acid, EDDA, produces little change in the stability constant of the copper complex, ( $\log K_{\text{Cu-EDTA}} = 18.3$ ,  $\log K_{\text{Cu-EDDA}} = 16.2$ ) whereas the change in the  $\log K$  value for most other metals which usually have a hexaco-ordinate nature

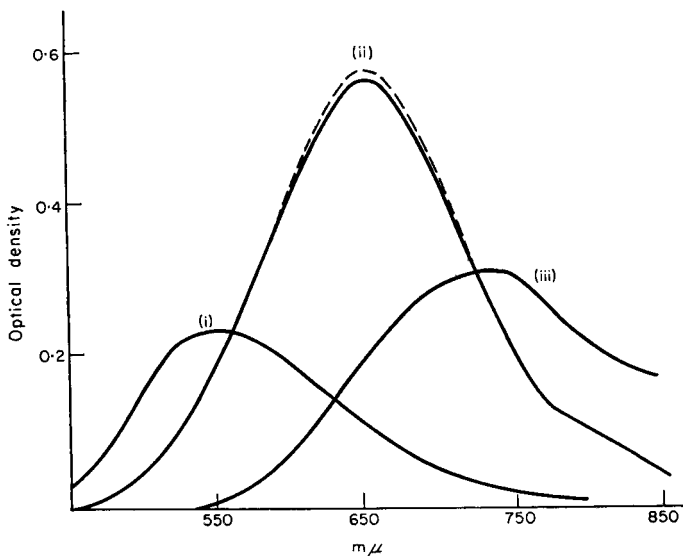


FIG. 2.—Spectra of  $\text{Cu}^{\text{II}}$  species  
 (i)  $\text{Cu}^{\text{II}}$ -ethylenediamine 1:2; (ii)  $\text{Cu}^{\text{II}}$ -EDTP 1:1 and 1:2 (dotted line);  
 (iii)  $\text{Cu}^{\text{II}}$ -EDTA 1:1

is more sharply defined. There appear to be good grounds for arguing that the chelating efficiency of EDTA towards most metal cations lies primarily in the five-membered acetic acid-imino nitrogen ring, rather than in the dative-bonded five-membered ring across the ethylene bridge. But this does not appear to be the case with copper<sup>II</sup>; for if the size of the "primary" ring is increased by forming the corresponding tetrapropionic or dipropionic compounds, the  $\log K$  value for copper<sup>II</sup> decreases further only slightly, whereas that of most other metals decreases very markedly (*cf.* Table 1). The presence of the five-membered ring with the ethylenediamine part of the molecule is sufficient to stabilise the square coplanar copper<sup>II</sup> ion. In this connection it is interesting to compare, at pH 9, the absorption spectra of (i) the Cu-bis-ethylenediamine, (ii) the Cu-EDTP and (iii) the Cu-EDTA complexes (Fig. 2). This shows that the second of these complexes is, as far as the spectra are concerned, half-way between the other two. The area under the curves is practically additive, and the absorption band is more intense than that of the others and more narrowly peaked. Thus the effect of substituting propionic for acetic acid groups is to

weaken the overall strength of the chelate only slightly in the case of Cu<sup>II</sup>, because the new reagent reacts more in the "normal" fashion of ethylenediamine. The EDTP chelate is, of course, stronger than that of ethylenediamine, partly because the inductive effect of the *N*-carboxylic acid on the availability of lone pair electrons on the nitrogen atoms may perhaps be favourable, but more certainly because of the entropy effect concomitant with 1:1 reaction in the case of EDTP as opposed to 2:1 in the case of ethylenediamine. Ethylenediamine does, of course, form a 1:1 complex with Cu<sup>II</sup>, and its absorption maximum at pH 9 falls almost exactly half way between Cu-EDTP and Cu(En)<sub>2</sub>; its intensity is lower than that of Cu(En)<sub>2</sub>, and the band falls almost wholly within that of Cu<sup>II</sup>-EDTP. The upper (dotted) peak in Fig. 2 at 650 m $\mu$  gives no indication of 2:1 complex formation between Cu<sup>II</sup> and EDTP, but only exhibits a slight hyperchromic effect from increased association of the 1:1 complex in the presence of a one-fold excess of reagent.

## EXPERIMENTAL

### Reagents

**0.02M EDTP:** Dissolve 6.967 g of EDTP in water containing 20 ml of 2M NaOH and dilute to 1 l. Both samples of pure acid prepared in this laboratory and a commercial sample obtained from the Dojindo Co. of Japan were used. The latter had an apparent purity >100% because it contained some di-acid, which is nearly equally reactive and selective towards copper<sup>II</sup>. Consequently the titrant should be standardised against a copper solution of known equivalence.

**pH 9 Buffer:** Dissolve 154 g of ammonium acetate and 12 ml of concentrated ammonia in water and dilute to 1 l. Check the pH on a pH meter.

**pH 5.8 Buffer:** Dissolve 150 g of sodium acetate and 4.6 ml of glacial acetic acid in water and dilute to 1 l. Check the pH on a pH meter.

**Ponceau 3R indicator:** Aqueous solution, 0.1%.

**Glycine Thymol Blue indicator:** Aqueous solution, 0.1% freshly prepared.

### Procedure

Pipette an aliquot of Cu<sup>II</sup> solution equivalent to 5 ml of 0.02M Cu<sup>II</sup> into a 250 ml conical flask, add 5 ml of pH 5.8 buffer and make up the volume to ca. 100 ml. Add 10 drops of freshly prepared 0.1% Glycine Thymol Blue indicator, and titrate with 0.02M EDTP till the blue colour changes to green-yellow or green, depending on the copper content. The end-point is sharply defined, though of low colour contrast when larger amounts of copper are involved.

When Ponceau 3R is used proceed as above, but add only the minimum amount of pH 9 buffer to obtain a clear solution, and then 0.5 ml more. Dilute as above, and use 6 drops of 0.1% Ponceau 3R indicator. Titrate from yellow-green or green depending on the copper concentration, to red-purple of purple-blue. The end-point is sharply defined, and with practice can be located to within 1 drop.

**Zusammenfassung**—Ein neues selektive Polyaminicarboxylsäure-Metallochromindikator-System wird vorgeschlagen um Kupfer genau zu titrieren. In wässrigem Medium wird durch Pb, Zn, Cd, Al, Mg, Ca, Ba, Sr, etc keine Störung verursacht. Trennungen oder Zugabe von Maskierungsmitteln ist unnötig. Nickel stört nur sehr wenig.

**Résumé**—Les auteurs proposent un nouvel indicateur, acide polyamino-carboxylique système pour le titrage précis du cuivre en solution aqueuse en présence d'autres ions métalliques tels que: Pb, Zn, Cd, Al, Mg, Ca, Ba, Sr, etc. La méthode n'exige ni séparations, ni addition d'agents complexants. Le nickel gêne peu.

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# VOLTAMMETRY OF SILVER IN MOLTEN SODIUM NITRATE-POTASSIUM NITRATE

## USE OF A CONTROLLED-POTENTIAL POLAROGRAPH AND A PLATINUM QUASI-REFERENCE ELECTRODE

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**Summary**—The voltammetry of silver in molten sodium nitrate-potassium nitrate has been investigated over the temperature range 246°–326°. The polarograms were recorded by means of a controlled-potential polarograph and a stationary platinum microelectrode coupled with a platinum quasi-reference electrode. A third platinum electrode, which was isolated, was the counter electrode. The reduction of  $\text{Ag}^+$  to  $\text{Ag}^0$  proceeds reversibly, and the limiting current is proportional to the concentration of silver. The activation energy for the current-limiting process has been determined to be approximately 6.4 kcal/mole.

THE polarography of redox systems in fused salts has been discussed extensively.<sup>1-5</sup> The majority of the fused salts have been either chlorides or nitrates. Both dropping and stationary indicator microelectrodes of various types have been used. The polarographs mostly appear to be of conventional design whereby the cell current flows through the reference electrode, which must either have a large surface area or be non-polarisable.

In this study, the voltammetry of silver in molten sodium nitrate-potassium nitrate was investigated by means of a controlled-potential polarograph<sup>6</sup> and a platinum quasi-reference electrode.<sup>7</sup> Silver was selected mainly because of convenience, and because the redox reaction  $\text{Ag}^+ + e \rightarrow \text{Ag}^0$  is reversible. Knowledge of the behaviour of the three-electrode system toward a known redox reaction in the molten electrolyte is necessary before more complex reactions can be studied with the system. The advantage of the controlled-potential polarograph, especially in fused-salt voltammetry, is that an inert substance can be used as a quasi-reference electrode because the cell current does not flow through the reference electrode. This quasi-reference electrode therefore remains at some constant potential as the current-voltage curve is recorded. Half-wave potentials relative to the quasi-reference electrode are strictly arbitrary; nevertheless, they are reproducible and should be especially useful in work with corrosive melts.

### EXPERIMENTAL

An equimolar  $\text{NaNO}_3$ - $\text{KNO}_3$  eutectic was prepared by mixing 213 g of  $\text{NaNO}_3$  and 253 g of  $\text{KNO}_3$  in a 1-litre tall-form beaker.

The ORNL model Q-1988 controlled-potential polarograph<sup>6</sup> was used to record the current-voltage curves.

The cell assembly consisted of a 1-litre, tall-form, Pyrex beaker that contained 466 g of equimolar  $\text{NaNO}_3$ - $\text{KNO}_3$  eutectic and accurately weighed quantities of  $\text{AgNO}_3$ . For heating, the cell was placed

\* Operated by Union Carbide Corporation for the Atomic Energy Commission.

in a stainless steel beaker in which was previously placed a small circular resistance heater of about 1000-w capacity. This assembly was then placed in a 5-inch (I.D.) resistance furnace. The temperature of the furnace was controlled to about  $\pm 2^\circ$  by means of a Wheelco model 407 temperature controller. Fine control of the temperature to  $\pm 1^\circ$  was achieved by regulating manually, through a Variac, the temperature of the small resistance heater. The temperature was measured with a mercury thermometer contained in a Pyrex well. In some of the experiments, a platinum-platinum-rhodium(10%) thermocouple was substituted. The thermocouple was also contained in a Pyrex well; its output was measured with a Leeds and Northrup precision temperature potentiometer connected through an ice bath to the thermocouple.

The 0.5-mm diameter platinum wire, used as the indicator microelectrode, was inserted in a 10-cm length of ceramic thermocouple insulator, which was then sheathed in 4-mm Pyrex tubing. The exposed electrode protruding through the sealed end of the Pyrex tubing was 7 mm long; the exposed area of the electrode was calculated to be 11 mm<sup>2</sup>. The platinum quasi-reference electrode was prepared in a similar manner; the protruding end was in the form of a spiral. The isolated counter electrode (anode) consisted of a third platinum wire (0.5 × 30 mm) that dipped into NaNO<sub>3</sub>-KNO<sub>3</sub> eutectic contained in a 12-inch by 8-mm Pyrex tube. An asbestos fiber was sealed through the bottom of the tube to serve as the conducting bridge while the tube was immersed in the cell. The depths of the melts in the counter-electrode compartment and in the cell were kept the same.

The experimental procedure for obtaining the current-voltage curves for silver in fused nitrates was relatively simple. The Pyrex beaker that contained the eutectic was heated in the furnace to the desired temperature. The melt was sparged with argon before and after the addition of the silver nitrate, and an inert atmosphere was maintained over the melt. The three electrodes were inserted in the melt and allowed to attain thermal equilibrium. The current-voltage curves were then recorded. The concentration of silver in the melt was changed by adding silver nitrate. The concentration of silver was calculated after ascertaining the volume of 466 g of the melt which, in this case, is 250 ml.

No particular difficulty was encountered in maintaining a reproducible surface on the microelectrode. At the end of each experiment, the deposited silver was removed anodically from the electrode by applying a potential of +0.5 v vs. the quasi-reference electrode until the cell current decreased to the residual-current value. All the electrodes were then removed from the melt, cooled, rinsed with distilled water to remove the solidified eutectic, dried, and stored in glass tubes.

## RESULTS AND DISCUSSION

Current-voltage curves of silver obtained at a stationary microelectrode *vs.* the quasi-reference electrode are shown in Fig. 1. Because of the three-electrode system that was used, the current did not flow through the quasi-reference electrode. Consequently, the quasi-reference electrode remained unpolarised and at the same potential (probably close to zero) throughout the recording of the curve. As shown by Curve B of Fig. 1, the limiting current is not constant but, instead, fluctuates randomly about an average value. The fluctuations are probably caused by uneven growth of dendritic deposits of silver and to thermal effects that produce convective motion of the molten electrolyte in the vicinity of the indicator electrode.

The effect of RC filtering on the shape of current-voltage curves is demonstrated by the difference between Curves B and C of Fig. 1. The filter is a parallel-T RC network<sup>6</sup> that rejects frequencies that are 1, 2, 4 and 10 times a null frequency of 0.2 cycle/sec. The filter was designed specifically for use with a dropping-mercury electrode. As noted from Curve C, however, the filter is very effective in improving the general definition of the current-voltage curve even though the fluctuations in current (Curve B) are random. There is some time lag in the RC filter which results in a slight shift of the half-wave potential. This shift is of no disadvantage in practice because the relationship between observed limiting current and concentration is linear for a fixed amount of filtering. Efforts to record derivative curves of silver in the melt were not successful. The current fluctuations, even after RC filtering, were of sufficient magnitude to distort, and in some cases almost to mask out, the derivative peaks.

The half-wave potential of the  $\text{Ag}^+ + e \rightarrow \text{Ag}^0$  reduction in the  $\text{NaNO}_3\text{-KNO}_3$  melt is approximately  $-0.1$  v vs. the quasi-reference electrode. This value agrees favourably with that reported previously<sup>2</sup> and depends, of course, on such factors as the use of RC filtering, the temperature of the melt, and the concentration of  $\text{Ag}^+$ . The half-wave potential should become less negative with increases in the temperature of the melt and in the concentration of the diffusing species.<sup>4</sup> Qualitatively, these

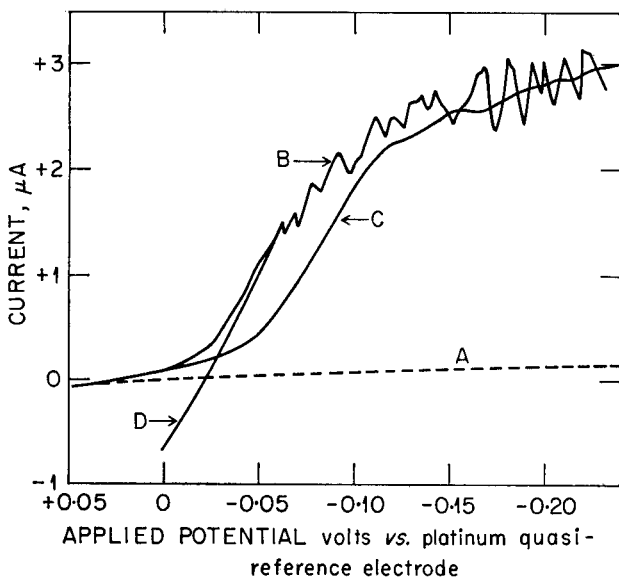


FIG. 1.—Automatically recorded current-voltage curves of  $\text{Ag}^+$ .

Concentration of  $\text{Ag}^+$ ,  $1.4 \times 10^{-4} M$

Temperature,  $246^\circ\text{C}$

Curve A, residual-current

Curve B, unfiltered

Curve C, RC-filtered

Curve D, reverse-scan

shifts were observed; however, they did not agree very well with those predicted. This poor agreement is probably due in part to the uncertainty in locating the half-wave point. The melt began to react at the microelectrode at approximately  $-0.5$  v vs. the quasi-reference electrode.

The equation that expresses the relationship between the limiting current,  $i_l$ , and concentration,  $C$ , of reducible ion at a solid microelectrode is<sup>8</sup>

$$i_l = \frac{nFADC}{l} = kAC \quad (1)$$

where  $k$  is the area-independent limiting-current constant,  $D$  is the diffusion coefficient of the diffusing species, and  $l$  is the effective thickness of the diffusion layer. The remaining terms are  $n$ , the electron change;  $A$ , the area of the electrode; and  $F$ , the faraday.

Values of  $k$  for the reduction of silver at  $246^\circ$ ,  $286^\circ$ , and  $326^\circ$  are given in Table I. The over-all relative standard deviation of the  $k$  values is about 14%, which demonstrates, in agreement with equation (1), that the limiting current is proportional to the concentration of silver and that the current-voltage curves are analytically useful.

The calculation of  $l$ , by means of equation (1) and based on an assumed value for  $D$  of  $10^{-5}$  cm<sup>2</sup>/sec at 246°, gives a value for  $l$  of about 0.1 mm. This value is reasonable and agrees favourably with previous values of  $l$  obtained at solid microelectrodes.<sup>5,8</sup>

TABLE I.—EFFECT OF TEMPERATURE ON THE VALUE OF THE LIMITING-CURRENT CONSTANT,  $k$ , AT VARIOUS CONCENTRATIONS OF Ag<sup>+</sup> (Indicator electrode area, 11 mm<sup>2</sup>)

Temperature, °C	Concentration of Ag <sup>+</sup> , mM	$k^*$
246	0.140	1.62
	0.140	1.30
	0.300	1.39
	0.785	1.16
		av. 1.37
286	0.132	2.60
	0.214	2.04
	0.350	2.12
	0.350	1.68
	0.890	1.63
	4.60	1.78
		av. 1.98
326	0.128	3.40
	0.218	3.32
	0.332	2.75
		av. 3.15

$$* k = \frac{\mu A}{(\text{mm}^2) \left( \frac{\mu\text{mole}}{\text{cm}^3} \right)}$$

The relationship between the diffusion coefficient,  $D$ , and temperature is shown by the equation<sup>5</sup>

$$D = Ae^{-E/RT} \quad (2)$$

where  $A$  is the frequency factor and  $e^{-E/RT}$  is the Boltzmann factor. By taking logarithms, *i.e.*,

$$\log D = \frac{-E}{2.3 RT} + \log A \quad (3)$$

and by plotting  $\log D$  (or  $\log k$ , since only  $D$  is temperature-dependent) *vs.*  $1/T$ , the activation energy  $E$  can be calculated. Such a plot is shown in Fig. 2, in which the logarithms of the averages of the  $k$  values at 246°, 286°, and 326° are plotted *vs.*  $1/T$ . From the slope of the line, an  $E$  value of 6.4 kcal/mole is obtained. This value can be compared with other activation energies relating to current-limiting processes in fused salts determined in essentially the same manner and ranging from 3.0 to 6.3 kcal/mole.<sup>1,5</sup>



The equation that describes the rising portion of the wave for a reversible process is<sup>4</sup>

$$E = E_m^\circ - \frac{RT}{nF} \left( \ln \frac{k_s}{f_s} \right) + \frac{RT}{nF} (\ln (i_l - i)) \quad (4)$$

where  $E$  is the applied potential;  $E_m^\circ$ , the standard potential of the solid silver;  $R$ , the gas constant;  $T$ , the temperature in  $^\circ\text{K}$ ;  $n$ , the electron change;  $F$ , the faraday;  $k_s$ , the proportionality constant;  $f_s$ , the activity coefficient of  $\text{Ag}^+$  at the electrode surface;  $i_l$ , the limiting current;  $i$ , the current on the rising portion of the current-voltage curve at any applied potential,  $E$ . For a reversible reaction, a plot of  $E$  vs.

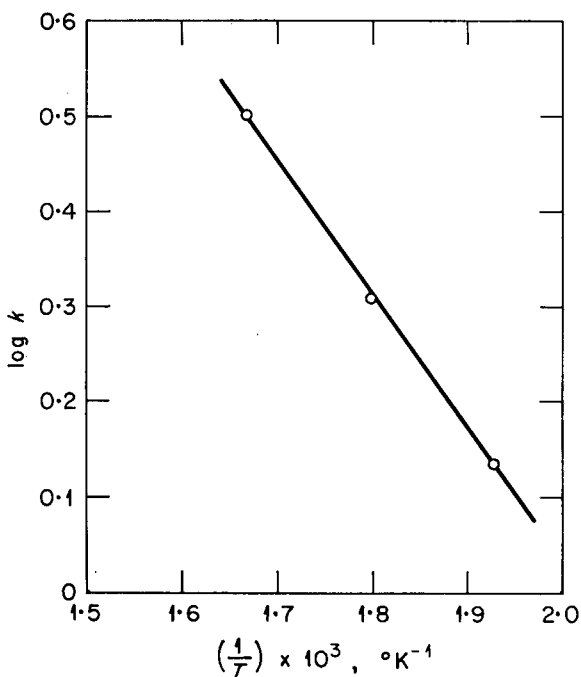


FIG. 2.—Plot of  $\log k$  vs.  $1/T$ ;  
slope of line,  $-1400$

$\log (i_l - i)$  should be a straight line having the slope  $2.3 RT/nF$  if  $k_s$  and  $F_s$  are constant. Such plots were made of the curves of silver recorded at  $246^\circ$ ,  $286^\circ$  and  $326^\circ$ . From the majority of the plots,  $n$  values that ranged from about 0.85 to 1.2 were calculated. The average  $n$  value was very nearly 1, and no particular trend with temperature was observed. The fluctuation of the  $n$  values appears to be in accord with the suggestions made by Laitinen, Liu and Ferguson<sup>3</sup> that a constant-thickness, Nernst diffusion layer is not strictly maintained around the microelectrode. Agreement of the results with equation (4) is therefore reasonable in view of the uncertain nature of the mass-transfer process. It is also demonstrated that such an analysis can be used, with caution, to estimate the value of  $n$  in an unknown reduction.

Reversibility is further substantiated by the fact that the stripping curve (Curve D of Fig. 1) does not hesitate as it passes through the zero-current axis. In all the reverse-scan tests, the deposited silver stripped off rapidly, which indicated that the

formation of alloy was not appreciable and that the silver deposited on the platinum microelectrode at unit activity.

To test the effect of scan rate, current-voltage curves were recorded at rates from 25 to 100 mv/min. No maximums or spurious peaks were observed. Apparently, steady-state conditions are achieved very rapidly in the melt. The limiting current of silver, within the precision of the measurements, was essentially independent of the scan rates in the range of scan rates used. Generally, however, curves obtained at 50 mv/min were somewhat better defined; therefore, the majority were recorded at this scan rate.

**Zusammenfassung**—Die Bestimmung von Silber mit einem Voltmeter wurde im Temperaturbereich 246 bis 326° in geschmolzenem Natriumnitrat-Kaliumnitrat untersucht. Die Polarogramme wurden mittels eines Polarographs mit gesteuertem Potential aufgezeichnet; eine stationäre Platinmicroelektrode war mit einer Platinquasireferenz-elektrode gekoppelt. Eine dritte, isolierte, Platinelektrode funktionierte als Gegenelektrode. Die Reduktion von  $\text{Ag}^+$  zu  $\text{Ag}^0$  verfährt reversibel, und der Grenzstrom ist der Silberkonzentration proportional. Die Aktivierungsenergie des strombeschränkten Prozesses war ungefähr 6,4 Kcal/mol.

**Résumé**—La voltamétrie de l'argent dans le nitrate de sodium-nitrate de potassium fondu, a été étudiée aux températures entre 246°C et 326°C. Les polarogrammes étaient enregistrés au moyen d'un polarographe à potentiel contrôlé et d'une microélectrode stationnaire reliée à une électrode de quasi-référence en platine. La contre-électrode était une troisième électrode en platine, isolée. La réduction de l' $\text{Ag}^+$  en  $\text{Ag}^0$  se produit de façon réversible et le courant limite est proportionnel à la concentration d'argent. L'énergie d'activation pour le processus limitant le courant a été déterminée égale à environ 6.4 kcal/mole.

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## THE CHRONOPOTENTIOMETRIC BEHAVIOUR OF ANTIOXIDANTS AND ANTIOZONANTS AT THE GRAPHITE ELECTRODE

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**Summary**—The chronopotentiometric behaviour of the phenylenediamines, dihydroxybenzenes, and several commercial antioxidants and antiozonants, has been studied using a graphite indicating electrode. The advantages of using non-aqueous solvents such as ethanol and acetonitrile in such work are pointed out—in particular, a significant increase in the precision of the technique arising from the ability of the solvent to wet the electrode efficiently.

### INTRODUCTION

SEVERAL colorimetric methods are available for the identification and determination of amine<sup>1</sup> and phenolic<sup>2</sup> antioxidants and antiozonants in polymers, but they are often time-consuming and are generally limited in scope to a few members of a particular chemical class.

Although nearly all the commonly used polymer antioxidants and antiozonants contain an electro-active functional group, and voltammetric methods would appear to be generally useful in this field, methods for the determination of *N,N'*-di-*sec*-butyl-*p*-phenylenediamine and *N*-butyl-*p*-aminophenol in gasoline<sup>3</sup> and of 2,6-di-*tert*-butyl-*p*-cresol<sup>4</sup> have been the only such applications reported.

Recently, the use of graphite electrodes in voltammetry<sup>5-8</sup> and chronopotentiometry<sup>9,10</sup> has been described. This electrode has been found to possess certain advantages, particularly in the analysis of organic compounds, but has suffered from the disadvantage of being extremely sensitive to variations in the experimental conditions. Most authors have recommended procedures involving re-surfacing of the electrode between runs, followed by rinsing in several solutions before insertion in the sample solution. Elving<sup>11</sup> has reported that many of the previous difficulties have been solved by immersing the electrode in a wetting agent before use in an aqueous solution.

Few applications of the method to non-aqueous solvents have been reported, although the system presents certain interesting advantages. First, of course, is the extension of the method to organic compounds insoluble in water. Also of importance is the fact that many nonaqueous solvents are found to wet a graphite electrode efficiently, and thus improve the precision of the method considerably.

This paper describes the results of an investigation of the chronopotentiometry of a number of commercial antioxidants and antiozonants in supporting electrolyte solutions of LiCl and LiClO<sub>4</sub> in acetonitrile and 95% ethanol.

## EXPERIMENTAL

*Reagents*

*LiCl*: Reagent Grade, J. T. Baker Co.

*LiClO<sub>4</sub>*: Reagent Grade, G. F. Smith Chemical Co.

*Hydroquinone*: C. P., Fisher Scientific Co.

*Catechol*: Practical, Eastman Kodak Co.

*Resorcinol*: Practical, The Matheson Co., Inc.

*o*-, *m*- and *p*-*Phenylenediamine*: Eastman Kodak White Label Grade.

All the antioxidants and antiozonants were typical commercial samples and were used as received, without further purification.

*Apparatus*

The apparatus used in the chronopotentiometric work described in this paper was similar in principle to that reported by Reilley.<sup>12</sup> The following components were used:

*Current source*: Kintel Meter Calibrator, Model MIDA-10, Kintel Co., San Diego, California.

*Potential measurement*: Leeds and Northrup Co. pH Meter, Cat. No. 7664.

*Recorder*: Brown Potentiometer, 20-mV. Range, 8 in./min Chart Speed, Minneapolis Regulator Co., Brown Instruments Div.

*Reference electrode*: Beckman high resistance aqueous saturated calomel electrode.

*Auxiliary electrode*: Platinum foil, 1 cm<sup>2</sup>.

A Sargent Model XXI Polarograph was used in voltammetric experiments, and a polarographic H cell served as the electrolysis cell in all work.

*Preparation and use of graphite electrodes*

Spectroscopic-grade carbon electrodes (diameter: 0.25 in.) were impregnated with paraffin wax by allowing the rods to stand for 1 hr in the molten wax at 100°. Although previous workers have used various sealing waxes and cements to coat the outer surface of the electrodes, such coatings are soluble in the solvent systems used in this investigation. Instead, Teflon tubing of nominal 1/4-in. diameter, which at room temperature was too small to fit over the graphite rods, was heated in boiling water, slipped over the graphite rod while hot, and allowed to cool. Electrodes prepared in this manner were effectively sealed from solvent penetration everywhere except at the exposed end which was dipped into the sample solution.

Except in the oxidation of *m*-phenylenediamine and resorcinol, the electrodes were not re-surfaced between runs. These compounds were found to form an insoluble coating on the electrode which could be removed only by re-surfacing.

*Chronopotentiometric procedure*

Approximately 10 ml of the sample solution were placed in the anode compartment of the electrolysis cell, and 10 ml of the supporting electrolyte solution were added to the cathode compartment. The graphite electrode was positioned in the sample solution, and the reference electrode and auxiliary electrode were placed in the cathode compartment. The starting potential of the indicating electrode was positioned at one side of the recorder chart by means of the zero adjustment, and the chart was started. As the pen passed an index line on the chart, the current was switched on.

Transition times were measured as described by Elving and Krivis.<sup>10</sup>

## DISCUSSION AND RESULTS

1. *Chronopotentiometry in acetonitrile*

Voorhies and Furman<sup>13</sup> have recommended the use of acetonitrile for the chronopotentiometry of organic compounds. These authors studied the oxidation of anthracene at a platinum electrode in a supporting electrolyte consisting of 0.1M NaClO<sub>4</sub> in CH<sub>3</sub>CN and reported that the diffusion coefficient of anthracene in this solvent was ten times the value obtained in aqueous solution. In the present investigation, the oxidation of hydroquinone, catechol, resorcinol, and the three isomeric phenylenediamines has been studied in a supporting electrolyte consisting of 0.1M LiClO<sub>4</sub> in CH<sub>3</sub>CN. These compounds were studied by Elving and Krivis in aqueous buffer

solutions<sup>9,10</sup> using the graphite electrode. The results obtained in the present investigation, when compared with those reported by Elving and Krivis, do not substantiate the observation of Voorhies and Furman that the diffusion coefficient of organic compounds in  $\text{CH}_3\text{CN}$  is an order of magnitude larger than in water.

Elving and Krivis found the value of  $\frac{i\tau^{\frac{1}{2}}}{C}$  in an 0.5M acetate buffer in water to be 156 for hydroquinone and 172 for catechol. (Note: In this paper, values of  $\frac{i\tau^{\frac{1}{2}}}{C}$  are given with the units  $\frac{\mu\text{A sec}^{\frac{1}{2}} \text{ litre}}{\text{millimole}}$ .) The corresponding values obtained by the author in acetonitrile, with an electrode of the same area, were 242 and 180. In an 0.25M  $\text{K}_2\text{HPO}_4$ -0.25M  $\text{K}_3\text{PO}_4$  aqueous buffer, Elving and Krivis reported  $\frac{i\tau^{\frac{1}{2}}}{C}$  to vary from 136 to 174 for *o*-phenylenediamine and from 125 to 174 for *p*-phenylenediamine. In the present investigation, the values obtained were 110 to 128 and 144 to 178, respectively, in the same concentration range.

Equation (1), derived by Sand<sup>14</sup> in 1901 expresses the relation between the applied current ( $i$ ), the concentration of electro-active species in the bulk of the solution ( $C$ ), and the transition time ( $\tau$ ). In this equation

$$\frac{i\tau^{\frac{1}{2}}}{C} = \frac{nFA\pi^{\frac{1}{2}}D^{\frac{1}{2}}}{2} \quad (1)$$

$n$  is the number of electrons involved in the electrode reaction,  $F$  is the Faraday,  $A$  is the electrode area, and  $D$  is the diffusion coefficient of the electroactive species in the solvent used. Equation (1) shows that the value of  $\frac{i\tau^{\frac{1}{2}}}{C}$  is a constant directly proportional to the square root of the diffusion coefficient of the electroactive species in the supporting electrolyte, so that these results show that the diffusion coefficients of the various compounds considered are nearly the same in water and acetonitrile.

The precision obtainable for repeated chronopotentiometric runs in acetonitrile was studied several times and was found to be better than  $\pm 1.0\%$  in cases in which no electrode fouling was observed, and  $\pm 1.7\%$  when the electrode was fouled by the products of the electrolysis and was re-surfaced between runs.

(a) *Isomeric dihydroxybenzenes*: Although hydroquinone, catechol, and resorcinol all gave well-defined potential-time curves in acetonitrile, a detailed investigation of the chronopotentiometry of these compounds in this system was not carried out because it was observed that the concentration of the dihydroxybenzenes decreased slowly because of a reaction between the solvent and solute, as the solutions were allowed to stand.

It is significant, however, that well-defined waves were obtained for all three isomers, since Elving and Krivis observed that resorcinol, because of electrode fouling, gives a poorly defined wave in aqueous solvent, in the absence of hydroquinone or catechol, and the same results were obtained in ethanol in the present investigation.

Many previous workers have reported electrode fouling during the electrochemical oxidation or reduction of organic compounds in aqueous solutions. The results obtained with resorcinol suggest that it may sometimes be possible to eliminate this

troublesome effect by using an organic solvent in which the reaction products are more soluble. Neither hydroquinone nor catechol caused electrode fouling in solutions as concentrated as  $10^{-2}M$ .

(b) *Isomeric phenylenediamines*: The chronopotentiometric behavior of the three phenylenediamine isomers in acetonitrile was found to be very similar. All three gave well-defined single waves which, from the  $\frac{i\tau^{\frac{1}{2}}}{C}$  values obtained, correspond to a  $2e^-$  oxidation. This agrees with results previously obtained for the electro-oxidation of the same compounds in aqueous solution,<sup>10</sup> and it appears that the reaction product is, in both cases, a di-imine.

Only with *m*-phenylenediamine was electrode fouling observed, and satisfactory results were obtained, even in this case, by polishing the electrode between runs.

The chronopotentiometric results obtained for the phenylenediamines in this system are presented in Table I.

From these results we see that  $\frac{i\tau^{\frac{1}{2}}}{C}$  increases as  $C$  is decreased, although  $i\tau^{\frac{1}{2}}$  remains constant as  $i$  is varied at a given  $C$ . This phenomenon, which has been observed by other workers, was observed with every compound studied in this investigation, and appears to be caused by the adsorption of the electroactive species on the electrode surface before the electrolysis. Although a plot of  $i\tau^{\frac{1}{2}}$  versus  $C$  deviates slightly from linearity at low concentrations ( $<10^{-4}M$ ) because of this effect, such plots have been found to be satisfactory for use as working curves over a wide concentration range ( $10^{-4}$  to  $10^{-2}M$ ).

## 2. Chronopotentiometry in 95% ethanol

A detailed study of the chronopotentiometric behaviour of various organic compounds in a supporting electrolyte solution consisting of  $0.5M$  LiCl or  $0.5M$  LiClO<sub>4</sub> in 95% ethanol was undertaken, since the method appeared promising for the qualitative identification and quantitative determination of commercial antioxidants, which may be extracted from rubber or polymer samples with 95% ethanol.

(a) *Isomeric dihydroxybenzenes*: The chronopotentiometric behaviour of the isomeric dihydroxybenzenes in 95% ethanol containing  $0.5M$  LiCl supporting electrolyte was investigated to study the effect of the alcoholic medium on reactions at the graphite electrode. Since Elving and Krivis had studied the behaviour of these compounds at a similar electrode in an aqueous buffer solution,<sup>9,10</sup> data were available for a comparison of the oxidation of these compounds in the two solvents.

In both solvent systems it was found that only hydroquinone and catechol gave a well-defined potential-time curve. Resorcinol appears to undergo a destructive oxidation which results in severe electrode fouling and a poorly shaped wave which is of little value for analytical purposes.

The chronopotentiometric results obtained for the oxidation of hydroquinone and catechol in 95% ethanol are presented in Table II. The values of  $\frac{i\tau^{\frac{1}{2}}}{C}$  obtained in aqueous solution by Elving and Krivis were 155 for  $1.01 \times 10^{-3}M$  hydroquinone and 172 for  $0.99 \times 10^{-3}M$  catechol. The difference between these values and those obtained in the present study (132 and 147, respectively) reflect a difference in the

TABLE I.—CHRONOPOTENTIOMETRY OF PHENYLENEDIAMINES IN CH<sub>3</sub>CN

<i>C</i> , millimoles/litre	<i>i</i> , $\mu A$	$\tau$ , sec	$\frac{i\tau^{\frac{1}{2}}}{C}$
A. <i>o</i> -Phenylenediamine			
1.13	50	8.42	128
	40	12.91	128
3.39	175	6.25	129
	130	10.30	123
6.78	220	11.55	113
	175	19.9	115
11.3	400	9.58	110
	300	17.6	112
B. <i>p</i> -Phenylenediamine			
0.103	6.0	9.23	178
	9.0	4.13	178
1.03	60	6.02	143
	40	13.83	145
3.09	160	4.89	115
	120	8.21	112
6.18	325	5.90	128
	250	9.28	123
10.3	500	5.93	118
	400	9.06	117
C. <i>m</i> -Phenylenediamine			
1.02	70	5.26	154
	50	9.62	158
3.07	190	4.37	130
	120	11.35	132
6.15	300	6.82	128
	200	15.44	128
10.3	500	4.88	109
	300	13.90	111

diffusion coefficients of the electro-active species in the two solvents, rather than a difference in  $n$  which would indicate a difference in the mechanism of the oxidation reaction at the graphite electrode. Plots of  $E$  versus  $\log \left( \frac{\tau^{\frac{1}{2}} - t^{\frac{1}{2}}}{t^{\frac{1}{2}}} \right)$  for typical chronopotentiometric waves resulted in straight lines. The value of  $\alpha n$  calculated from these plots was 0.56 for both hydroquinone and catechol. The values obtained by Elving and Krivis were 0.59 and 0.60, respectively.

TABLE II.—CHRONOPOTENTIOMETRY OF HYDROQUINONE AND CATECHOL IN 95% ETHANOL (0.5M LiCl SUPPORTING ELECTROLYTE)

$C$ , millimoles/litre	$i$ , $\mu A$	$\tau$ , sec	$\frac{i\tau^{\frac{1}{2}}}{C}$
A. Hydroquinone			
1.01	35	13.4	128
	50	7.30	134
4.04	100	19.7	110
	150	9.69	115
7.07	160	22.4	107
	300	6.83	111
10.1	200	27.1	103
	300	12.1	103
B. Catechol			
1.11	37	18.8	145
	50	10.8	148
4.44	130	18.4	125
	230	5.96	127
7.77	200	24.0	128
	280	12.6	128
11.1	300	22.5	128
	550	6.51	127

(b) *Chronopotentiometry of commercial antioxidants*: The results of a study of the chronopotentiometry of various commercial antioxidants are given in Table III. The  $E^{\frac{1}{2}}$  values for the various compounds were not measured, because an aqueous saturated calomel electrode was used as a reference electrode and the potentials measured in the ethanol solution with respect to this reference were not corrected for the liquid-liquid junction potential.

Although  $\frac{i\tau^{\frac{1}{2}}}{C}$  always increased as  $C$  was decreased, plots of  $i\tau^{\frac{1}{2}}$  versus  $C$  gave a nearly straight line suitable for use as an analytical working curve.

The antioxidant concentrations were calculated on the assumption that the commercial product was a pure compound. If the product is impure, the  $\frac{i\tau^{\frac{1}{2}}}{C}$  values will be slightly low. The purity of the compounds is usually greater than 95%, however, so that the  $\frac{i\tau^{\frac{1}{2}}}{C}$  values provide a useful estimation of the range of concentration over which the method is applicable. In general, chronopotentiometry appears well suited to the determination of antioxidants in the concentration range from  $10^{-4}$  to  $10^{-2}M$ . This range places a lower limit of 0.2–0.5% by weight on the concentration of antioxidant which could be measured in actual samples, depending on the molecular weight of the antioxidant, if the antioxidant content of a 2.0-g sample is extracted



TABLE III.—CHRONOPOTENTIOMETRY OF VARIOUS COMMERCIAL ANTI-OXIDANTS IN 95% ETHANOL

<i>C</i> , millimoles/litre	$\frac{ir^{\frac{1}{2}}}{C}$	Supporting electrolyte
A. *Dalpac: 2,6-Di- <i>t</i> -butylcresol		
10.1	124	LiClO <sub>4</sub>
6.06	126	
3.03	136	
1.01	152	
B. Age-Rite Alba: Hydroquinone monobenzyl ether		
10.1	111	LiCl
6.04	112	
3.02	122	
1.01	136	
C. Flexone 6H: <i>N'</i> -Phenyl- <i>N'</i> -cyclohexyl phenylenediamine		
9.83	84.2	LiCl
5.90	88.3	
2.95	89.8	
0.98	105	
D. Age-Rite Stalite: Heptylated diphenylamine		
10.0	73.2	LiCl
6.02	74.6	
3.01	80.3	
1.00	93.0	
E. Santovar A: 2,5-Di- <i>t</i> -amylhydroquinone		
10.1	91.1	LiCl
6.06	94.0	
3.03	98.0	
1.01	107.0	
F. Flexone 3C: <i>N</i> -Isopropyl- <i>N'</i> -phenyl phenylenediamine		
10.3	96.3	LiCl
6.17	99.4	
3.09	110.6	
1.03	119.3	
G. Age-Rite Powder: <i>N</i> -Phenyl- $\beta$ -naphthylamine		
10.3	159	LiCl
6.21	157	
3.11	160	
1.03	186	
H. Antioxidant 2246: 2,2'-Methylene-bis-(6- <i>t</i> -butyl-4-ethylphenol)		
10.0	237	LiClO <sub>4</sub>
6.00	229	
3.00	231	
1.00	243	
I. Santowhite Powder Refined: 4,4'-Butylidene-bis-(3-methyl-6- <i>t</i> -butylphenol)		
11.2	323	LiClO <sub>4</sub>
6.73	316	
3.36	348	
1.12	410	

\* Trademark—Hercules Powder Company

into 10 ml of solution (a procedure which has been described previously in the literature). This sensitivity, of course, may be greatly improved by procedures for increasing the sample—extractant ratio or concentration of the extract.

None of the substances studied and listed in Table III was found to cause electrode fouling at any concentration level.

At a given concentration of electro-active species, the product  $i\tau^{\frac{1}{2}}$  was constant as  $i$ , and thus  $\tau$ , were varied over a 2- to 3-fold range.

The range of transition times measured was limited to not less than 5, nor more than 30 sec. The lower limit was imposed by the accuracy with which it was possible to measure  $\tau$  with the recorder used. The upper limit results from disturbance of the diffusion layer by such effects as vibration, convection, *etc.* Within these limits, the precision with which transition times could be reproduced was  $\pm 1.0\%$ , even when the electrode was removed from the solution between runs and dried before being replaced. This increase in reproducibility appears to arise from the ability of the solvent to wet the electrode and suggests an important advantage to be gained by the use of non-aqueous solvents with carbon electrodes.

### 3. Voltammetry with the graphite indicating electrode

Current-voltage curves for the anodic oxidation of the various antioxidants in 95% ethanol were obtained, using the same graphite indicating electrode used in the chronopotentiometric study. While a preliminary investigation has shown that this method is not as rapid or reproducible as chronopotentiometry for the quantitative determination of organic compounds, at least under the conditions used in this work, it is much superior for qualitative work.

The peak potential ( $E_p$ ) for a current-potential wave obtained with a solid electrode is characteristic of the electro-active species and is potentially very useful for the qualitative identification of unknown antioxidants in rubber and polymer samples. A list of  $E_p$  values for the various antioxidants studied in this work is given in Table IV.

## CONCLUSIONS

Chronopotentiometry, using a graphite indicating electrode and non-aqueous supporting electrolyte solutions, has been found to be a useful method for the quantitative determination of polymer antioxidants and antiozonants. The method possesses a considerable advantage over other methods in this field, such as ultraviolet

TABLE IV.—PEAK POTENTIALS ( $E_p$ ) FOR VARIOUS ANTIOXIDANTS

Trade names	Supporting electrolyte	No. of waves	$E_p$ (vs. S.C.E.)
Age-Rite Powder	LiCl	1	+·73
Age-Rite Alba	LiCl	1	+·66
2246	LiClO <sub>4</sub>	2	+·80, +1·22
UOP-88	LiCl	2	+·04, +·39
Flexone 6H	LiCl	1	+·41
Santovar A	LiCl	1	+·43
Age-Rite Stalite	LiCl	1	+·65
Flexone 3C	LiCl	2	+·14, +·43
Dalpac	LiClO <sub>4</sub>	2	+·82, +1·21
Santowhite Powder	LiClO <sub>4</sub>	1	+·80

spectrophotometry, in speed and simplicity. It appears to be useful in the concentration range  $10^{-4}$  to  $10^{-2}M$ , and is applicable to a wide variety of compounds.

Voltammetry with the graphite indicating electrode was found to be a valuable tool for the qualitative identification of these compounds, although, under the present conditions, it is quantitatively less precise than chronopotentiometry.

**Zusammenfassung**—Das chronopotentiometrische Verhalten von der Phenylendiamine und Dioxybenzole und mehrerer, anderer Antioxydantia und Antiozonate wurde an einer graphitene Indicatorelektrode studiert. Der Vorteil bei solchen Untersuchungen, nichtwässrige Lösungsmittel wie Athanol und Acetonitril zu verwenden, wird betont. Im besonders ist es wert hervorzuheben, dass die Genauigkeit der Methode erheblich gesteigert wird, weil die Lösemittel imstande sind die Elektrode gut zu benetzen.

**Résumé**—L'auteur a étudié le comportement chronopotentiométrique des phénylène diamines, des dihydroxybenzènes et de différents antioxydants et antiozonisants commerciaux, à une électrode indicatrice de graphite. Les avantages des solvants non aqueux comme l'éthanol et l'acétonitrile sont dégagés, en particulier une augmentation importante de la précision de la technique due à la propriété du solvant de mouiller efficacement l'électrode.

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## COMPARISON OF SOLVENTS FOR THE DIFFERENTIATING TITRATION OF PHENOLS

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**Summary**—Nine of the more commonly used solvents for the differentiating titration of acids have been compared for their ability to resolve phenols. Two methods of defining the differentiating quality of a solvent were used for this investigation. The first technique utilises the  $\Delta\text{HNP}$  (solvent) *vs.*  $\text{pKa}$  ( $\text{H}_2\text{O}$ ) curves described by Streuli. The magnitude of the slope of such curves determines the resolving power of the solvent. The other method used is based upon the practical observation that the extent of the first "break",  $\Delta E$  e. pt., for the potentiometric titration of a mixture of two phenols of similar  $\text{pKa}$  ( $\text{H}_2\text{O}$ ) will define the differentiating quality of the solvent. A nearly linear relationship exists between these two methods of defining the differentiating quality of the solvent. A good correlation has been observed between  $\Delta E$  e. pt. and the dielectric constant of the solvent, and, in general, solvents with the lower dielectric constants have greater resolving powers. On the basis of this study *t*-butanol, the solvent recommended by Fritz and Marple, is superior to the other solvents investigated.

### INTRODUCTION

IN recent years considerable progress has been made in the ability to distinguish among acids by differentiating titrations in non-aqueous media. Progress in this field has been reviewed semi-annually by Riddick,<sup>1-4</sup> and theoretical considerations for such titrations have been presented by Kolthoff and Bruckenstein.<sup>5</sup> Among the factors that reflect or determine the ability of a solvent to distinguish among acids are the steepness of the titration,<sup>6,7</sup> the basicity of the solvent and the ionisation constants of the acids titrated,<sup>8</sup> and the potential scale of the solvent.<sup>9</sup> Each of these factors has been used to define the differentiating quality of the many solvents proposed for the titration of acids in non-aqueous media. A technique utilising an empirical acidity potential of the solvent and the half-neutralisation potential of the acid has been used to predict the optimum solvent-titrant combination for any given titration.<sup>9</sup>

A technique of characterising a solvent by relating the aqueous ionisation constant of the acid to a measurable potential difference in the solvent has been presented by Streuli.<sup>10,11</sup> The measured potential difference between the half-neutralisation potential of the acid and the half-neutralisation potential of the reference, benzoic acid, was called the  $\Delta\text{HNP}$  value of the acid. Linear relationships were found between the aqueous ionisation constants and  $\Delta\text{HNP}$  for phenols and carboxylic acids in pyridine. The equation for the plot,  $\Delta\text{HNP}$  *vs.*  $\text{pKa}$  ( $\text{H}_2\text{O}$ ), for phenols in pyridine was found to be  $\text{pKa}$  ( $\text{H}_2\text{O}$ ) = 0.00661 $\Delta\text{HNP}$  + 7.52. This curve had a slope of 155 mv per  $\text{pKa}$  ( $\text{H}_2\text{O}$ ) unit.

The relative acidity work of Streuli suggests that the slope of the  $\Delta\text{HNP}$  *vs.*  $\text{pKa}$  curve will define the differentiating quality of a solvent for acids of the same structural

type, *i.e.*, the steeper the slope the greater the resolving character of the solvent. In order to test this principle, and to compare solvents for their ability to differentiate among phenols, nine of the more commonly used solvents were examined and the slopes of their  $\Delta\text{HNP}$  *vs.*  $\text{pK}_a(\text{H}_2\text{O})$  curves determined.

### EXPERIMENTAL

All solvents used in this survey were examined as received without further purification. The phenols titrated were purchased from the Eastman Kodak Chemicals Company and were used without purification. The titrant, 0.1*N* tetrabutylammonium hydroxide, was prepared by diluting with 2-propanol a 1*N* stock solution purchased from Southwestern Analytical Chemicals, Austin, Texas. The titrant was not standardised, but was protected from the atmosphere by an Ascarite guard tube.

All potentiometric titrations were performed using a Metrohm automatic recording "Potentiograph E-336" manufactured in Herisau, Switzerland. A glass indicator electrode and a calomel (saturated tetrabutylammonium perchlorate in methanol) reference electrode pair was employed for all titrations.

Equal molar concentrations of phenols and benzoic acid reference were used for all titrations. This requirement was necessary in order to prevent changes in half-neutralisation potential with concentration<sup>5,8</sup>. Titrations were performed in 100 ml of solvent and the total acid titer was 5 ml. The small titer was used to minimise the influence of the 2-propanol in the titrant upon the characteristics of the solvent. Grounding of the magnetic stirrer and instrument, and shielding of the titration vessel proved to be necessary in the solutions of low dielectric constant.

### RESULTS AND DISCUSSION

#### $\Delta\text{HNP}$ results

The  $\Delta\text{HNP}$  results for the solvents studied were obtained following a procedure similar to that used by Streuli.<sup>10,11</sup> The HNP of benzoic acid was arbitrarily assigned a value of zero and the HNP's for the phenols were referred to this reference to obtain the  $\Delta\text{HNP}$ 's. The  $\Delta\text{HNP}$  (solvent) *vs.*  $\text{pK}_a(\text{H}_2\text{O})$  curves for some of the solvents investigated are shown in Fig. 1. Some of the curves obtained are not shown, in order to improve clarity. Solvents whose  $\Delta\text{HNP}$  *vs.*  $\text{pK}_a(\text{H}_2\text{O})$  curves fall to the right of the water line are generally more basic towards phenols than water. Presumably the curves for solvents more acidic than water would be displaced to the left; however, this cannot be established because titrations in such media are impractical if not impossible.

With the exception of ethylene glycol, all of the non-aqueous solvents investigated tend to intersect at a  $\Delta\text{HNP}$  of approximately 15 and a  $\text{pK}_a(\text{H}_2\text{O})$  of approximately 7.5. This means that the acidity of a phenol with a  $\text{pK}_a(\text{H}_2\text{O})$  of 7.5 would be nearly the same as benzoic acid [ $\Delta\text{HNP}(\text{H}_2\text{O}) = 0$ ] in these solvents. In water and ethylene glycol, however, large differences would be observed, and presumably carboxylic acids could be readily titrated in the latter solvents in the presence of such a phenol. With phenols with  $\text{pK}_a(\text{H}_2\text{O})$  weaker than 7.5, larger differences are observed among the non-aqueous solvents.

The  $\Delta\text{HNP}$  values for the phenols selected for this investigation in the various solvents are contained in Table I. In addition, the slopes of the  $\Delta\text{HNP}$  (solvent) *vs.*  $\text{pK}_a(\text{H}_2\text{O})$  curves for the various solvents are also listed. For pyridine a slope of 137 mv per  $\text{pK}_a(\text{H}_2\text{O})$  unit was obtained. This compares with a value of 155 obtained by Streuli. The discrepancy, no doubt, results from different conditions used to obtain the values. In particular, variations in acid concentrations will affect the  $\Delta\text{HNP}$  values and such values cannot be compared unless obtained at the same concentrations.

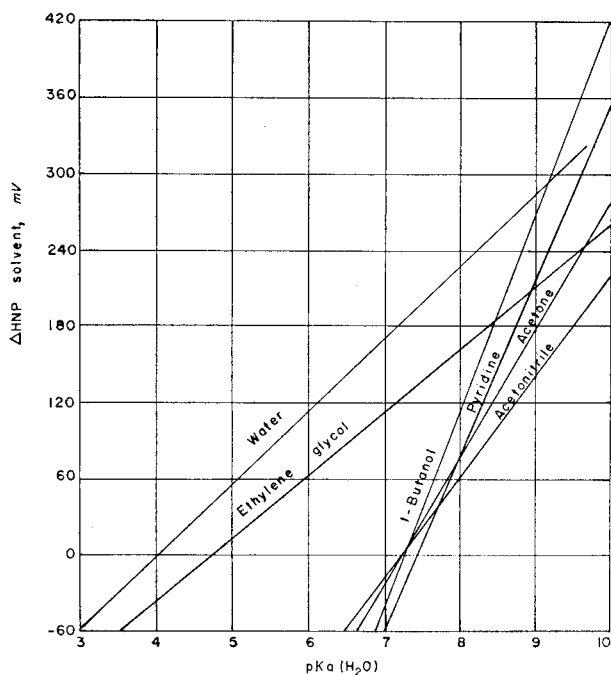
FIG. 1.—HNP (solvent) vs. pKa (H<sub>2</sub>O) curves for phenols in various solvents.

TABLE I.—ΔHNP VALUES FOR THE SOLVENTS EXAMINED

Acid	pKa (H <sub>2</sub> O)	Solvent*								
		1	2	3	4	5	6	7	8	9
o-Bromobenzoic	2.84	—	—	—	—	—	—	—	—	-120
2,4-Dinitrophenol	4.13	-240	—	-325	—	—	—	—	-84	—
<i>p</i> -Nitrophenol	7.14	-6	-44	-100	-50	-15	-12	-32	+126	+260
2,4,6-Trichlorophenol	7.59	—	—	-95	—	+65	—	—	—	+170
2,4-Dichlorophenol	7.85	—	+96	—	+78	—	+90	—	+146	—
<i>m</i> -Nitrophenol	8.35	+137	—	+150	+139	+210	+112	+76	+180	—
<i>m</i> -Chlorophenol	8.85	—	—	+155	—	—	—	—	—	+470
Phenol	9.95	+450	+326	+295	+340	+195	—	+224	—	+550
Slope of ΔHNP vs. pKa (H <sub>2</sub> O)		157	137	137	130	125	100	87	62	57

\* Solvents

- |                       |                    |
|-----------------------|--------------------|
| 1.— <i>t</i> -Butanol | 6.—Acetone         |
| 2.—Pyridine           | 7.—Acetonitrile    |
| 3.—Tetrahydrofuran    | 8.—Ethylene glycol |
| 4.—2-Propanol         | 9.—Water           |
| 5.—Dimethylsulphoxide |                    |

### Degree of differentiation

If the assumption is made that the magnitude of the slope of the ΔHNP (solvent) vs. pKa (H<sub>2</sub>O) curves determines the differentiating quality of a solvent, then on this basis *tert*-butanol, suggested by Fritz and Marple,<sup>7</sup> is the best solvent investigated. In order to test this assumption, an alternative method of defining the differentiating quality of the solvent was sought. From a practical standpoint, the differentiating

quality of the solvent can be defined from the character of the potentiometric titration curves obtained for a mixture of phenols of similar  $pK_a$  ( $H_2O$ ). If the solvent is a good differentiating solvent, then a well-defined "break" will be obtained for the potentiometric titration of the stronger acid. The better the differentiating quality of the solvent, the greater the "break" will be. This method of defining the differentiating quality of the solvent is shown in Fig. 2. An equimolar mixture of *p*-nitrophenol and *m*-nitrophenol,  $\Delta pK_a$  ( $H_2O$ ) = 1.88, was selected for this purpose. In order to determine the magnitude of the potentiometric "break" for the stronger acid, the two straight portions of the potentiometric curves are extrapolated and the height of the break,  $\Delta E$  e. pt., measured as indicated.

$\Delta E$  e. pt. values were obtained for all of the solvents investigated and these values are shown in Table II. The largest  $\Delta E$  e. pt. value, and consequently the best resolution, was obtained in *t*-butanol. A value of zero was obtained in water because no potentiometric "break" was evident. In ethylene glycol only a suggestion of a

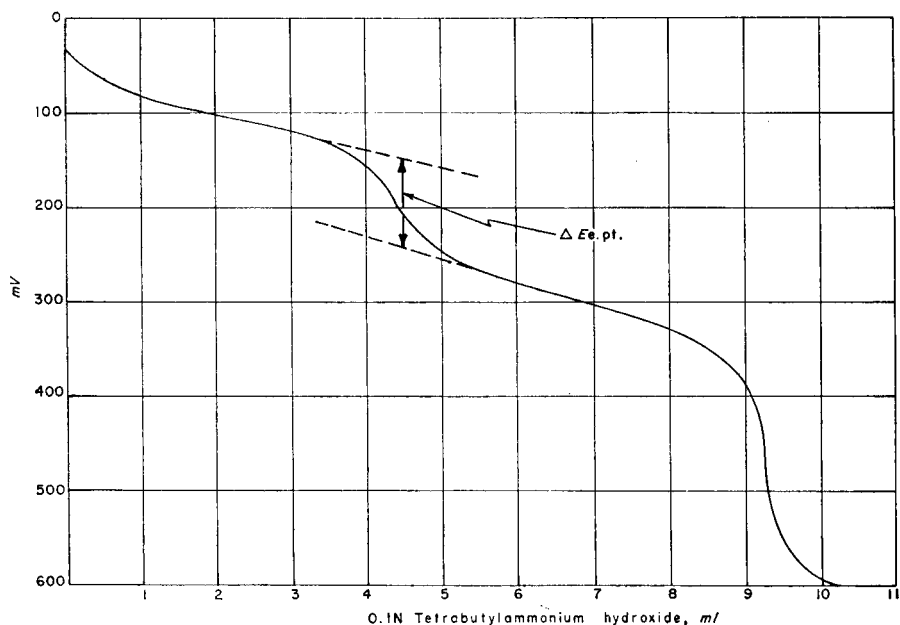


FIG. 2.—Determination of  $\Delta E$  e. pt. Titration of *p*-nitrophenol [ $pK_a$  ( $H_2O$ ) = 7.14] and *m*-chlorophenol [ $pK_a$  ( $H_2O$ ) = 8.85] in *t*-butanol as solvent.

TABLE II.— $\Delta E$  e. pt. AND DIELECTRIC CONSTANT VALUES FOR THE SOLVENTS EXAMINED

	Solvent*								
	1	2	3	4	5	6	7	8	9
$\Delta E$ e. pt., <i>p</i> -Nitrophenol and <i>m</i> -Chlorophenol <i>mV</i>	95	72	64	64	56	36	22	—	0
Dielectric constant	15.8	12.3	7.4	18.3	46.7	20.7	37.5	37	79.5

\* See Footnote to Table I

break was observed and this value was not calculated. Fig. 3 shows that a nearly linear relationship exists between  $\Delta E$  e. pt. and the slope of the  $\Delta HNP$  (solvent) *vs.*  $pK_a$  ( $H_2O$ ) curves. This, of course, means that the greater the slope of the  $\Delta HNP$  (solvent) *vs.*  $pK_a$  ( $H_2O$ ) curve, the better the differentiating quality of the solvent.

In order to determine the relative differentiating qualities of a series of solvents for phenols, two simple methods can be used:

(1) Determine the magnitude of the slopes of the  $\Delta HNP$  (solvent) *vs.*  $pK_a$  ( $H_2O$ ) curves (this will require at least 5 potentiometric titrations for each solvent), or

(2) Determine  $\Delta E$  e. pt. as previously discussed (this will require only one titration for each solvent). The latter technique permits rapid scanning of solvents, whereas the former technique will give additional information pertaining to relative acidities.

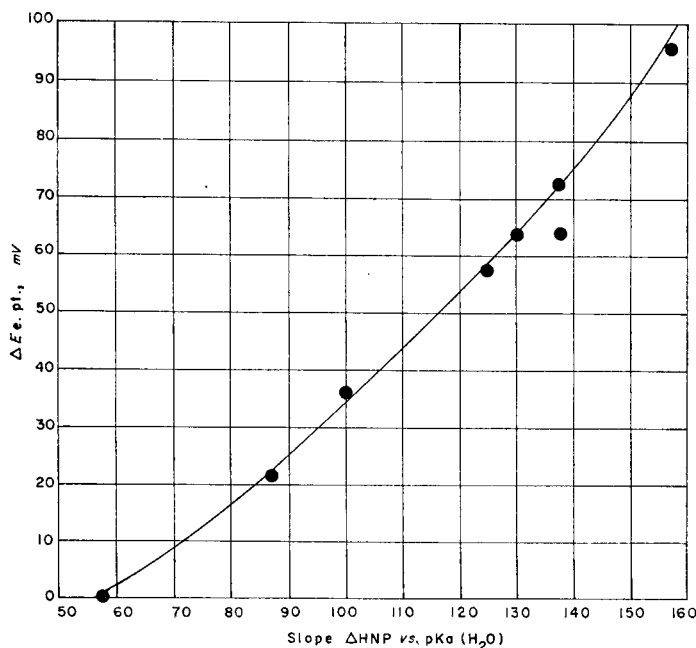


FIG. 3.—Relationship between slope of  $\Delta HNP$  (solvent) *vs.*  $pK_a$  ( $H_2O$ ) curve and  $\Delta E$  e. pt.

#### *Factors affecting differentiation*

Of the solvents investigated, those with the lower dielectric constants were the better differentiating solvents. This correlation, although not exact, is shown in Fig. 4. Major exceptions to this generalisation are dimethyl sulphoxide and ethylene glycol. Dimethylsulphoxide has a fairly high dielectric constant, 46.7, and is still a fairly good differentiating solvent. Ethylene glycol is a poorer differentiating solvent than would be predicted on the basis of its dielectric constant (37). The reasons for these exceptions are not known; however, other factors obviously affect the differentiating quality of the solvent.

On the basis of this study, solvents with dielectric constants in the range of 2 to 5 would be expected to possess excellent differentiating qualities, at least for the resolution of phenols. However, such solvents have low conductivities which produce poor electrode response and accompanying instrumental difficulties.



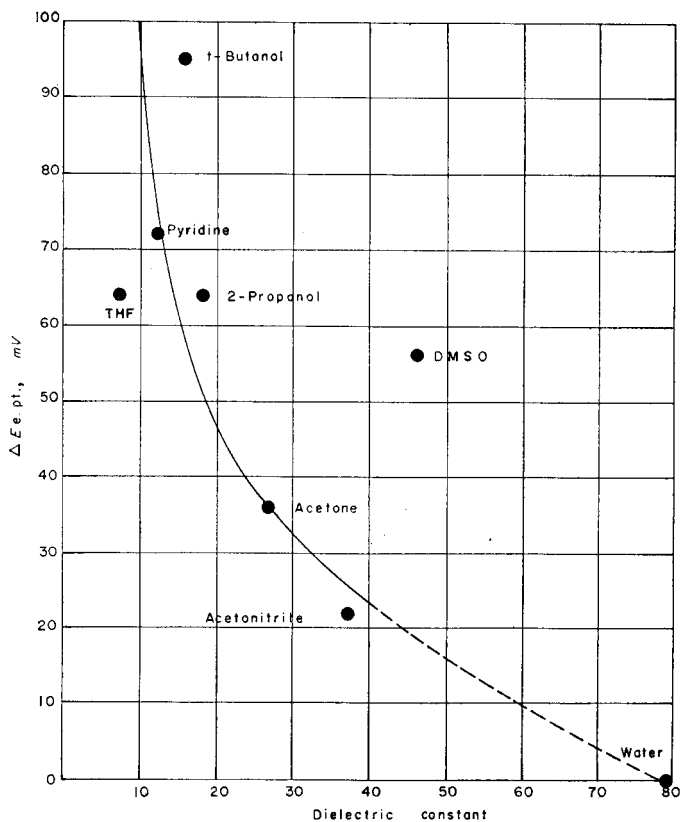


FIG. 4.—Correlation between  $\Delta E$  e. pt. and dielectric constant.

The unusual acid-anion equivalence point for *m*-nitrophenol in acetone<sup>6</sup> was also observed in acetonitrile but not in the other non-protolytic solvents or in the solvents with low dielectric constants. Acid-anion formation of this type occurs when there is a greater tendency for the non-dissociated acid to form a hydrogen bond with the anion than with the solvent.<sup>6</sup> Such an effect would no doubt be observed in hydrocarbons or other solvents in which solvolysis is poor. Acid-anion formation will have a detrimental effect upon the resolution of phenols, particularly if it occurs with the stronger acid.

**Zusammenfassung**—Neun der mehr gewöhnlichen Lösemittel für differenzierende Titration von Säuren wurden auf ihre Fähigkeit zur Differenzierung von Phenolen untersucht. Zwei Methoden um die Differenzierfähigkeit zu definieren wurden bei der Untersuchung angewendet. Die erste Methode verwendet die  $\Delta HNP$  (Solvent)- $pK_a$  ( $H_2O$ )-Kurven nach Streuli. Die Steigung dieser Kurven bestimmt den Differenzierungsgrad des Lösemittels. Die andere Methode benützt die experimentell erhaltenen Sprünge in potentiometrischen Titrations zweier Phenole mit ähnlichem  $pK_a$  ( $H_2O$ ); und zwar wird die Höhe des ersten Sprunges als bewertendes Kriterium gewählt. Eine nahezu lineare Beziehung zwischen den nach den beiden Methoden erhaltenen Differenzierungsgraden wird erhalten. Gute Korrelation besteht zwischen dem  $\Delta E$  im Endpunkte und der Dielektrizitätskon-

stante des Solvents. Im allgemeinen haben Lösemittel mit niedriger Dielektrizitätskonstante ein höheres Differenziervermögen. Aufgrund der Studien wurde der von Fritz und Marple empfohlene tert. Butylalkohol als den anderen Lösemitteln überlegen gefunden.

**Résumé**—Neuf des solvants les plus couramment utilisés pour le titrage différentiel des acides ont été comparés au point de vue de leur facilité à séparer les phénols. Deux méthodes ont été utilisées pour définir la qualité différentielle d'un solvant. La première technique utilise les courbes  $\Delta HNP$  (solvant) en fonction de  $pK_A (H_2O)$  décrites par Streuli. La valeur de la pente de telles courbes détermine le pouvoir séparateur du solvant. L'autre méthode utilisée est basée sur l'observation pratique suivante: l'importance de la première "cassure",  $\Delta E$  e. pt. dans le titrage potentiométrique d'un mélange de deux phénols de  $pK_A (H_2O)$  semblables définira la qualité différentielle du solvant. Une relation à peu près linéaire existe entre ces deux méthodes de définition de la qualité différentielle d'un solvant. Un bon accord a été observé entre  $\Delta E$  e. pt. et la constante diélectrique du solvant, et en générale les solvants de plus faible constante diélectrique ont des pouvoirs séparateurs plus grands. D'après cette étude, le tert-butanol, solvant recommandé par Fritz et Marple, est supérieur aux autres solvants étudiés.

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## THE DETERMINATION OF TRACES OF SELENIUM AND TELLURIUM IN SAMPLES OF PLATINUM BY NEUTRON-ACTIVATION ANALYSIS

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**Summary**—A method is described for the determination of submicrogram amounts of selenium and tellurium in platinum by neutron-activation analysis. After a sample has been irradiated in a nuclear reactor, known amounts of tellurium and selenium carriers are added and a chemical separation of the elements is made. The activities of  $^{127}\text{Te}$  and  $^{75}\text{Se}$  isolated from the samples are then compared with corresponding activities separated from comparators irradiated simultaneously with the samples. The results obtained on 7 batches of pure platinum are reported.

NEUTRON-ACTIVATION analysis can provide a simple method for the determination of submicrogram quantities of selenium and tellurium in a variety of materials. Application of the technique to the determination of traces of the two elements as impurities in samples of purified platinum is described here.

The nuclear characteristics of selenium and tellurium relevant to activation with thermal neutrons are summarised in Tables I and II.<sup>1,2</sup>

Selenium-75 proved to be the most convenient radionuclide for the determination

TABLE I.—NUCLEAR DATA FOR THERMAL NEUTRON ACTIVATION OF SELENIUM

Target nuclide	Abundance, %	Isotopic activation cross section, barns	Product on thermal neutron irradiation	Radiation and energy, Mev	Half-life
$^{74}\text{Se}$	0.87	$26 \pm 6$	$^{75}\text{Se}$	EC; $\gamma$ 0.265, 0.136, 0.280, 0.402, others	121 d
$^{76}\text{Se}$	9.02	$7 \pm 3$	$^{77m}\text{Se}$	IT $e^- \gamma$ 0.162 ( $Q_{IT}$ )	17.5 s
$^{78}\text{Se}$	23.52		$^{79m}\text{Se}$	IT 0.096 ( $Q_{IT}$ )	3.91 m
$^{80}\text{Se}$	49.82	$0.03 \pm 0.01$	$^{81m}\text{Se}$	IT $e^- (\gamma)$ 0.103 (Q)	56.8 m
		$0.5 \pm 0.1$	$^{81}\text{Se}$	$\beta^-$ 1.38 (Q)	18.2 m
$^{82}\text{Se}$	9.19	$0.050 \pm 0.025$	$^{83}\text{Se}$	$\beta^-$ 3.4; $\gamma$ 1.01, 2.02, 0.65, 0.35	70 s
			$^{83}\text{Se}$	$\beta^-$ 1.5; $\gamma$ 0.35 (both $^{83}\text{Se}$ radionuclides decay independently to yield $^{83}\text{Br}$ , $t_{1/2}$ 2.3 h)	25 m

TABLE II.—NUCLEAR DATA FOR THERMAL NEUTRON ACTIVATION OF TELLURIUM

Target nuclide	Abundance, %	Isotopic activation cross section, barns	Product on thermal neutron irradiation	Radiation and energy, Mev	Half-life
$^{120}\text{Te}$	0.089		$^{121\text{m}}\text{Te}$	IT $e^-$ ( $\gamma$ ) 0.082 $\gamma$ 0.214; $Q_{\text{IT}} = 0.296$	153 d
$^{122}\text{Te}$	2.46	$1.1 \pm 0.5$	$^{121}\text{Te}$	EC; $\gamma$ 0.573, 0.506	17 d
$^{124}\text{Te}$	4.61	$5 \pm 3$	$^{123\text{m}}\text{Te}$	IT $e^-$ ( $\gamma$ ) 0.089, 0.159	104 d
			$^{125\text{m}}\text{Te}$	IT $e^-$ ( $\gamma$ ) 0.110, 0.0355; $Q_{\text{IT}} = 0.146$	58 d
$^{126}\text{Te}$	18.71	$0.09 \pm 0.02$	$^{127\text{m}}\text{Te}$	IT (98%) $e^-$ ( $\gamma$ ) 0.0885 ( $Q_{\text{IT}}$ ); $\beta^-$ (2%)	105 d
		$0.8 \pm 0.2$	$^{127}\text{Te}$	$\beta^-$ 0.70 (99%)	9.4 h
$^{128}\text{Te}$	31.79	$0.015 \pm 0.005$	$^{129\text{m}}\text{Te}$	IT $e^-$ ( $\gamma$ ) 0.1063 ( $Q_{\text{IT}}$ )	33.5 d
		$0.13 \pm 0.03$	$^{129}\text{Te}$	$\beta^-$ 1.45 (71%), 0.99 (15%) 0.29 (10%) 0.69 (4%); $\gamma$ 0.0268, 0.475, 1.14, others	72 m
$^{130}\text{Te}$	34.49	$<0.008$	$^{131\text{m}}\text{Te}$	$\beta^-$ (78%) 0.42, 0.57 others; IT (22%) 0.1817	30 h
		$0.22 \pm 0.05$	$^{131}\text{Te}$	$\beta^-$ 2.14 (60%), 1.69 (25%), 1.35 (15%); $\gamma$ 0.15, 0.45, others. Parent of $^{131}\text{I}$ $t_{1/2} = 8.08$ d	24.8 m

of selenium, even though a shorter irradiation time and a greater sensitivity can be achieved by measuring the radiations of other selenium isotopes produced by neutron activation of the element.<sup>3</sup> Tellurium was determined by measurement of  $^{127}\text{Te}$ . Shorter-lived tellurium radionuclides were not convenient, and the use of longer-lived radionuclides was excluded since they do not provide as good a sensitivity as  $^{127}\text{Te}$ .

The fact that the half-lives of  $^{127}\text{Te}$  and  $^{75}\text{Se}$  are 9.4 h and 121 d, respectively, made it possible to perform determinations on a given sample in the order tellurium, selenium.

In Table III are shown the estimated activities formed after irradiation in a flux of  $10^{12}$  thermal neutrons.cm<sup>-2</sup>.sec<sup>-1</sup> by 1  $\mu\text{g}$  of each element. With 12 days irradiation and a counting efficiency of 10%, it follows that 1  $\mu\text{g}$  of selenium will give  $6.9 \times 10^2$  cpm, so that it should be possible to determine the element down to a level of  $2 \times 10^{-8}$  g. Similarly, it should be possible to determine as little as  $5 \times 10^{-9}$  g of tellurium if it is assumed that one half-life elapses between the end of irradiation and counting.

Nuclear reactions other than radiative capture which might result in the formation of  $^{75}\text{Se}$  or  $^{127}\text{Te}$  or other radioisotopes of selenium or tellurium are listed by Koch,<sup>4</sup> but these do not give rise to interference in the present case.

In order to avoid errors from self-shielding, standardisation has been provided by irradiating similar known quantities,  $a$  and  $b$ , of a sample with very small known amounts of selenium and tellurium mixed with  $b$ .

## EXPERIMENTAL

### Irradiation

About 0.1-g samples of platinum, in the form of powdered sponge, were accurately weighed and sealed in silica irradiation tubes of 4-mm internal diameter. Standardisation was provided by the

TABLE III.—ACTIVITIES PRODUCED FROM 1  $\mu\text{g}$  OF SELENIUM AND 1  $\mu\text{g}$  OF TELLURIUM AFTER IRRADIATION IN A FLUX OF  $1 \times 10^{12}$  THERMAL NEUTRONS. $\text{CM}^{-2}.\text{SEC}^{-1}$ 

Radionuclide	Half-life	Activity, disintegrations/min	
		After 6 d irradiation	After 12 d irradiation
$^{75}\text{Se}$	121 d	$3.5 \times 10^3$	$6.9 \times 10^3$
$^{127}\text{Te}$	9.4 h	$4.2 \times 10^4$	$4.2 \times 10^4$

addition of weighed portions (*ca.* 0.05 g) of standard solutions of selenium (150 mg of Se/litre as  $\text{Se}^{\text{IV}}$  in 1M NaOH) and tellurium (120 mg of Te/litre, as  $\text{Te}^{\text{IV}}$  in 1M NaOH) to 0.1-g samples of platinum in silica irradiation tubes. The liquids were allowed to soak into the metal powder, which was then carefully dried at 70°, after which the tubes were sealed.

Comparators containing the added selenium and tellurium, together with samples to which no selenium or tellurium had been added, were packed with silica wool in standard aluminium screw-top cans and sent to the Atomic Energy Research Establishment, Harwell, for activation. Irradiations were for 12 days in the nuclear reactor BEPO with a flux of  $10^{12}$  thermal neutrons. $\text{cm}^{-2}.\text{sec}^{-1}$ .

#### Radiochemical separation

Following delivery from Harwell after irradiation, the samples and comparators were put through a radiochemical procedure to separate tellurium and selenium radionuclides free from interfering activities. Several radiochemical procedures for the elements have been described in monographs on their radiochemistry.<sup>5,6</sup> The radiochemical separations used in the present work were based to a considerable extent on the procedures of Schindewolf<sup>7</sup> and Glendenin<sup>8</sup>. Ten mg of inactive tellurium and 15 mg of inactive selenium were added as carriers, and the radiochemically pure elements obtained from the chemical separations were mounted for counting as dioxide and metal, respectively. The chemical yields were determined gravimetrically, and were usually ~60% for tellurium and ~80% for selenium.

Preliminary experiments with  $^{127}\text{Te}$  and  $^{75}\text{Se}$  tracers showed that there were no losses of tellurium or selenium before exchange with carriers had been brought about.

#### Radiochemical separation procedure

*Step 1:* Remove the irradiation tubes from the can, open them, and transfer samples and comparators quantitatively to 50-ml round-bottom Quickfit flasks each containing 10 mg of Te and 15 mg of Se carriers (*Note 1*). In every case wash the tube out thoroughly with warm 6M  $\text{HNO}_3$  and add the washings to the respective flask. Attach a water-cooled reflux-condenser to each flask, add 5 ml of 12M HCl, and dissolve the platinum by warming at 60° on a water-bath (*Note 2*).

*Step 2:* Rapidly remove  $\text{HNO}_3$  by adding small portions of 12M HCl and heating with a microburner. Cool, and transfer the contents of the flask to a 50-ml glass centrifuge tube. Dilute the solution to a volume of 35 ml with  $\text{H}_2\text{O}$ . Place in an ice bath and add 1 g of  $\text{NH}_4\text{Cl}$  to precipitate  $(\text{NH}_4)_2\text{PtCl}_6$ . Allow to stand for 10 min and centrifuge.

*Step 3:* Separate the supernate into a clean 50-ml centrifuge tube. Pass  $\text{SO}_2$  rapidly (*Note 3*) through the solution until the precipitates of Te and Se have coagulated (2–3 min). Centrifuge, and wash well with  $\text{H}_2\text{O}$  (*Note 4*).

*Step 4:* Dissolve the Se and Te in the minimum necessary amount of 12M  $\text{HNO}_3$ . Add 2 mg of Pd carrier and dilute to 20 ml with  $\text{H}_2\text{O}$ . Heat nearly to boiling, neutralise with 6M NaOH and add 1 ml more of the reagent. Add 1 to 2 mg of  $\text{Fe}^{\text{III}}$  carrier dropwise with stirring. Centrifuge and discard the precipitate of  $\text{Fe}(\text{OH})_3$  (*Note 5*).

*Step 5:* Add 1 ml of 6M  $\text{HNO}_3$  to the supernatant solution and then add with stirring 1 ml of a 1% solution of dimethylglyoxime in 95%  $\text{C}_2\text{H}_5\text{OH}$ . Allow to stand for 10 min and filter through a Whatman No. 41 paper. Evaporate the filtrate to dryness adding a few drops of 10% KI during the evaporation, and then dissolve with 5 ml of 12M HCl.

*Step 6:* Pour the solution on a Deacidite FF (100–200 mesh, pre-equilibrated with 12M HCl) anion-exchange column 5 cm in length and 1 cm in diameter. Elute with 20 ml of 3M HCl into a 50-ml glass centrifuge tube and retain the eluate for selenium determination. Then elute with 20 ml of 0.3M HCl into a clean centrifuge tube and proceed on this solution with tellurium determination (*Note 6*).

*Step 7: Procedure for tellurium:* Add 2 mg of Pd carrier and 1 ml of 1% dimethylglyoxime reagent and filter through a Whatman No. 41 paper. Separate the filtrate into a clean centrifuge tube. Add a slight excess of dilute  $\text{NH}_4\text{OH}$ , and just acidify with 6M  $\text{CH}_3\text{COOH}$ . Centrifuge and wash the precipitate with  $\text{H}_2\text{O}$  and then with  $\text{C}_2\text{H}_5\text{OH}$ . Transfer the precipitate with a little  $\text{C}_2\text{H}_5\text{OH}$  on a

weighed aluminium counting tray and dry at 105° to constant weight. Weigh as TeO<sub>2</sub> and determine the chemical yield.

*Step 8: Procedure for selenium:* Take the solution for selenium determination from Step 6 and add 20 ml of 12M HCl. Place the centrifuge tube in an ice bath and precipitate selenium with SO<sub>2</sub>. Centrifuge and discard the supernate. Wash the precipitate well with H<sub>2</sub>O and then dissolve it in the minimum quantity of 6M HNO<sub>3</sub>. Evaporate to dryness. Add 1 ml of 6M NaOH and then 20 ml of 6M HCl and boil for 15 min after addition of 10 ml of a 20% solution of hydroxylamine hydrochloride. Centrifuge and discard the supernate. Wash the selenium, which is the black modification, with H<sub>2</sub>O and then with C<sub>2</sub>H<sub>5</sub>OH. Transfer the precipitate with a little C<sub>2</sub>H<sub>5</sub>OH on to a weighed aluminium counting tray, and dry at 110°. Weigh as Se and determine the chemical yield.

#### Notes

(1) The tellurium carrier may conveniently be standardized gravimetrically as TeO<sub>2</sub> and the selenium carrier by precipitation of metallic Se by means of hydroxylamine. For experimental details see Schoeller and Powell.<sup>9</sup>

(2) Before exchange between the radionuclides and carriers has been achieved the temperature must be carefully controlled to avoid the possibility of losses of selenium or tellurium by volatilization.<sup>10</sup>

(3) A rapid stream of SO<sub>2</sub> hastens precipitation and aids coagulation.

(4) A few drops of Manoxol OT (British Drug Houses Ltd.), 0.1% solution in water, prevents scum formation and aids in centrifuging.

(5) Scavenging with Fe(OH)<sub>3</sub> removes general contamination. An excessive loss of tellurium by coprecipitation with Fe(OH)<sub>3</sub> is prevented by the addition of only a small amount of Fe<sup>III</sup> carrier after the solution has been made alkaline.

(6) The anion-exchange step<sup>7</sup> can give a separation factor of selenium from tellurium of greater than 10<sup>4</sup>.

#### Measurement of radioactivity

In the present work the isolated precipitates of TeO<sub>2</sub> were counted under similar conditions with a Geiger-Müller counter of the EHM 2/S type. All measured counting rates were corrected for paralysis, background, and chemical yield, and for decay between counting precipitates from samples and comparators. The sources for counting were of similar weight, and no correction for self absorption was necessary. Radiochemical purity was demonstrated by plotting decay curves. A typical experimental decay curve is shown in Fig. 1.

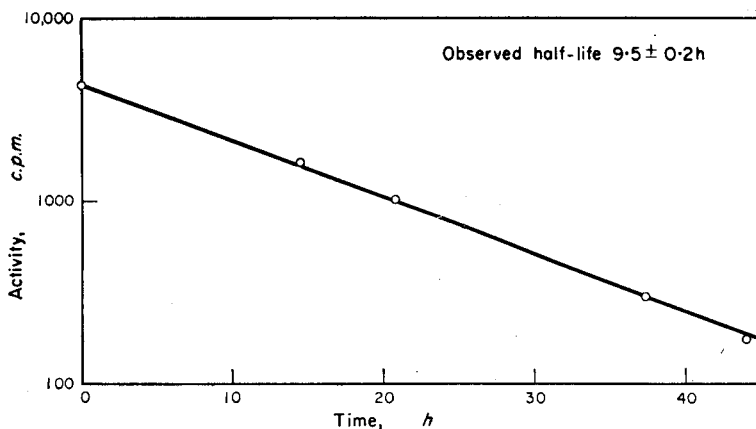


FIG. 1.—Typical decay curve of a final sample of TeO<sub>2</sub>.

The final precipitates of Se were counted with a NaI(Tl) crystal scintillation counter type 1186A. All measured activities were corrected for background and chemical yield. No coincidence correction was necessary. Radiochemical purity was shown by  $\gamma$ -spectrometer measurements and by measurements of decay (see Figs. 2 and 3).

## RESULTS

In Table IV are shown results of analyses of purified samples of platinum.

FIG. 2.—Gamma-ray spectrum of a separated sample of Se. Measured with a  $1 \times 1.5$ -inch NaI(Tl) crystal scintillation spectrometer with single-channel pulse-height analyser.

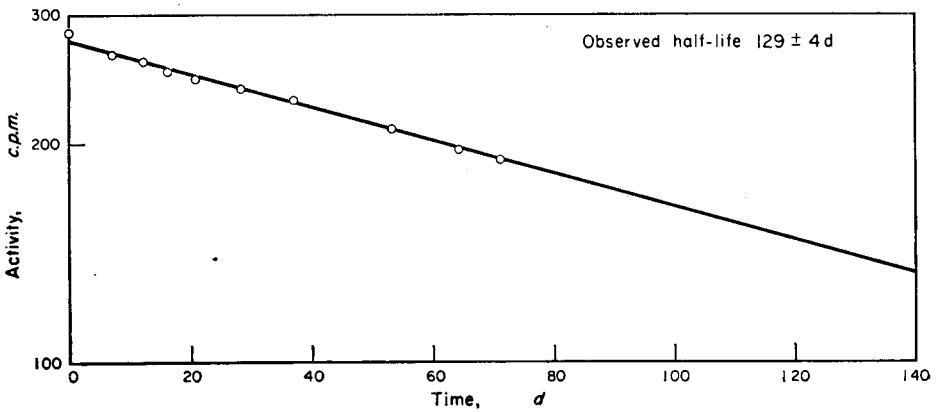
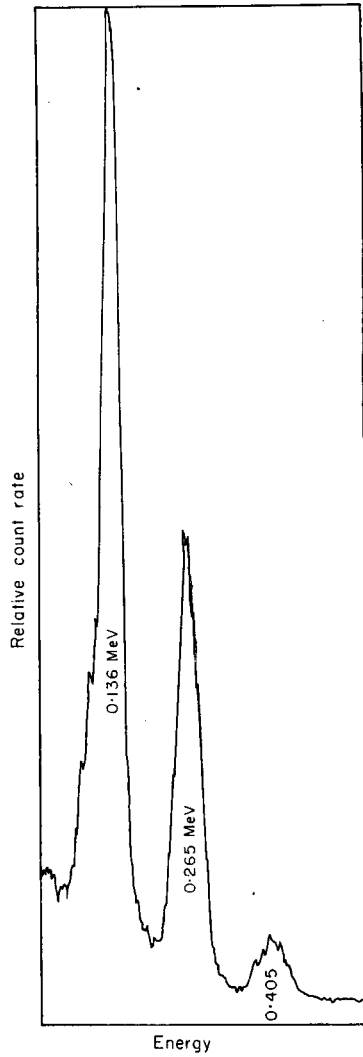


FIG. 3.—Typical decay curve of a final sample of Se.

TABLE IV.—SELENIUM AND TELLURIUM CONTENTS OF SAMPLES OF PLATINUM DETERMINED BY NEUTRON-ACTIVATION ANALYSIS

Sample	Selenium found, <i>ppm</i>	Tellurium found, <i>ppm</i>
Pt 1	0.84	2.5
	0.85	2.6
	0.89	2.2
	0.90	2.2
Pt 2	1.1	3.0
	1.2	3.1
Pt 3	1.8	2.7
	1.6	2.8
Pt 4	1.7	2.7
	1.8	2.8
Pt 5	2.7	2.4
	3.2	2.2
	3.1	2.1
	3.1	2.0
	2.6	
	2.6	
Pt 6	0.72	1.2
	0.71	1.3
Pt 7	0.9	0.76
	0.9	0.78

*Acknowledgement*—We are grateful to The International Nickel Company (Mond) Ltd., for supplying samples of platinum, for financial support, and for a Research Fellowship to one of us (R. A. K.).

**Zusammenfassung**—Eine Methode zur Bestimmung von Submikrogrammengen Selens und Tellurs in Platin mittels Neutronenaktivierung wird beschrieben. Nach Bestrahlung der Probe in einem Kernreaktor werden gemessene Mengen von Tellur und Selen zur Probe zugesetzt und die chemische Trennung der Elemente wird durchgeführt. Die Aktivität von  $^{127}\text{Te}$  und  $^{76}\text{Se}$  wird gezählt und mit unter gleichen Bedingungen bestrahlten Standardproben verglichen. Resultate für 7 verschiedene Proben werden mitgeteilt.

**Résumé**—Les auteurs décrivent une méthode de dosage au moyen de l'analyse par activation de neutrons, du sélénium et du tellure dans le platine pour des quantités inférieures au microgramme. Après l'irradiation d'un échantillon dans un réacteur nucléaire, on ajoute des quantités connues de sélénium et de tellure, et l'on effectue une séparation chimique. Les activités de  $^{127}\text{Te}$  et  $^{76}\text{Se}$  provenant de l'échantillon considéré sont comparées aux activités correspondantes de témoins irradiés en même temps que les échantillons à analyser. Les résultats obtenus pour sept séries de platine pur ont été signalés.

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# A NEW PRINCIPLE OF ACTIVATION-ANALYSIS SEPARATIONS—I

## THEORY OF SUBSTOICHIOMETRIC DETERMINATIONS

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**Summary**—Separation procedures in the activation analysis of elements mainly consist of many steps which are usually derived from classical analysis schemes. In all cases an excess of reagent (precipitating, complexing, etc.) is used for separation of the element to be determined. In the present paper separations by means of a smaller amount of reagent than corresponds to the stoichiometric ratio of element to be determined are discussed. The use of an insufficient amount of the reagent has two advantages: greater selectivity (possibility of eliminating many steps) and elimination of the necessity for determining the chemical yield of the element in question. As a result the analysis is more rapid.

### INTRODUCTION

IN activation analysis procedures involving separations the principle of reversal isotopic dilution is commonly used. For a determined element, the activity  $A$  induced in the analysis sample by irradiation, is calculated from the relation

$$A = a \frac{x}{m} \quad (1)$$

where  $a$  = the activity of the recovered fraction of weight  $m$ ,  
and  $x$  = the amount of carrier added.

The same relation is valid for a standard sample irradiated simultaneously with the analysed sample

$$A_s = a_s \frac{x_s}{m_s} \quad (2)$$

where

$A_s$  = the activity of the determined element induced in the standard sample by irradiation,

and

$a_s$  = the activity of the fraction of weight  $m_s$  recovered from the irradiated standard sample.

Because the analysed sample (containing an unknown amount  $y$  of the element to be determined) and the standard sample (containing a known amount  $y_s$  of the same element) are irradiated simultaneously, the following equation is valid

$$y:y_s = A:A_s \quad (3)$$

For  $x = x_s$  and  $m = m_s$

$$y = y_s \frac{a}{a_s} \quad (4)$$

From equation (4) it follows that for the determination of the element by activation analysis, it is not necessary to determine the chemical yield if the following two conditions are fulfilled:

1. The amounts of carrier added to the standard and analysed samples are equal ( $x = x_s$ ).
2. The amounts of the element (compound) isolated from the standard and analysed samples for measurement of the activity are equal ( $m = m_s$ ).

To fulfill the first condition is very simple; after irradiation, when starting chemical analysis any amount of carrier can be chosen. The second condition is far more difficult. It can be fulfilled by adding a smaller amount of the reagent (precipitating, complexing, *etc.*) than corresponds to the stoichiometric ratio of the metal to be determined. The compound formed must be easily separated from the excess of unreacted metal by solvent extraction, ion exchange, precipitation, electrolysis or by some other separation technique.

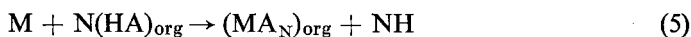
This principle was successfully used for the selective determination of metals by isotopic dilution analysis by solvent extraction<sup>1-5</sup> or by ion exchange.<sup>6</sup> In these cases the determinations were more difficult because the separated amounts of the determined metals were very small (down to  $10^{-10}$  g). In substoichiometric activation analysis separations the conditions are far more simple because the amount of carrier added is greater (approximately  $10^{-2}$  g). For this reason it will be possible to use other methods (precipitation, electrolysis, *etc.*) and a larger number of reagents for substoichiometric separations.

## THEORY

### *Solvent extraction*

In a previous paper<sup>1</sup> the general theory of extraction of metal chelates by an insufficient amount of reagent was given. The basic equation derived is, in general, applicable for activation analysis separations.

From the equilibrium constant  $K$  (extraction constant) of the extraction process\*



and from the condition that more than 99.9% of the organic reagent HA has been used in forming the extractable complex  $\text{MA}_N$ , the pH of the determination is:

$$\text{pH} > \frac{1}{N} \log \frac{c_{\text{HA}}}{N} - \frac{1}{N} \log \left[ c_{\text{M}} - \frac{c_{\text{HA}} V_{\text{org}}}{NV} \right] - \frac{1}{N} \log K - \log 0.001 c_{\text{HA}} \quad (6)$$

where

$c_{\text{HA}}$  = the original concentration of organic reagent in the organic phase,

$c_{\text{M}}$  = the original concentration of the metal M,

and

$V_{\text{org}}$  and  $V$  = the volumes of organic and aqueous phase, respectively.

From equation (6) it is evident that the first two terms on the right-hand side have relatively little influence on the value of the threshold pH-value. If, for example, the

\* The charges are omitted for simplicity.

amount of organic reagent is half of that amount which would correspond to the stoichiometric ratio, the sum of these two terms for  $V_{\text{org}} = V$  is zero.

In activation analysis the amount of carrier added is usually of the order of  $10^{-2}$  g/10 ml. This corresponds approximately to a  $10^{-2}M$  solution of metal ion. The initial concentration of organic reagent must be of the same order. For this case equation (6) may be simplified to

$$\text{pH} \geq 5 - \frac{1}{N} \log K \quad (6')$$

It follows from this equation that the pH-values for the determination of many metals may be easily predicted from the known values of  $\log K$  (see Table I).<sup>7</sup>

In the presence of masking agent  $H_nB$ , used to increase the selectivity, the threshold pH can be calculated from the following equation

$$\text{pH} \geq 5 - \frac{1}{N} \log K + \frac{1}{N} \log (1 + K_s[B]^n) \quad (7)$$

where

$$K_s = \frac{[MB_n]}{[M][B]^n} \quad (8)$$

TABLE I.—LOG K-VALUES FOR VARIOUS EXTRACTION SYSTEMS

Metal	Acetyl- acetone in benzene	Benzoyl- acetone in benzene	Dibenzoyl- methane in benzene	Thenoyl- trifluor- acetone in benzene	8-hydroxy- quinoline in chloro- form	Dithizone in carbon tetrachlo- ride
Ag <sup>I</sup>		-7.8	-8.6		-4.5*	8.9
Al <sup>III</sup>	-6.5	-7.6	-8.9	-5.2	-5.2	
Ba <sup>II</sup>				-14.4	-20.9†	
Be <sup>II</sup>	-2.8	-3.9	-3.5	-3.2	-9.6	
Bi <sup>III</sup>				-3.2	-1.2	9.6
Ca <sup>II</sup>		-18.3	-18.0	-12.0	-17.9*	
Cd <sup>II</sup>		-14.1	-14.0	-11.4	-5.3†	2.1
Co <sup>II</sup>		-11.1	-10.8	-6.7	-2.2†	0.0
Cu <sup>II</sup>	-3.9	-4.2	-3.8	-1.3	-1.8	9.6
Fe <sup>III</sup>	-1.4	-0.5	-1.9	3.3	4.1	
Ga <sup>III</sup>	-5.5	-6.3	-5.8		3.7	
Hg <sup>II</sup>						26.8
In <sup>III</sup>	-7.2	-9.3	-7.6	-4.3	-0.9	4.8
La <sup>III</sup>		-20.5	-19.5	-10.5	-16.4	
Mg <sup>II</sup>		-16.6	-14.7		-15.1	
Mn <sup>II</sup>		-14.6	-13.7		-9.3	
Ni <sup>II</sup>		-12.1	-11.0		-2.2	-0.6
Pb <sup>II</sup>	-10.2	-9.6	-9.4	-5.2	-8.0	1.2
Pd <sup>II</sup>	>2	1.2			15.0	>26
Sc <sup>III</sup>	-5.8	-6.0	-6.0	-0.8	-6.6*	
Sr <sup>II</sup>		-20.0	-20.9	-14.1	-19.7†	
Th <sup>IV</sup>	-12.2	-7.7	-6.4		0.8	
Tl <sup>I</sup>				-5.2	-7.2	-3.3
U <sup>VI</sup>	-5.2*	-4.7*	-4.1*	-2.0	-1.6*	
Zn <sup>II</sup>		-10.8	-10.7		-2.4†	2.7
Zr <sup>IV</sup>				9.0		

\* Complexes  $MA_NHA$  are formed.

† Complexes  $MA_NHA_2$  are formed.

### Selectivity of the method

Each organic reagent forms extractable complexes with a certain number of metals. It is, therefore, evident that an extractable metal can be determined in the presence of any excess of non-extractable metals.

A selective determination of a certain metal may be worked out, however, even in the presence of the metals which also form extractable complexes with the reagent employed. The concentration ratio of the two metals ( $M'$  and  $M''$ ) in the organic phase is easily determined from the individual  $K$ -values:

$$\frac{[M'A_{N'}]_{\text{org}}}{[M''A_{N''}]_{\text{org}}} = \frac{K'[HA]_{\text{org}}^{N'-N''} [M']}{K''[H]^{N'-N''} [M'']} \quad (9)$$

Metals having higher values of extraction constant  $K$  can be selectively separated from metals with lower  $K$ -values. Using an insufficient amount of organic reagent (*i.e.* providing substoichiometric separation), the selectivity of the determination increases for the following reasons:

1. As may be seen from equation (9), for quantitative (*i.e.*  $\frac{[M'A_{N'}]_{\text{org}}}{[M''A_{N''}]_{\text{org}}} > 100$ , and  $\frac{[M']}{[M'']} < 0.01$ ) separation of metal  $M'$  from the interfering metal  $M''$  (initial concentrations of both metals are equal and the charges are also equal) by means of the excess of organic reagent, the ratio  $\frac{K'}{K''}$  has to be higher than  $10^4$ . For a substoichiometric separation using only half of the amount of the reagent that corresponds to the amount of metal  $M'$  present, the ratio  $\frac{K'}{K''}$  has to be higher than 200 for the same condition (*i.e.*  $\frac{[M'A_{N'}]_{\text{org}}}{[M''A_{N''}]_{\text{org}}} > 100$  for  $\frac{[M']}{[M'']} = 0.5$ ).
2. For the case  $N' = N''$ , the selectivity of the separation does not depend on the pH-value.

The selectivity of the separation may be further increased by adding masking agent  $H_nB$ . In this case equation (9) is transferred into the form:

$$\frac{[M'A_{N'}]_{\text{org}}}{[M''A_{N''}]_{\text{org}}} = \frac{K'[HA]_{\text{org}}^{N'-N''} c_{M'}(1 + K_s''[B]^S)}{K''[H]^{N'-N''} c_{M''}(1 + K_s'[B]^S)} \quad (10)$$

The higher is the value  $\frac{1 + K_s''[B]^S}{1 + K_s'[B]^S}$ , the more selective is the separation provided.

From the theory and from the results of previous work<sup>2-5</sup> the conditions for determination of many metals in various materials by means of substoichiometric activation analysis may be predicted. Thus, it will be possible to determine by dithione extraction mercury, zinc, silver and copper in various materials. The determination of mercury in 5-50% sulphuric acid will be very selective.<sup>3</sup> Zinc can be determined with high selectivity at pH 7-9 in the presence of a masking agent—diethanoldithiocarbamate.<sup>2</sup> Copper may be determined at pH 1-3 in the presence of potassium iodide.<sup>4</sup> Determination of silver can be carried out at pH 4-5 in the presence of EDTA.<sup>9</sup> Using cupferron extraction, iron<sup>5</sup> may be selectively determined in the presence of thiourea and hexamethylenetetramine at pH 4-5.

The basic procedure for all cases is as follows:

1. Both standard and analysed samples are irradiated under the same conditions.
2. After dissolution, exactly the same amounts of carrier (*ca.* 1 mg) are added to both samples. (Holdback carrier may be also added.)
3. Both solutions are simultaneously extracted with dithizone-carbon tetrachloride (or with cupferron-chloroform) solution under the above described conditions. The amount of organic reagents used for the extraction must be exactly the same and less than corresponds to the stoichiometric amount of the carrier added.
4. The activities of aliquots of the extracts are measured under the same conditions. The amount of determined element in the analysis sample is calculated from equation (4).

In conclusion it may be said that ion association systems may also be used for substoichiometric separations in activation analysis. It can be expected, for example, that it will be possible to determine antimony by substoichiometric extraction as a complex with methyl violet from concentrated hydrochloric acid.<sup>8</sup>

### *Ion exchange*

The theory of isotopic dilution analysis<sup>6</sup> by ion exchange can also be generally used for activation analysis by substoichiometric separations. The method consists of adding a smaller amount of complexing agent than stoichiometrically corresponds to the amount of metal present. The complex formed is then separated from the excess of unreacted metal by means of ion exchange. The complexing agent  $H_nY$  has to form with the metal to be determined a neutral or negatively charged complex  $MY$ , the stability of which has to fulfil the following condition:

$$K_{MY} = \frac{[MY]}{[M][Y]} \geq \frac{c_{H_nY} \sum_{n=0}^{\infty} \frac{[H]^n}{k_0 \dots k_n}}{(c_M - c_{H_nY}) 0.001 c_{H_nY}} \quad (11)$$

where

$c_{H_nY}$  = the original concentration of complexing agent,  
and

$$k_n = \frac{[H][H_{n-1}Y]}{[H_nY]} \quad (k_0 = 1) \quad (12)$$

For our case where the amount of element to be isolated is approximately 1 mg of metal/ml and the amount of complexing agent is half of the amount which corresponds to the metal present, equation (12) can be simplified to

$$K_{MY} \geq 10^5 \sum_{n=0}^{\infty} \frac{[H]^n}{k_0 \dots k_n} \quad (13)$$

From this equation it follows that  $Fe^{III}$ , Tn, Th, Ga can be determined as EDTA-complexes at a pH higher than 2 ( $K_{MY}$  values are higher than  $10^{19}$ ); Cu, Ni, Pb, *etc.*, may be determined as EDTA-complexes at a pH higher than 3 ( $K_{MY}$  values are higher than  $10^{16}$ ), *etc.* The selectivity of ion exchange substoichiometric separations is the same as in the case of solvent extraction. Using an insufficient amount of complexing agent increases the selectivity of the separation.

From this theory and from our previous experiments<sup>6</sup> it follows, for example, that it will be possible to determine iron as its EDTA-complex at pH 2-3. This negatively charged complex is separated from the excess of unreacted iron<sup>III</sup> on a cation exchanger (Dowex 50 in Na-form). The basic procedure is principally the same as described above.

### Precipitation reactions

The conditions for substoichiometric separations with the use of precipitation agent HA can be derived from the solubility product

$$S_{MA_N} = [M][A]^N = [M] \frac{K_{HA}^N [HA]^N}{[H]^N} \quad (14)$$

where

$$K_{HA} = \frac{[H][A]}{[HA]} \quad (15)$$

From the condition that more than 99.9% of organic reagent HA should react to form precipitate MA<sub>N</sub> (i.e. [HA] < 0.001c<sub>HA</sub>, where c<sub>HA</sub> is the original concentration of HA) it follows that

$$S_{MA_N} < [M] \frac{K_{HA}^N (0.001c_{HA})^N}{[H]^N} \quad (16)$$

from which the threshold pH-value of the determination may be derived:

$$pH > \frac{1}{N} (NpK_{HA} - pS_{MA_N} - \log [M] - N \log c_{HA} + 3N) \quad (17)$$

For our case c<sub>M</sub> and c<sub>HA</sub> are of order 10<sup>-2</sup>M, i.e.

$$pH > \frac{1}{N} (NpK_{HA} - pS_{MA_N} + 2 + 5N) \quad (18)$$

From equation (18) it follows that iron<sup>III</sup>, for example, can be determined as iron<sup>III</sup> cupferrate at pH higher than 1.5 (pS<sub>MA<sub>N</sub></sub> = 25, pK<sub>HA</sub> = 4.2); aluminium can be precipitated as aluminium cupferrate at a pH higher than 3.7 (pS<sub>MA<sub>N</sub></sub> = 18.6).

The selectivity of separation by substoichiometric precipitation, like that for solvent extraction and ion exchange, is much higher than for precipitation with an excess of reagent. It may be further increased by masking interfering metals. In this case, the pH of the determination is

$$pH > \frac{1}{N} \left[ NpK_{HA} - pS_{MA_N} + 2 + 5N + \log(1 + K_s[B]^S) \right] \quad (19)$$

where K<sub>s</sub> is the stability constant of the water soluble complex MB<sub>s</sub>.

### CONCLUSION

It has been shown that the use of substoichiometric separations in activation analysis increases the speed of many activation analysis procedures for the following reasons:

1. Separation procedures using substoichiometric amounts of reagent are far more selective than current methods using an excess of reagent, and thus it will be possible to reduce the time required for an analysis.
2. The necessity of determining the chemical yield is eliminated. Because equal amounts of the element (compound) are isolated from the standard and analysed solution, the activities of these two fractions are directly proportional to the amounts of the determined element originally present in the standard and analysed samples.

The experimental possibilities of substoichiometric separations in activation analysis are now being investigated in our laboratory.

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**Zusammenfassung**—Trennungsmethoden in der Aktivierungsanalyse von Elementen sind gewöhnlich aufgrund klassischer Analysengänge ausgearbeitet und bestehen aus zahlreiche Einzeloperationen. In allen Fällen wird ein Überschuss an Reagens (Fällungsmittel, Komplexbildner usw.) zugesetzt. In der vorliegenden Arbeit wird gezeigt, dass man Trennungen mit weniger als der stöchiometrischen Menge an Reagens durchführen kann. Die Anwendung eines Unterschusses hat zwei Vorteile: höhere Selektivität (Möglichkeit eine mehrstufige Operation zu vermeiden) und Ausschaltung der Notwendigkeit quantitativ zu arbeiten. Im Endergebnis resultiert höhere Analysengeschwindigkeit.

**Résumé**—Le procédé de séparation des éléments dans l'analyse par activation consiste en une suite d'étapes habituellement dérivées des schémas de l'analyse classique. Dans tous les cas pour la séparation de l'élément considéré, on utilise un excès de réactif (précipitation, formation de complexes, etc.) Cet article est consacré à une technique de séparation des éléments, en utilisant des quantités de réactif plus faibles que celles correspondant à la formule stoechiométrique, ce qui présente deux avantages: une sélectivité (possibilité d'élimination de plusieurs étapes) et l'affranchissement de l'obligation de déterminer le pourcentage chimique de l'élément considéré. L'analyse est ainsi plus rapide.

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## A NEW REDUCTIMETRIC REAGENT: IRON<sup>II</sup> IN A STRONG PHOSPHORIC ACID MEDIUM—III\*

### TITRATION OF VANADIUM<sup>IV</sup> OR VANADIUM<sup>V</sup> WITH IRON<sup>II</sup> AT ROOM TEMPERATURE: DETERMINATION OF CHROMIUM<sup>VI</sup> AND VANADIUM<sup>V</sup> IN THE SAME SOLUTION

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**Summary**—The formal redox potential of the V<sup>IV</sup>/V<sup>III</sup> couple has been determined in a medium of varying phosphoric acid concentration. From these results and those previously reported for the Fe<sup>III</sup>/Fe<sup>II</sup> couple, the formal redox potential of the V<sup>IV</sup>/V<sup>III</sup> couple is higher than that of the Fe<sup>III</sup>/Fe<sup>II</sup> couple for a concentration of phosphoric acid above 4.0M, the difference between the formal redox potentials increasing with increasing concentration of phosphoric acid. At a concentration of 10.5M phosphoric acid the V<sup>IV</sup>/V<sup>III</sup> couple has a potential which is about 0.27 V higher than that of the Fe<sup>III</sup>/Fe<sup>II</sup> couple, so that iron<sup>II</sup> then rapidly reduces vanadium<sup>IV</sup> to vanadium<sup>III</sup> even at room temperature. Using this reaction a titrimetric procedure has been developed for determination of vanadium<sup>IV</sup> either with a potentiometric end-point or with a visual end-point using methylene blue or thionine as redox indicators. Titrations using these indicators must be carried out in an inert atmosphere. The new reagent is more advantageous than titanium<sup>III</sup> or chromium<sup>II</sup> which require special storage conditions. Moreover, iron<sup>III</sup> and tungsten<sup>VI</sup> do not interfere with the use of this reagent as they do with titanium<sup>III</sup> or chromium<sup>II</sup>. Further, the new reagent enables the determination of chromium<sup>VI</sup> and vanadium<sup>V</sup> in a single solution to be carried out with a potentiometric end-point. The first break in the potential curve corresponds to the reduction of chromium<sup>VI</sup> to chromium<sup>III</sup> and of vanadium<sup>V</sup> to vanadium<sup>IV</sup>, and the second break corresponds to the further reduction of vanadium<sup>IV</sup> to vanadium<sup>III</sup>. Iron<sup>III</sup>, manganese<sup>II</sup>, cobalt<sup>II</sup> and tungsten<sup>VI</sup> do not interfere. This procedure is likely to be of considerable value in the analysis of special steels.

In previous parts<sup>1,2</sup> of this series the use of iron<sup>II</sup> was reported as a new reductimetric reagent for the direct titration of uranium<sup>VI</sup> and molybdenum<sup>VI</sup> in a strong phosphoric acid medium at room temperature. It has now been found that vanadium<sup>IV</sup> is quantitatively reduced to vanadium<sup>III</sup> by iron<sup>II</sup> under similar conditions. In a dilute sulphuric or hydrochloric acid medium iron<sup>II</sup> normally has no action on vanadium<sup>IV</sup>; on the other hand, iron<sup>III</sup> slowly oxidises vanadium<sup>III</sup> to vanadium<sup>IV</sup>. In order to elucidate the mechanism of the reversal of the normal redox reaction now observed in a strong phosphoric acid medium, the formal redox potential of the V<sup>IV</sup>/V<sup>III</sup> couple has been measured in media of varying phosphoric acid concentration. The potential was found to increase with increasing phosphoric acid concentration, while that of the Fe<sup>III</sup>/Fe<sup>II</sup> couple decreases.<sup>1</sup> From Fig. 1, the formal redox potential of the V<sup>IV</sup>/V<sup>III</sup> couple begins to have a value higher than that of the Fe<sup>III</sup>/Fe<sup>II</sup> couple in a phosphoric acid concentration above 4.0M, the difference between the formal redox potentials

\* Part II: see reference 2.

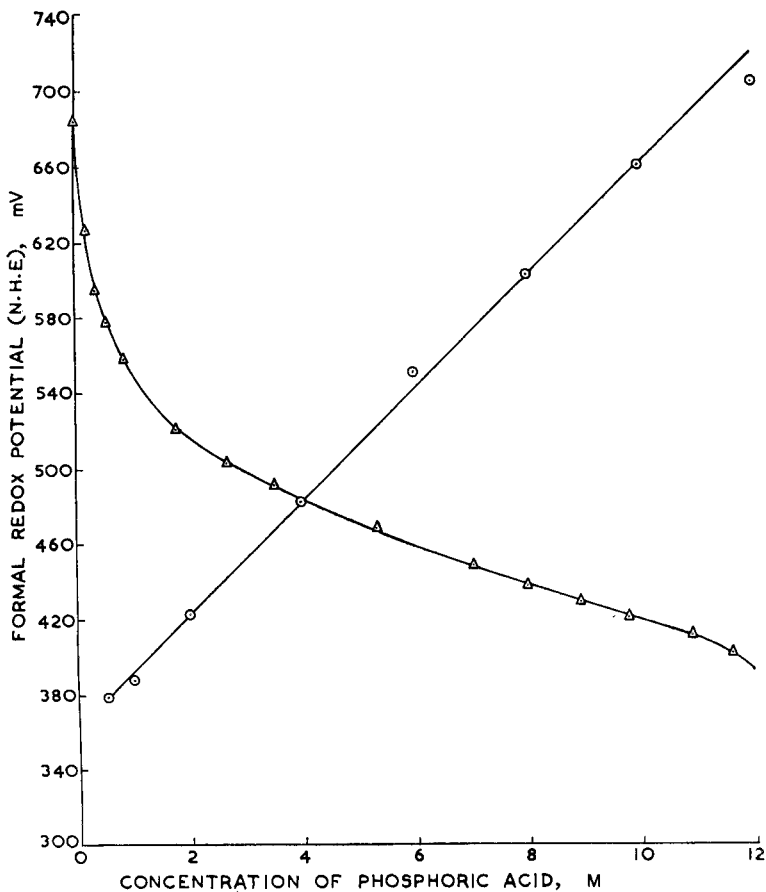


FIG. 1.—Formal redox potentials of the  $V^{IV}/V^{III}$  and  $Fe^{III}/Fe^{II}$  couples in a medium of varying phosphoric acid concentration:

○—○— $V^{IV}/V^{III}$  couple,  
 △—△— $Fe^{III}/Fe^{II}$  couple.

increasing with increasing concentration of phosphoric acid. At a concentration of 10.5M phosphoric acid the  $V^{IV}/V^{III}$  couple has a potential which is about 0.270 V higher than that of the  $Fe^{III}/Fe^{II}$  couple. Because this difference is sufficiently large for a speedy reaction to take place between vanadium<sup>IV</sup> and iron<sup>II</sup> a study of the various factors involved in the reaction was undertaken. This study enabled a new redoximetric titration of vanadium<sup>IV</sup> to be developed with iron<sup>II</sup> in a strong phosphoric acid medium at room temperature, using either a potentiometric end-point in 12.0–13.0M phosphoric acid or a visual end-point with methylene blue or thionine as internal redox indicator in 10.5–13.0M phosphoric acid. Also, a potentiometric titration procedure for the differential determination of chromium<sup>VI</sup> and vanadium<sup>V</sup> in the same solution has been developed with the new reagent. This procedure is much more convenient than the procedures currently available.

The redoximetric reagents previously proposed for the titrimetric determination of vanadium<sup>IV</sup> are not very satisfactory. Thus, Kolthoff and Tomiček<sup>3</sup> found that more than the theoretical amount of titanium<sup>III</sup> was consumed in the redoximetric

titration of vanadium<sup>IV</sup> at room temperature. They reported better results when the titration was carried out at 50–60° in the presence of Rochelle salt. Zintl and Zaimis<sup>4</sup> found that vanadium<sup>IV</sup> can be titrated at room temperature with chromium<sup>II</sup>. Both titanium<sup>III</sup> and chromium<sup>II</sup> have the disadvantage that their aqueous solutions require special storage conditions on account of their instability to the oxygen of the air. Moreover, they cannot be used for the determination of vanadium<sup>IV</sup> in the presence of iron<sup>III</sup>. In a recent short communication, Miller<sup>5</sup> proposed the use of iron<sup>II</sup> for the reductimetric titration of vanadium<sup>IV</sup> in catechol solutions in an ammonical medium (pH 9.5) in an inert atmosphere. The strong reducing power of iron<sup>II</sup> under his experimental conditions is attributed to the high stability of the iron<sup>III</sup>-catechol complex as compared with that of the iron<sup>II</sup>-catechol complex. Miller did not give any details of the experimental procedure for an accurate assay of vanadium<sup>IV</sup> with his new reagent. Our reagent has the advantage over that of Miller in that it can be used for the titrimetric determination of vanadium<sup>IV</sup> or vanadium<sup>V</sup> even in the presence of air. Another disadvantage of the Miller reagent is that the complexing agent used therein, namely catechol, is not inert. For instance, it reduces vanadium<sup>V</sup> to vanadium<sup>IV</sup>, whereas the phosphoric acid forming part of our reagent is perfectly inert by itself.

## EXPERIMENTAL

### *Determination of Formal Redox Potential of V<sup>IV</sup>/V<sup>III</sup> Couple in Media of Varying Phosphoric Acid Concentration*

#### *Reagents*

**0.05M Vanadium<sup>IV</sup> sulphate solution:** Prepared as described previously,<sup>6</sup> then standardised with cerium<sup>IV</sup> sulphate using rhodamine 6G as fluorescent indicator and a small amount of syrupy phosphoric acid as catalyst.<sup>6</sup> From this solution an exactly 0.05M solution of vanadium<sup>IV</sup> is prepared, the over-all acidity with respect to sulphuric acid being adjusted to 0.25M.

**0.05M Vanadium<sup>III</sup> sulphate solution:** Prepared by cathodic reduction of an aliquot volume of 0.1M sodium vanadate solution in 0.25M sulphuric acid using a diaphragm cell. Reduction is carried out by means of four 2-V batteries connected in series, using a bright platinum gauze as the cathode and a platinum rod as the anode, and it is continued until the solution is deep green in colour. The reduced solution is diluted to give the desired strength, keeping the over-all acidity with respect to sulphuric acid at 0.25M, then transferred to a reservoir fitted with a burette to be stored under nitrogen. The solution contains mostly vanadium<sup>III</sup> and a little vanadium<sup>IV</sup> sulphate. Vanadium<sup>III</sup> present is determined by titration with a standard solution of sodium vanadate.<sup>7</sup> Another aliquot of the solution is titrated with a standard solution of cerium<sup>IV</sup> sulphate using Rhodamine 6G as fluorescent indicator,<sup>6</sup> which gives the total of vanadium<sup>III</sup> and vanadium<sup>IV</sup> present. From these two titrations the composition of the solution is calculated with respect to vanadium<sup>III</sup> and vanadium<sup>IV</sup>.

**Syrupy phosphoric acid:** Syrupy phosphoric acid of "Pro Analsi" grade supplied by E. Merck (Germany) is used in this investigation. The strength of phosphoric acid is determined, after suitable dilution, by titration with a standard solution of sodium hydroxide using a mixture of phenolphthalein and  $\alpha$ -naphtholphthalein (1:1) as indicator.

#### *Apparatus*

The potentiometric assembly consists of a Cambridge potentiometer and a suspension galvanometer. A bright platinum rod (about 0.2 mm in diameter) serves as the indicator electrode and a saturated calomel electrode as the reference electrode. An inverted U-tube with porous end-plates, filled with a saturated solution of potassium chloride, is used as the salt bridge.

#### *Procedure*

After determining the concentrations of vanadium<sup>III</sup> and vanadium<sup>IV</sup> in the vanadium<sup>III</sup> sulphate solution, a volume corresponding to 5.0 ml of 0.05M solution of vanadium<sup>III</sup> is taken. Enough vanadium<sup>IV</sup> solution is then added such that the total concentration with respect to vanadium<sup>IV</sup> also corresponds to 5.0 ml of 0.05M. After adding enough phosphoric acid to give the required strength, the mixture is made up to 50 ml. Because of the considerable heat of dilution of phosphoric acid, the mixed vanadium solutions and phosphoric acid are taken in a 50 ml measuring flask along with

most of the water and allowed to cool to room temperature before the final dilution to the mark. The mixture is placed in a 3-necked flask through one neck of which passes an inlet tube for nitrogen. A bright platinum rod fitted in a stopper is inserted through the second neck and a salt bridge is inserted through the third neck, which also serves as an outlet for nitrogen. The three-necked flask is kept in a thermostat maintained at 28°.

The potential of the mixture is read against a saturated calomel electrode. Oxygen-free nitrogen is passed through the mixture continuously during the measurement of potentials. The potentials show considerable drift and steady values are not obtained even after 3 hr. However, the interesting observation was made that the addition of 1 drop of a 0.05M solution of iron<sup>III</sup> chloride helps a more speedy attainment of steady potentials. This has also been the experience of Coryell and Yost<sup>8</sup> in determination of the potentials of the V<sup>V</sup>/V<sup>IV</sup> couple. In the presence of iron<sup>III</sup> chloride, it takes 60 min for the potentials to reach steady values. The added iron<sup>III</sup> chloride does not react with the vanadium<sup>III</sup> in the presence of phosphoric acid. The drift in potential has been observed to decrease as the concentration of phosphoric acid is increased. When the concentration of phosphoric acid is  $\geq 4M$ , equilibrium potentials are obtained within 30 min; when it is 10–12M, the potentials reach steady values within 15 min. The potentials obtained in a medium of varying phosphoric acid concentration are given in Table I. They are not corrected for the liquid-liquid junction potential.

TABLE I.—FORMAL REDOX POTENTIALS OF V<sup>IV</sup>/V<sup>III</sup> COUPLE IN A MEDIUM OF VARYING PHOSPHORIC ACID CONCENTRATION (temperature: 28°; total vanadium concentration: 0.01M).

Concentration of phosphoric acid, M	Formal redox potential (N.H.E.), V
0.50	0.379
1.00	0.388
2.00	0.422
4.00	0.481
6.00	0.550
8.00	0.601
10.00	0.658
12.00	0.702

The data presented in Table I are shown graphically in Fig. 1. In the same figure the curve showing the variation of the potential of the Fe<sup>III</sup>/Fe<sup>II</sup> couple with changing phosphoric acid concentration is also included.<sup>1</sup>

#### *Reduction of Vanadium<sup>IV</sup> to Vanadium<sup>III</sup> with Iron<sup>II</sup> in a Strong Phosphoric Acid Medium*

Canning and Dixon<sup>8</sup> observed that vanadium<sup>IV</sup> is reduced to vanadium<sup>III</sup> by iron<sup>II</sup> in a 40% (by volume) phosphoric acid medium when heated to boiling for 5 min. We have now observed that vanadium<sup>IV</sup> is completely reduced to vanadium<sup>III</sup> within 1 min at room temperature when mixed with an equivalent amount of iron<sup>II</sup> in a 50% (by volume) phosphoric acid medium. That the reduced solution contains only the vanadium<sup>III</sup> species has been established by quantitative spectrophotometry. Vanadium<sup>III</sup> was prepared by electrolytic reduction of vanadium<sup>IV</sup> in 0.25M sulphuric acid, then treated with enough phosphoric acid to give an over-all concentration of 80% (by volume). The absorption spectrum of this solution (Fig. 2) shows two absorption maxima. The vanadium<sup>III</sup> solution prepared by reduction of vanadium<sup>IV</sup> with iron<sup>II</sup> in 80% (by volume) phosphoric acid gives an absorption curve showing similar maxima. Moreover, the molecular extinction coefficients of the vanadium<sup>III</sup> prepared by the two different methods agree quite closely, having values of 13.1 and 8.6 at 460 and 690 m $\mu$ , respectively. The two curves are also seen to overlap. The solution of vanadium<sup>III</sup> in 80% phosphoric acid is yellow-green in colour while the corresponding solution in 1.0M sulphuric acid is deep green in colour.

#### *Electrometric Titration of Vanadium<sup>IV</sup> with Iron<sup>II</sup> in a Concentrated Phosphoric Acid Medium*

In view of the foregoing observations, experiments were made to ascertain the conditions under which vanadium<sup>IV</sup> can be titrated with iron<sup>II</sup> using a potentiometric end-point.

#### *Reagents*

0.05M Vanadium<sup>IV</sup> sulphate solution: Prepared in 0.25M sulphuric acid and standardised according to the procedure already described.

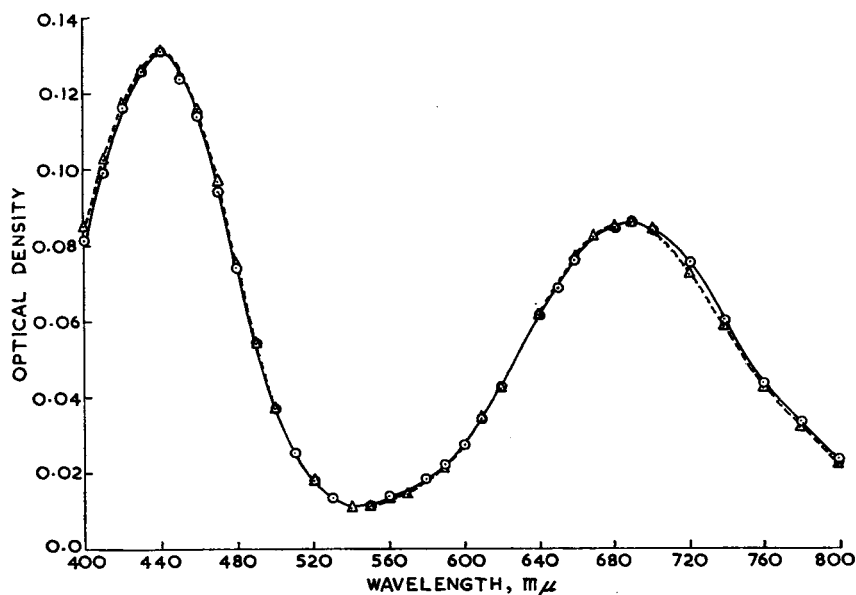


Fig. 2.—Absorption spectrum of vanadium<sup>III</sup> in 80% phosphoric acid:

○—○—V<sup>III</sup> by reduction with Fe<sup>II</sup>,  
 △—△—V<sup>III</sup> by electrolytic reduction.

0.10M Iron<sup>II</sup> solution: Prepared from Mohr's salt in 0.25M sulphuric acid and standardised against a standard solution of cerium<sup>IV</sup> sulphate using ferroin as indicator.

Syrupy phosphoric acid: For the bulk of the electrometric titrations syrupy phosphoric acid of B.P. grade supplied by Albright and Wilson Ltd., Birmingham, England, has been used. Control experiments with Merck's "Pro Analysi" syrupy phosphoric acid have shown that phosphoric acid obtained from Albright and Wilson is quite satisfactory.

A number of potentiometric titrations of vanadium<sup>IV</sup> were carried out with iron<sup>II</sup> at room temperature, varying the phosphoric acid concentration such that it was 9.0M, 10.5M or 12.0M at the end-point. Typical results are represented graphically in Fig. 3. A satisfactory break in potential is obtained only when the concentration of phosphoric acid is 12.0M at the end-point.

#### Stability of vanadium<sup>III</sup> in a phosphoric acid medium

The stability of vanadium<sup>III</sup>, when exposed in titration flasks to air, was studied in media containing phosphoric acid at two different concentrations. The results presented in Table II show that vanadium<sup>III</sup> is stable to aerial oxidation for 2 hr in a 7.5M phosphoric acid medium and for 6 hr (at least) in a 12M phosphoric acid medium.

TABLE II

Concentration of phosphoric acid, M	Volume of vanadium <sup>V</sup> (0.05492M) consumed by 10.0 ml of vanadium <sup>III</sup> at various time intervals, ml							
	Initial	0.5 hr	1 hr	2 hr	3 hr	4 hr	6 hr	24 hr
7.5	3.36	3.36	3.36	3.36	3.34	3.32	3.30	3.21
12.0	3.36	3.36	3.36	3.36	3.36	3.36	3.36	3.34

In view of the above results an inert atmosphere need not be maintained during the titration of vanadium<sup>IV</sup> with iron<sup>II</sup> in a concentrated phosphoric acid medium. However, titrations were carried out both in air and in an inert atmosphere. In both cases the results were equally satisfactory.

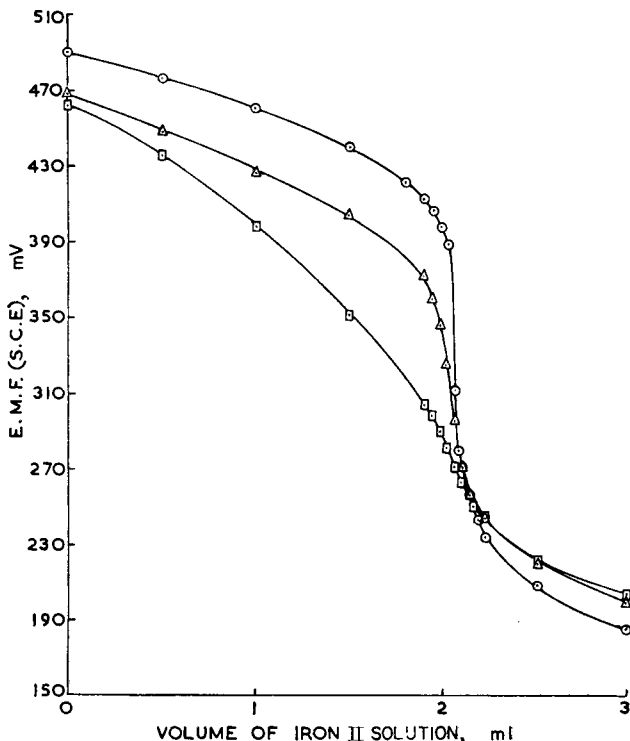


FIG. 3.—Effect of phosphoric acid concentration on the potentiometric titration of vanadium<sup>IV</sup> with iron<sup>II</sup>:

- 12.0M H<sub>3</sub>PO<sub>4</sub>,  
 △—△—10.5M H<sub>3</sub>PO<sub>4</sub>,  
 □—□—9.0M H<sub>3</sub>PO<sub>4</sub>.

#### Procedure

About 3–10 ml of an approximately 0.05M solution of vanadium<sup>IV</sup> are taken in a 150-ml Pyrex beaker and 40–65 ml of syrupy phosphoric acid are added, then the mixture is titrated with 0.1M iron<sup>II</sup> solution while it is stirred by means of a B.T.L. magnetic stirrer. Potentials are measured from time to time using the potentiometric assembly already described, using a platinum rod as an indicator electrode (steady values are more easily attained with a platinum rod electrode than with a gauze electrode). The measurements are made 1 min after each addition of the titrant. Once the end-point is reached, the potentials attain steady values almost immediately after the addition of iron<sup>II</sup>. After a platinum rod electrode is used continuously for a number of titrations, it becomes inert and cannot easily be activated by heating with or without preliminary treatment with concentrated hydrochloric acid. Such an electrode can, however, serve quite satisfactorily if the titrant is added close to the electrode but not on the electrode itself. If the iron<sup>II</sup> solution is added on the electrode itself, a low potential is immediately obtained and it takes about 10 min to attain the usual value. The break in potential at the end-point amounts to 80–100 mV/0.04 ml of 0.1M iron<sup>II</sup> solution when the titration is carried out in 12M phosphoric acid, the total volume of the titration mixture being 50 ml. Under the conditions described, the concentration of phosphoric acid will be about 90% initially and 80% at the end of the titration. Some typical results are given in Table III.

#### Interferences

Chromium<sup>III</sup>, iron<sup>III</sup> and manganese<sup>II</sup> do not interfere in this titration. Tungsten<sup>VI</sup> gives a precipitate but does not interfere with the determination of vanadium<sup>IV</sup>.

#### Ferrometric Determination of Vanadium<sup>IV</sup> Using Methylene Blue or Thionine as Redox Indicators

In a 12M phosphoric acid medium, the formal redox potential of the V<sup>IV</sup>/V<sup>III</sup> couple is about 0.720 V, while that of the Fe<sup>III</sup>/Fe<sup>II</sup> couple is about 0.390 V. Therefore, any redox indicator having

a transition potential of about 0.5–0.6 V should work satisfactorily in the above titration. Hence, the use of methylene blue and thionine as internal redox indicators in this titration was attempted.

Experiments in a concentrated phosphoric acid medium have shown that reduction of thionine (or methylene blue) by iron<sup>II</sup> is rapid, while oxidation of the leuco-dye by vanadium<sup>IV</sup> is somewhat slow, requiring about 3–5 sec at the concentrations of reactants obtaining near the close of a titration of vanadium<sup>IV</sup> with iron<sup>II</sup>.

As leuco-methylene blue or leuco-thionine is not stable to the oxygen of the air, even in a concentrated phosphoric acid medium, it is essential to use an inert atmosphere for titrations with these indicators. Further, it has been found that visual titrations using these redox indicators are possible only when the concentration of phosphoric acid is at least 10.5M at the end-point. When methylene blue is used as indicator, the colour transition at the end-point from deep green (blue of the dye + yellow-green of vanadium<sup>III</sup>) to yellow-green is difficult to detect when the amount of vanadium<sup>IV</sup> exceeds 0.30 millimole/50 ml of titration mixture. With thionine as indicator, however, as much as 0.50 millimole of vanadium can be tolerated.

TABLE III

Amount of vanadium <sup>IV</sup> , millimole	
Taken	Found
0.1742	0.1732
0.1812	0.1827
0.2153	0.2163
0.2503	0.2515
0.3589	0.3580
0.4130	0.4156

#### Reagents

*Vanadium<sup>IV</sup> and iron<sup>II</sup> solutions:* Prepared and standardised as described above.

*Methylene blue and thionine:* Prepared as described previously.<sup>1</sup>

#### Procedure

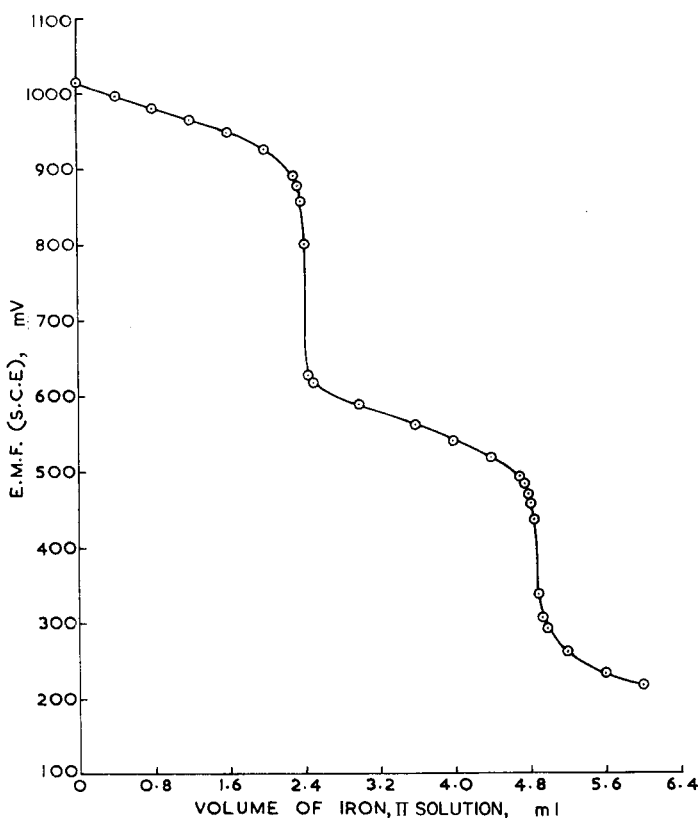
An aliquot volume of vanadium<sup>IV</sup> solution containing less than 0.5 millimole of vanadium (for titrations using thionine as indicator) and less than 0.3 millimole (for titrations using methylene blue as indicator) is taken in a 150-ml Pyrex three-necked flask. One of the necks is fitted with a stopper carrying the inlet tube for nitrogen, the second with a stopper carrying the tip of the micro burette and the third with a stopper carrying the outlet tube for nitrogen. Enough phosphoric acid is added to the titration vessel to give an end-point strength of at least 10.5M when diluted to 50 ml, followed by 0.5 ml of the indicator solution. The mixture is stirred by means of a B.T.L. magnetic stirrer during the course of the titration. After the air is removed from the titration vessel by passage of nitrogen for about 10 min, the mixture is titrated with 0.1M iron<sup>II</sup> solution while continuing to pass nitrogen. The initial colour of the titration mixture is blue and it changes to deep green just before the end-point, the green colour being a mixture of the blue of the dye and the yellow-green of vanadium<sup>III</sup>. At the end-point the deep green colour changes to yellow-green. The indicator correction is negligible. Cylinder nitrogen is used after passage through alkaline pyrogallol. Typical results obtained from many such titrations are given in Table IV.

#### Potentiometric Titration of Vanadium<sup>V</sup> with Iron<sup>II</sup> in a Strong Phosphoric Acid Medium

Using the experimental arrangement already described, the titration of vanadium<sup>V</sup> with iron<sup>II</sup> has been carried out in a 12.0M phosphoric acid medium and two distinct breaks in the potential curve were observed; the first break very nearly corresponds to the reduction of vanadium<sup>V</sup> to vanadium<sup>IV</sup> and the second break to the further reduction of vanadium<sup>IV</sup> to vanadium<sup>III</sup>. The second break occurs at the stoichiometric end-point ( $\pm 0.5\%$ ), but the first break occurs about 1% earlier than the theoretical value. The potential obtained at the first break shows considerable drift and becomes reasonably stable only after about 10 min. At the second break, however, it attains a fairly stable value in about 1 min. The first break in potential amounts to about 200 mV whereas the second will be about 80 mV/0.04 ml of 0.1M iron<sup>II</sup> solution when the total volume of the titration solution is 50 ml. Fig. 4 shows a typical titration curve of vanadium<sup>V</sup> with iron<sup>II</sup> in a 12M phosphoric acid medium.

TABLE IV

Methylene blue as redox indicator		Thionine as redox indicator	
Amount of vanadium <sup>IV</sup> , millimoles		Amount of vanadium <sup>IV</sup> , millimoles	
Taken	Found	Taken	Found
0.0551	0.0556	0.1101	0.1101
0.1361	0.1361	0.1702	0.1697
0.1856	0.1850	0.2660	0.2648
0.1918	0.1936	0.2907	0.2883
0.2350	0.2340	0.3773	0.3743
0.3033	0.3025	0.4701	0.4671

FIG. 4.—Potentiometric titration of vanadium<sup>V</sup> with iron<sup>II</sup> in a phosphoric acid medium.**Reagents**

**0.05M Sodium vanadate solution:** Prepared from pure ammonium vanadate and standardised by titration against a standard iron<sup>II</sup> solution using *N*-phenylanthranilic acid as indicator. The iron<sup>II</sup> solution, in turn, is standardised against a standard solution of potassium dichromate using the same indicator.

**0.1M Iron<sup>II</sup> solution:** Prepared from Mohr's salt and standardised as described above.

**Syrupy phosphoric acid:** B.P. grade, supplied by Albright & Wilson Ltd., Birmingham, England, is used.



*Procedure*

About 3–10 ml of vanadium<sup>V</sup> solution are taken in a 150-ml Pyrex beaker, 40–80 ml of syrupy phosphoric acid are added, and the solution is titrated with iron<sup>II</sup> solution using the potentiometric assembly already described. The potentials are observed immediately after each addition of iron<sup>II</sup> solution until the first break in potential is obtained. The potential obtained at the first break is noted after waiting for about 10 min, only by which time does it become reasonably constant. After the first break is obtained the potentials are noted 1 min after each addition of iron<sup>II</sup> solution. Some typical results are given in Table V.

TABLE V

Amount of vanadium <sup>V</sup> , millimole		
Taken	Found	
	First break (reduction to vanadium <sup>IV</sup> )	Second break (reduction to vanadium <sup>III</sup> )
0.1310	0.1300	0.1305
0.2037	0.2078	0.2091
0.2516	0.2511	0.2511
0.2823	0.2795	0.2811
0.5123	0.5073	0.5135

*Determination of Chromium<sup>VI</sup> and Vanadium<sup>V</sup> in the Same Solution*

Kolthoff and Tomiček<sup>3</sup> employed titanium<sup>III</sup> chloride for the differential determination of vanadium<sup>V</sup> and chromium<sup>VI</sup>. The first jump in potential occurs when all of the chromium<sup>VI</sup> has been reduced to chromium<sup>III</sup> and the vanadium<sup>V</sup> to vanadium<sup>IV</sup>. If iron<sup>III</sup> is present, the second jump occurs when the iron<sup>III</sup> is reduced to iron<sup>II</sup>. At this stage, Rochelle salt is added and the titration continued until a third inflexion occurs corresponding to the reduction of vanadium<sup>IV</sup> to vanadium<sup>III</sup>. The last part of the titration is better carried out at 50–60°. The Rochelle salt should not be added at the beginning because it will react with chromium<sup>VI</sup> and vanadium<sup>V</sup>. Zintl and Zaimis<sup>10</sup> were unable to obtain good results by this method. They<sup>4</sup> employed chromium<sup>II</sup> chloride for the determination of chromium<sup>VI</sup> and vanadium<sup>V</sup> in mixtures. The chromium<sup>VI</sup> and vanadium<sup>V</sup> are simultaneously reduced: chromium<sup>VI</sup> to chromium<sup>III</sup> and vanadium<sup>V</sup> to vanadium<sup>IV</sup>. If iron<sup>III</sup> is present it is then reduced to iron<sup>II</sup>, and finally vanadium<sup>IV</sup> is reduced to vanadium<sup>III</sup>. Great care should be taken when iron<sup>III</sup> is present. The solution should be ice-cold during the titration of chromium<sup>VI</sup> and vanadium<sup>V</sup> and the acidity should correspond to 20% sulphuric acid. After the reduction of chromium<sup>VI</sup> and vanadium<sup>V</sup>, the solution is diluted in order to decrease the acidity to about 5% sulphuric acid. Under these conditions a pronounced jump in potential is observed after the reduction of iron<sup>III</sup> to iron<sup>II</sup>. When the amount of iron<sup>III</sup> is very high relative to vanadium<sup>V</sup> and chromium<sup>VI</sup>, Zintl and Zaimis did not achieve good results by their procedure.

In the presence of large amounts of iron<sup>III</sup>, Zintl and Zaimis employed arsenic<sup>III</sup> for the reduction of chromium<sup>VI</sup>. If the solution contains at least 20% sulphuric acid, chromium<sup>VI</sup> is readily reduced, giving a large jump in potential at the end-point. Vanadium<sup>V</sup> is almost unaffected by arsenic<sup>III</sup>. A large excess of iron<sup>III</sup> is believed to completely prevent the reduction of vanadium<sup>V</sup>. After the reduction of chromium<sup>VI</sup> is complete, the vanadium<sup>V</sup> is determined by titration with a standard iron<sup>II</sup> solution.

This method has the disadvantage that it requires two reagents for the determination of chromium<sup>VI</sup> and vanadium<sup>V</sup>. Further, manganese<sup>II</sup> interferes. Arsenic<sup>V</sup> which is formed in the titration favours the formation of rather stable complex manganese compounds of higher valency. Oxidation of manganese<sup>II</sup> by chromium<sup>VI</sup> is induced by the reaction between arsenic<sup>III</sup> and chromium<sup>VI</sup>, probably through the intermediate formation of chromium<sup>V</sup>. In the presence of manganese<sup>II</sup>, the results for chromium<sup>VI</sup>

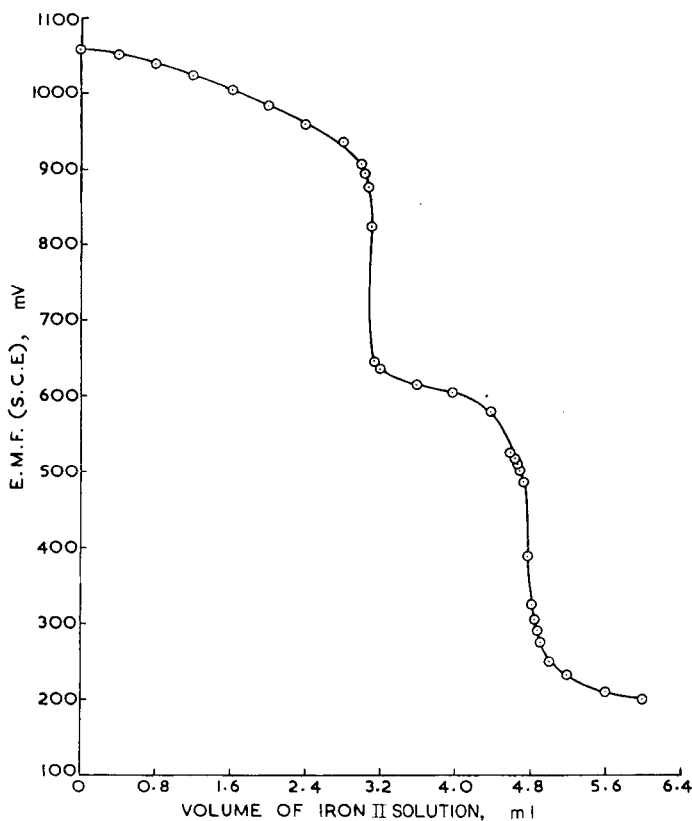


FIG. 5.—Potentiometric titration of a mixture of chromium<sup>VI</sup> and vanadium<sup>V</sup> with iron<sup>II</sup> in a phosphoric acid medium.

are much too low. On the other hand, too much iron<sup>II</sup> solution is required for the subsequent titration of vanadium<sup>V</sup>, because the higher valent manganese compound is also reduced along with vanadium<sup>V</sup>. Cobalt<sup>II</sup> also interferes somewhat similarly.

Independently of Zintl and Zaimis, the same titration was described by Lang and Zwerina.<sup>11</sup> They stated, however, that the method could be applied only if very small amounts of vanadium<sup>V</sup> were present in solution in the presence of chromium<sup>VI</sup>. They suggested a modified procedure.

According to Zintl and Zaimis<sup>12</sup> tungsten<sup>VI</sup> interferes in that part of the titration where vanadium<sup>V</sup> is titrated with iron<sup>II</sup>. In order to eliminate the interference of tungsten<sup>VI</sup>, they proposed the addition of phosphoric acid.

From the above, it appears that the existing methods for the differential potentiometric determination of chromium<sup>VI</sup> and vanadium<sup>V</sup> are complicated and subject to

interferences. We have found that chromium<sup>VI</sup> and vanadium<sup>V</sup> can be titrated potentiometrically with an iron<sup>II</sup> solution in a strong phosphoric acid medium (12*M* at the second inflexion point). The first inflexion corresponds to the reduction of chromium<sup>VI</sup> and vanadium<sup>V</sup> to chromium<sup>III</sup> and vanadium<sup>IV</sup>, respectively; the second inflexion corresponds to the reduction of vanadium<sup>IV</sup> to vanadium<sup>III</sup>. From the two titres, the chromium<sup>VI</sup> and vanadium<sup>V</sup> present can be calculated. It has been found that the amounts of chromium<sup>VI</sup> and vanadium<sup>V</sup> can be altered within sufficiently wide limits relative to each other. In titrations conducted with 0.1*M* iron<sup>II</sup> solution, the jump at the first inflexion point is found to be about 200 mV/0.04 ml of titrant; the jump at the second inflexion point is found to be about 80 mV/0.04 ml of titrant. Manganese<sup>II</sup>, iron<sup>III</sup>, cobalt<sup>II</sup> and tungsten<sup>VI</sup> do not interfere. This procedure is therefore likely to be of considerable value for the determination of chromium<sup>VI</sup> and vanadium<sup>V</sup> in the same solution, being less complicated and subject to much less interference than the methods currently available. Typical results for the determination of chromium<sup>VI</sup> and vanadium<sup>V</sup> are given in Table VI.

TABLE VI

Amount of vanadium <sup>V</sup> , <i>millimole</i>		Amount of chromium <sup>VI</sup> , <i>millimole</i>	
Taken	Found	Taken	Found
0.1048	0.1056	0.0500	0.04963
0.1452	0.1457	0.02175	0.02192
0.1468	0.1478	0.02400	0.02392
0.1573	0.1561	0.01667	0.01659
0.2537	0.2551	0.04033	0.04053
0.3145	0.3159	0.01667	0.01657

A typical potentiometric curve is given in Fig. 5.

**Zusammenfassung**—Die Formalpotentiale von V(IV)/V(III) wurden in Lösungen wechselnden Phosphorsäuregehaltes bestimmt. Ein Vergleich dieser Resultate, mit denen für das System Fe(III)/Fe(II) zeigt, dass das Vanadinsystem von einer Phosphorsäurekonzentration 4.0 m an das höhere Potential hat, und dass die Differenz zwischen den beiden Potentialen mit ansteigender Phosphorsäurekonzentration grösser wird. In 10.5 m Phosphorsäure beträgt die Differenz 0.27 V, sodass zweiwertiges Eisen Vanadin (IV) bei Zimmertemperatur leicht reduziert. Auswertung dieser Reaktion erlaubte die titrimetrische Bestimmung von Vanadin mit potentiometrischer oder visueller Indication unter Verwendung von Methylenblau oder Thionin als Indicator. Das neue Reagens hat vorteile gegenüber Ti(III) und Cr(II), die spezielle Lagerung erfordern. Ferner stören Fe(III) und W(VI) nicht. Weitens kann man nach dem neuen Verfahren Chrom und Vanadin in einer Lösung bestimmen. Bei potentiometrischer Anzeige entspricht der erste Sprung der Reduktion Cr(VI) zu Cr(III) und V(V) zu V(IV), der zweite Sprung zeigt die Reaktion V(IV) zu V(III) an. Das Verfahren kann grosse Bedeutung für die Analyse von Spezialstählen haben.

**Résumé**—Les auteurs ont déterminé le potentiel normal apparent du couple V<sup>IV</sup>/V<sup>III</sup> en milieu acide phosphorique de concentrations variées. Des résultats obtenus et de ceux obtenus précédemment dans ce laboratoire pour le couple Fe<sup>III</sup>/Fe<sup>II</sup>, on a pu déterminer que pour une concentration en acide phosphorique supérieure à 4,0 M le potentiel normal apparent du couple V<sup>IV</sup>/V<sup>III</sup> est plus élevé que celui du couple

$\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ . La différence entre les potentiels normaux apparents croît lorsque la concentration de l'acide phosphorique augmente. En milieu phosphorique 10,5 M le potentiel du couple  $\text{V}^{\text{IV}}/\text{V}^{\text{III}}$  est supérieur d'environ 0,27 V à celui du couple  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ . Ceci va permettre la réduction du vanadium (IV) en vanadium (III) par le fer (II) même à la température ordinaire. Cette réaction a permis de mettre au point un dosage du vanadium (IV); le point équivalent est déterminé par potentiométrie ou par colorimétrie en utilisant le bleu de méthylène ou la thionine comme indicateurs d'oxydo-réduction. Ce nouveau procédé mis au point pour réaliser le dosage est plus commode que les méthodes qui mettent en jeu le titane(III) et le chrome(II), et qui demandent des précautions spéciales pour la conservation des solutions. La présence du fer(III) et du tungstène(VI) ne gêne pas lorsqu'on utilise ce réactif comme cela se produisait avec le titane(III) et le chrome(II). D'autre part, on peut doser potentiométriquement le chrome (VI) et le vanadium(V) dans la même solution. Si l'on trace la courbe du potentiel en fonction du volume versé: le premier point équivalent correspond à la réduction du chrome(VI) et à celle du vanadium(V) en vanadium(IV); le second correspond à la réduction du vanadium(IV) en vanadium(III). La présence du fer(III), du manganèse (II), du cobalt(II) et du tungstène(VI) ne gêne pas. Ce procédé peut avoir une application importante dans le dosage des aciers spéciaux.

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## SHORT COMMUNICATIONS

### Indirect spectrophotometric determination of sulphate ion

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#### INTRODUCTION

IN 1904 Ruer<sup>1</sup> discovered that the thorium ion formed relatively stable soluble complexes with the sulphate ion. About fifty years later Kuzněcov<sup>2</sup> suggested that the sulphate ion could be detected from the decomposition of the soluble coloured thorium complex of 2-(1,8-dihydroxy-3,6-disulpho-2-naphthylazo)-benzoic acid in a slightly acidic solution. This azo dye was later used by Čuta and Hanušová<sup>3</sup> as the indicator in a direct titrimetric determination of the sulphate ion. The titrant was a thorium nitrate solution. Lambert, Yasuda and Grotheer<sup>4</sup> developed an indirect spectrophotometric method for determination of the sulphate ion. The method was based on conversion of the slightly soluble thorium complex of 4-(2-hydroxy-3,6-disulpho-1-naphthylazo)-naphthalene-1-sulphonic acid. The amount of the free acid, proportional to the concentration of the sulphate ion, was determined spectrophotometrically. Soluble thorium complexes of alizarin,<sup>5</sup> salicylfluorone<sup>6</sup> and Pyrocatechol Violet<sup>7</sup> have also been used for this purpose. In these investigations, either the liberated free indicator or the decomposed thorium complex were determined spectrophotometrically and their amount found to be proportional to the sulphate ion concentration.

All of these methods<sup>4,5,6,7</sup> have the common advantages of simplicity and sensitivity. A serious disadvantage under experimental conditions, however, is the interference of all cations which form complexes or oxidise the indicator, and of all anions which form either soluble complexes or slightly soluble salts with the thorium ion.

The optimum pH value for any of these methods depends on the type of indicator employed. This value, therefore, varies from pH 3.0 to 4.5. The sulphanilate buffer, used in most methods, has a low buffer capacity and is poorly stable. Acetate, chloracetate and similar buffer solutions are unsuitable because these anions also form soluble complexes with the thorium ion, and even if such complexes are poorly stable they can considerably lower the sensitivity of the method. Also, it is important to note that in this pH range thorium is present not only in the form of  $\text{Th}^{+4}$ , but mainly as hydroxo-complexes,  $\text{Th}(\text{OH})_n^{4-n}$ .

In order to avoid some of the disadvantages mentioned above, metallochromic indicators containing an iminodiacetic group were tried, mainly because their thorium complexes were known to be stable at a considerably lower pH value. The indicator found to be suitable was Xylenol Orange. The optimum pH for this dye was such that a perchlorate buffer solution at its maximum buffer capacity could be used. The maximum absorption of the thorium complex occurs at 553 m $\mu$ , and the absorption of the free indicator at this wavelength is negligible. Very narrow slits can be used because most photocells have a maximum spectral sensitivity at this range. As far as interfering ions are concerned, it has been possible to employ a simple procedure for their removal. Interfering anions could be precipitated as slightly soluble lanthanum salts, while interfering cations were adsorbed on an ion-exchange resin.

#### EXPERIMENTAL

##### Reagents

**Thorium perchlorate, 10<sup>-3</sup>M stock solution:** Prepared by evaporating to dryness several times the exact amount of thorium nitrate tetrahydrate with 70% perchloric acid and dissolving the residue in water. This solution was standardised by EDTA titration, employing Methylthymol Blue as indicator. In the procedure a 2 × 10<sup>-4</sup>M solution was used, prepared by appropriate dilution of the stock solution.

**Xylenol Orange, 10<sup>-3</sup>M solution:** Prepared by dissolving the calculated amount of indicator in water. The titre of the commercially available reagent had to be determined preliminarily by either potentiometric titration or molar ratio method, because it contained a considerable amount of

inactive substances. In the determination, a  $4 \times 10^{-4}M$  solution was used, prepared by dilution of the stock solution. In the procedure employed no changes were observed for these two solutions after 2 months.

*Perchlorate buffer solutions, 0.4 M:* Prepared by mixing 100 ml of 1M perchloric acid with the respective volume of 1M sodium hydroxide and diluting to 250 ml. In order to obtain the optimum pH of 1.40, the volume of sodium hydroxide solution had to be 50 ml.

*Standard solution of sulphate ion:*  $10^{-3}M$  Potassium sulphate solution; secondary standards were prepared by appropriate dilution.

*Lanthanum chloride, 0.05M solution:* Prepared from hydrated lanthanum chloride. The titre of the solution was determined by EDTA titration. Lanthanum hydroxide was prepared by precipitation of the lanthanum chloride solution, and decanted ten times with water.

Demineralsed water was used for the preparation of all solutions. All reagents were of A.G. purity or better, and were checked for possible sulphate contamination.

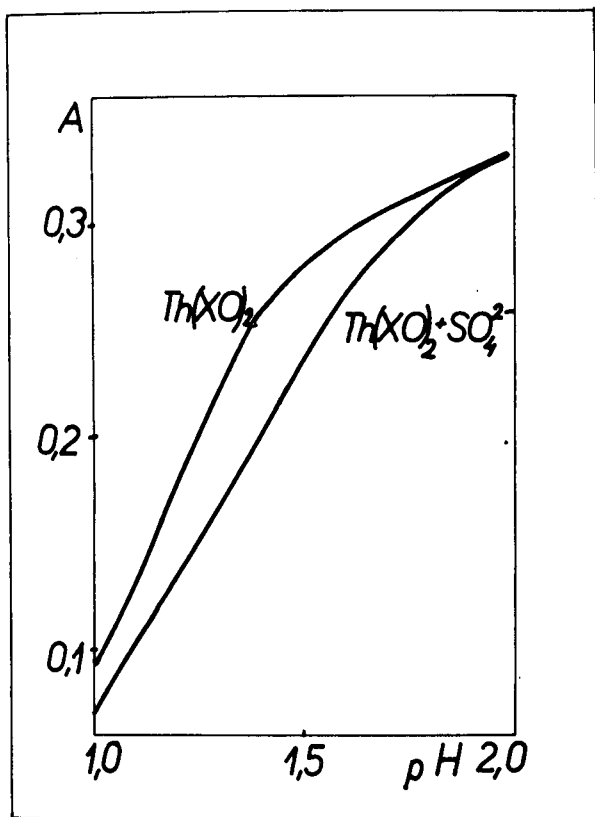


FIG. 1.—Absorbance of the thorium complex of Xylenol Orange, in the presence and absence of sulphate ion, as a function of pH.

#### Apparatus

Universal spectrophotometer VEB Zeiss Jena with glass optics and MVS photocell; slit widths 0.02 mm; matched cells with 3.00-cm path length. Water was used as blank. All measurements were performed at the wavelength of the thorium complex maximum, 553 m $\mu$ . Precision as well as reproducibility were better than 1 relative %.

pH meter Radiometer Model 22, standardised with NBS pH<sub>s</sub> standards.

Xylenol Orange, as well as other metallochromic indicators, can form several complexes with varying content of thorium. The most suitable one for determination of the sulphate ion is obviously that which contains the maximum number of indicator molecules per one thorium atom, because its decomposition causes the maximum change of absorbance. This postulate has been proved by measuring the absorbances of two series of solutions containing a constant concentration of the

thorium ion and a varying concentration of the indicator. To the second series of solutions a constant amount of sulphate ion was added. By this method the assay of the commercially available dye was also checked. The optimum ratio found was two molecules of Xylenol Orange per one thorium atom. In a similar way the optimum pH value for this complex was found to be 1.40 (Fig. 1).

#### Procedure

To a 100-ml volumetric flask, 25 ml of the buffer solution, 5 ml of  $2 \times 10^{-4}M$  thorium perchlorate solution and 5 ml of  $4 \times 10^{-4}M$  Xylenol Orange solution were transferred. After mixing, 50 ml of the sample or of the secondary standard were added and water was added to the mark. The absorbance was measured immediately after thorough mixing.

The calibration curve obtained in this way is shown in Fig. 2. No changes in the values of the absorbances were observed during 24 hr. Reproducibility of the calibration curve was found to be better than 1%.

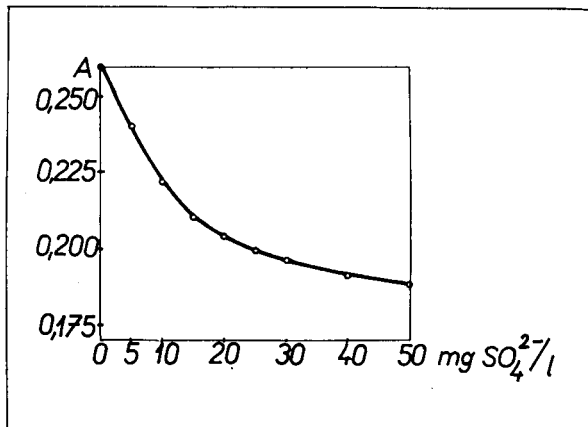


FIG. 2.—Calibration curve

#### Interferences

As mentioned in *Introduction*, a great number of ions interfere with this type of method. An attempt was made to eliminate their interference in order to increase the selectivity of the method. All cations forming similar complexes or reacting in other ways with both indicator and sulphate ion interfere. To this group belong all quadrivalent cations and most of the trivalent ones, such as iron, aluminium, bismuth. Tervalent rare earth metal cations do not belong to this group. Interfering cations can be easily removed by passing the sample through a strongly acidic cation column in the  $H^+$ - or  $Na^+$ -form. The latter cannot be used for quadrivalent cations. No adsorption of the sulphate was observed even in the presence of quadrivalent cations, including that of thorium, if the  $H^+$ -form was used.

If only iron and aluminium in moderate concentrations (less than 5 mg/l.) are present in the sample, as is the case of most waters, there is no need for this procedure, because iron can be easily reduced to non-interfering iron<sup>II</sup> by hydroxylamine (not by ascorbic acid). Because the aluminium ion reacts slowly with the indicator under these conditions its effect can be diminished to a negligible one if the absorbance is measured immediately after finishing the procedure. If some potassium perchlorate precipitates, it must be removed by filtration. This has no interfering effect.

Anions forming soluble complexes or slightly soluble salts with the thorium cation seriously interfere, but they can be easily removed as slightly soluble lanthanum salts. In this manner all interfering inorganic anions—phosphates, fluorides, tungstates, molybdates and arsenates—can be removed. Organic hydroxyacids usually cannot be removed by this procedure. According to the content of interfering anions either the solution of lanthanum chloride or the suspension of lanthanum hydroxide was added to a 100-ml volume of the sample in slight excess. The hydroxide was used if the content of interfering anions was low. After thorough stirring, the precipitate was allowed to settle and was removed by filtration. A correction for the added volume was made. The determination is not interfered with by excessive lanthanum ion left in the sample. The pH of the sample should be approximately 7.0 before the precipitation. If aluminium is present, it is also removed by this procedure. The procedure was tested for the removal of fluorides and/or phosphates up to the concentration  $10^{-3}M$  in the presence of  $10^{-1}M$  sulphate. The maximum error observed was -3%, and was probably caused by adsorption on the precipitate.

## DISCUSSION

The indirect method for the determination of the sulphate anion as described in this paper has some advantages over those mentioned in *Introduction*. Perhaps the most important one, caused by the use of Xylenol Orange, is the possibility of using the perchlorate buffer solution with its high buffer capacity, which means that in most cases there is no need for a prior adjustment of the pH of the sample. The type of indicator employed enables the use of a very simple procedure for elimination of interfering anions. The method is sensitive and simple.

All necessary reagents are commercially available, with the exception of thorium perchlorate for which thorium nitrate can be substituted in this method. In this work the perchlorate was used because an attempt was made to determine stability constants of thorium sulphate complexes, and the nitrate ion is known to form complexes with the thorium ion even if extremely unstable. It revealed that under the experimental conditions of this determination mainly the complex  $[\text{Th}(\text{SO}_4)]^{+2}$  was formed,<sup>9</sup> and that the nitrate anion has no interfering effect up to a concentration of  $10^{-2}M$ .

Some actual determinations of sulphate by the proposed method and a comparison with other methods are now being carried out. The results will be published in due course.

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**Summary**—A method for the indirect spectrophotometric determination of sulphate ion has been developed, based on its decomposition of the thorium-Xylenol Orange complex. The amount of decomposed complex is proportional to the concentration of sulphate ion. Optimum conditions for this method are given.

**Zusammenfassung**—Eine Methode zur indirekten spectrophotometrischen Bestimmung von Sulfaten wurde entwickelt und die optimalen Bedingungen werden mitgeteilt. Die Methode basiert auf der Zersetzung des Thorium- Xylenol Orange-Komplexes, die Menge an zersetztem Komplex ist der Konzentration von Sulfat proportional.

**Résumé**—Une méthode indirecte de dosage spectrophotométrique des ions sulfates fondée sur la destruction du complexe thorium-xylénil orange a été mise au point. La quantité de complexe détruit est proportionnelle à la concentration des ions sulfates. Les conditions optimales d'application de cette méthode sont données.

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## Use of the argon gas chromatograph in the determination of carbon in steel

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THE determination of carbon in steel may be considered to consist of (a) the quantitative conversion of the carbon to a suitable single compound (usually carbon dioxide), and (b) the quantitative measurement of the amount of that compound formed. A detailed analytical technique, recommended as being of particular value as a referee method, is given in British Standard 1121.<sup>1</sup> In this method the sample of steel is burned in oxygen under conditions designed to ensure complete oxidation of carbon [(a) above] and the carbon dioxide is subsequently weighed after being absorbed in soda



asbestos [part (b)], the products of combustion having been first treated to remove oxides of sulphur.

The present paper reports results of experiments in which carbon dioxide, formed on combustion of steel as described in reference 1, is determined by gas chromatography using the radioactive ionisation detector.<sup>2</sup> This modification to part (b) has been investigated in an attempt to reduce the time spent by an analyst in the routine determination of carbon in steels, through instrumental detection and recording of the amount of carbon dioxide formed. The method proposed would obviate the necessity for the difference weighing of the adsorbent and also it seems possible that the method could be further developed to make it largely automatic.

### EXPERIMENTAL

Samples of steel were burned as recommended in reference 1 at 1050–1100° with the modifications that (i) no lead foil or red lead was used to accelerate combustion, and (ii) the combustion boats were not ignited before use. Several blank experiments were, however, carried out. The products of combustion were passed into the gas handling apparatus, shown diagrammatically in Fig. 1, which

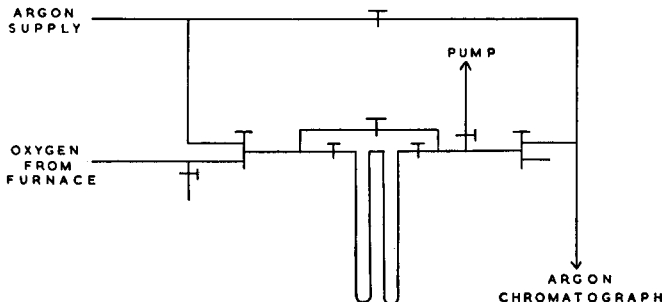


FIG. 1.—Diagrammatic sketch of apparatus.

enabled carbon dioxide in the oxygen stream leaving the furnace to be collected in the thin-walled double U-tube trap (4-mm diameter tubing), which was chilled in liquid oxygen. Subsequently, this carbon dioxide was measured in a standard Pye Argon Chromatograph. Preliminary chromatographic measurements showed that carbon dioxide was separated from oxygen and sulphur dioxide and that the response of the radioactive ionisation detector (to carbon dioxide) was suitable for quantitative studies after passage of the gas through a charcoal column (100–120 mesh B.S.S. standard screen and 60 cm long) held at 100°, using the thermostat of the instrument as supplied, and an argon flow controlled at  $25 \pm 1$  ml/min. The detector was operated at 2000 V and " $\times 10$ " sensitivity and the output was connected to a 10 mV "Sunvic" recorder. These conditions were adopted as standard throughout the work. Initially the column was heated to about 225°, then cooled in argon overnight. This process was repeated at intervals during the work so that a constant zero line was maintained on the chromatograph recorder chart.<sup>2</sup> The position of this zero did not change appreciably throughout the period of the work.

Before each analysis the position and stability of the recording unit base line was checked, with the argon flow directed through the "long by-pass" (see Fig. 1). If this was satisfactory a weighed sample of steel was burned in oxygen and the gases from the furnace swept through the trap which was chilled in liquid oxygen, gaseous oxygen leaking to the atmosphere at the second two-way tap. Liquid oxygen is used as coolant because liquid nitrogen would cause condensation of the oxygen flow from the furnace. Some 10–15 min after combustion both two-way taps were closed and oxygen from the furnace allowed to leak to the atmosphere. All the tubing between the two-way taps was *very carefully* evacuated to remove excess oxygen (leaving solid particles of condensed gases, including carbon dioxide), the taps at each side of the trap were closed and the trap warmed to room temperature. The tap to the pumps was closed, the argon flow diverted to the "short by-pass" and, as soon as the recorder disturbance response was completed, the U-tube trap was swept out with argon with *both* by-passes closed. Special care was taken to avoid evacuation of the U-tube while it was connected to the argon or oxygen supply, and to avoid immersing the trap in liquid oxygen while argon was flowing through it.

Carbon determinations were made with four samples of British Chemical Standards, carbon steels, issued by the Bureau of Analysed Standards, Ltd. details as under:

B.C.S. No.	Carbon, %
237	0.083
238/1	0.21
240/1	0.45
163/1	1.21

Provision was also made, not shown in Fig. 1, for the admission of a measured volume of carbon dioxide to the U-tube trap, and the recorder response could then be determined by the method detailed above.

Care was taken throughout the work to adopt a rigidly standardised experimental technique.

## RESULTS AND DISCUSSION

A typical recorder response trace is shown in Fig. 2, the order of elution of the three peaks being oxygen, carbon dioxide and sulphur dioxide (poorly defined). Most of the oxygen must be pumped from the condensed sample gases before sweeping the residual gases, which contain the carbon dioxide, on to the chromatographic column, otherwise the oxygen peak obscures most of the carbon dioxide peak. The shape of the carbon dioxide peak observed here differs from that reported previously.<sup>2</sup> This is believed to be because of some tailing of the oxygen peak resulting in modification of the latter stages of the carbon dioxide peak.

The most satisfactory procedure for determination of carbon dioxide from the recorder trace was found to be measurement of peak "area" which is here defined as peak height multiplied by peak width at half peak height. The method for measurement of peak height was carefully considered because, for small amounts of carbon dioxide the peak maximum was below the zero deflection line and, as shown on Fig. 2, for larger amounts of carbon dioxide the later part of the peak shows inversion below the base line. Accordingly, the line shown dotted in Fig. 2, some 5 mm below the zero

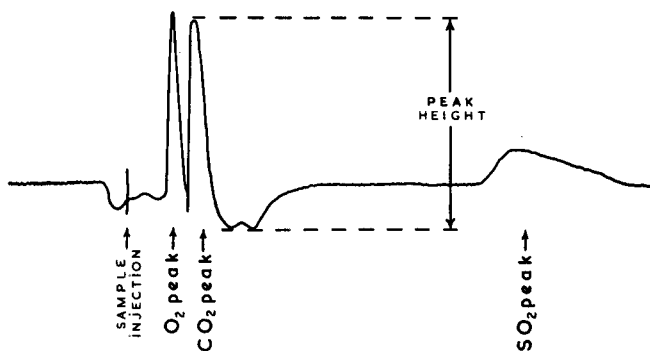


Fig. 2.—A typical recorder response trace showing the approximate positions of products detected from combustion of a typical sample of steel.

recorder deflection, was selected as datum and this was satisfactory because (a) this was the average 'below the line' deflection found for carbon dioxide, and (b) it was close to the peak maximum of the very small, almost constant, blank determined for the apparatus when no sample had been weighed into the boat. A constant zero datum line for peak height measurement was used rather than the position of the maximum inversion below the zero line for individual carbon dioxide responses because the latter were somewhat variable and depended on a number of undetermined factors. Providing a consistent and standardised procedure is adopted, the exact position of the datum line may be expected to be of lesser importance.

Of the functions of response tested, peak "areas" gave the most nearly linear plot of response function against weight of carbon in the sample analysed. A plot of peak "area" against weight of carbon in steel samples is shown in Fig. 3. Five sources of carbon dioxide were used in all; approximately equal numbers of analyses of the four carbon steels of different percentage carbon (as detailed above) and, in addition, measured volumes of cylinder carbon dioxide transferred directly to the U-tube trap. All results obtained in the present work for analyses made under identical conditions for which sample sizes were equivalent to less than 3 mg of carbon have been included in Fig. 3. The calibration plot is seen to be linear and pass through the origin. With sample sizes equivalent to more than 3 mg of carbon the results showed a decrease in accuracy undoubtedly because of the decrease in accuracy of measurement of peak area. With larger volumes of carbon dioxide the peaks became broader and there appeared to be a decrease in the sensitivity of the detector to this compound.

Carbon could be determined with an accuracy of  $\pm 0.1$  mg in the range 0–3.0 mg of total carbon on steel samples 0.1 to 2.0 g in weight, the weight taken for these calibrations depending on the percentage carbon in the steel. The accuracy of the method, therefore, for a 1-g sample of steel containing 0.0–3% of carbon is  $\pm 0.01\%$  and rather less for higher carbon steels. The particular application of the method would therefore appear to be in the analysis of low carbon steel and, by

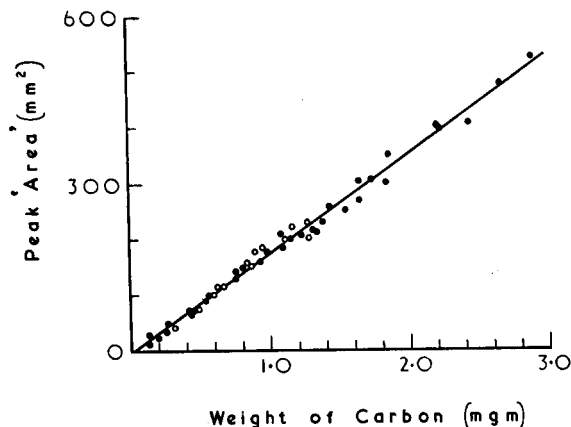


FIG. 3.—Plot of peak "area" against weight of carbon in sample:  
 ●—steels containing 0.083, 0.21, 0.45 or 1.21% of carbon,  
 ○—gaseous carbon dioxide.

the use of more stringent control of chromatograph conditions, in particular if the constant temperature of the detector could be more accurately thermostatted, it might be possible to increase the accuracy of the method and also the maximum weight of carbon which could be analysed within the limit of accuracy  $\pm 0.01\%$ .

Because the response trace is automatically recorded, it seems probable that an apparatus of the type detailed in the present paper could reduce the time spent by trained staff on routine determinations of carbon in steel.

Small sulphur dioxide peaks were obtained for every sample analysed by the method detailed above and during quantitative analyses care was taken to avoid overlap of carbon dioxide responses with sulphur dioxide peaks still in the column from analysis of the condensable products of the previous sample. If desired, sulphur dioxide could readily be removed by standard methods<sup>1</sup> in the gas handling apparatus prior to condensation in the U-tube trap. Furthermore, it may be possible to determine both sulphur and carbon in a single combustion of steel by the above method. The determination of sulphur necessitates quantitative conversion to sulphur dioxide and preliminary results obtained in the present study gave irreproducible results, possibly because the steels were ignited at an insufficiently high temperature. Quantitative calibrations of response of sulphur dioxide in the argon chromatograph have shown<sup>2</sup> that reproducible deflections can be obtained and there is evidence to suppose that, if quantitative sulphur dioxide formation can be achieved on combustion, both carbon and sulphur could be determined on a single sample. More work is, however, necessary before this could be established. It must also be remembered that sulphur dioxide may cause corrosion of the detector, which contains strontium-90, and this should be inspected at regular and frequent intervals when there is any possibility of attack by corrosive gases.

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**Summary**—A method is described in which carbon dioxide, formed by the combustion of steel, can be determined in the argon gas chromatograph. Results indicate that 0.0–0.3% carbon may be determined with an accuracy of about  $\pm 0.01\%$ , but the accuracy is rather less for higher carbon steels. The method may be useful in the determination of small concentrations of carbon and it may be possible to make it largely automatic. The possibility of determining both carbon and sulphur in a single sample of steel by gas chromatographic methods is also discussed.

**Zusammenfassung**—Eine Methode zur quantitativen Bestimmung des bei der Verbrennungsanalyse von Stahl erhaltenen Kohlendioxydes in einem Argon-Gaschromatographen wird beschrieben. 0–0.3% C können auf etwa  $\pm 0.01\%$  genau bestimmt werden. Die Genauigkeit für höhere Kohlenstoffgehalte ist geringer. Die Methode ist vorteilhaft für kleine C-Mengen und kann möglicherweise als Grundlage zu einer Automatisierung dienen. Die Möglichkeit, Kohlenstoff und Schwefel in einer Probe zu bestimmen werden diskutiert.

**Résumé**—Description d'une méthode de dosage de l'anhydride carbonique formé par la combustion de l'acier, au moyen de la chromatographie gazeuse dans l'argon. Les résultats indiquent que des quantités inférieures à 0,3% de carbone peuvent être déterminées avec une précision d'environ  $\pm 0,01\%$ , mais cette précision est moindre pour les aciers à forte teneur en carbone. La méthode est utile pour déterminer de faibles concentrations de carbone et elle peut être rendue automatique dans une large mesure. Discussions des possibilités d'estimation du carbone et du soufre dans un échantillon d'acier par les méthodes de chromatographie gazeuse.

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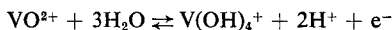
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### The determination of oxidising and reducing cations in transition-metal oxides using vanadium sulphate solutions

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THE oxides and mixed oxides of the transition metals have been studied extensively in recent years. Much of this work has been stimulated by the technological importance of certain families of materials such as the ferrimagnetic mixed oxides containing iron (ferrites); those with the spinel crystal structure of formula type  $(M', Fe)_3O_4$  and those with the garnet crystal structure,  $M_3(M'Fe)_5O_{12}$  ( $M'$  is usually a transition metal). An important aspect of these studies has been the finding of relationships between physical properties and chemical composition. It is routine to determine the total quantities of the metals present but a quantitative knowledge of the oxidation states of the various cations present is also important. It is not always possible to obtain this kind of information by chemical methods. One can discover, however, that the over-all stoichiometry is correct, allowing one to know, for example, the value of  $\lambda$  if the formula for a spinel is written  $M_3O_{4+\lambda}$ .

A ferrite or other mixed oxide prepared by ignition at high temperature is very well crystallised and inert towards many reagents. Extended periods of digestion are often required to dissolve the sample. We have found that solutions of quinquevalent and quadrivalent vanadium sulphates in dilute sulphuric acid, because of their stability, are very satisfactory reagents for the determination of several reducing and oxidising cations, respectively, in solids. For the half-cell reaction



the standard oxidation potential<sup>1</sup>  $E_0$  is  $-1.000$  v while in  $1M$   $H_2SO_4$  the potential is  $-1.02$  v. Thus strongly oxidising cations like  $Co^{III}$ ,  $Mn^{III}$ , and  $Mn^{IV}$  will oxidise  $V^{IV}$  in dilute  $H_2SO_4$  solutions and reducing cations such as  $Fe^{II}$ ,  $V^{III}$  and  $Ti^{III}$  will reduce  $V^V$  in similar solutions.<sup>1,2</sup> After the solid has dissolved the  $V^{IV}$  which is left over from an excess of reagent by oxidising cations or that produced from  $V^V$  by reducing cations is titrated with a standard solution of  $KMnO_4$ . The accuracy and precision obtainable is indicated by these results for the analyses of some pure oxides:

OXIDATION (REDUCTION) EQUIVALENTS PER 100 g OF MATERIAL

Oxide	Found	% of theoretical	Expected
$V_2O_3$	$1.3319 \pm 0.0007$	99.42	1.3342
$Mn_2O_3$	$1.267 \pm 0.003$	100.02	1.2668
$Co_3O_4$	$0.8297 \pm 0.0003$	99.90	0.8305

The amount of  $V^{IV}$  and  $V^{V}$  reagents to be used, the quantity of sample, the concentration of  $H_2SO_4$  (maximum used equals  $2.4M$ ), etc., can be varied to accommodate a particular problem. Some materials are dissolved with such difficulty that only the finest available can be taken for samples; e.g., that passing through a 325-mesh screen or that obtained by making a suspension of the sample and collecting the slowest settling material. Among the most difficult substances to dissolve is yttrium-iron garnet,  $Y_3Fe_5O_{12}$ . The finest material must be separated and boiled with the  $V^{V}$  reagent for several days under reflux to effect complete solution before determination of the  $Fe^{II}$  content can be done.

We have used the  $V^{IV}$  and  $V^{V}$  reagents chiefly to check the stoichiometry of transition-metal mixed-oxide preparations in order to find suitable preparative methods before studying physical properties. We have thus been able to study, in addition to those already mentioned, the preparation of substances such as  $VO_2$ ,  $LiVO_2$ ,  $Co_2VO_4$  and  $Y_3Fe_5O_{12}$ ; solid solutions in the systems  $Fe_2GeO_4$ — $ZnFe_2O_4$ ,  $Co_2GeO_4$ — $ZnMn_2O_4$ ,  $LiMn_2O_4$ — $ZnMn_2O_4$ ,  $Fe_2VO_4$ — $FeV_2O_4$ ,  $Co_3O_4$ — $Mn_3O_4$ ,  $NiMn_2O_4$ — $Mn_3O_4$ , and  $MgFe_2O_4$ — $Mn_3O_4$ .

Pure ferrites with compositions very close to that given by the formula,  $MFe_2^{III}O_4$  have been found to exhibit physical properties different than those of slightly non-stoichiometric materials.<sup>3</sup> Observed electrical and magnetic properties, for example, can often be related to the presence of small amounts of  $Fe^{II}$ . The compounds  $Mn_2SnO_4$  and  $Mn_2TiO_4$  were known to be intrinsically ferrimagnetic only after magnetic measurements had been made on samples known to be stoichiometric, i.e., containing no  $Mn^{II}$ .<sup>4</sup>

In several of these systems the study of physical properties of stoichiometric materials has yielded some evidence concerning specific oxidation states present in the solid. The oxidation states in  $Co_2^{IV}V^{IV}O_4$  were discovered by analysis of magnetic susceptibility measurements.<sup>5</sup> The constitution of substances in the  $Co_3O_4$ — $Mn_3O_4$  system has been deduced from studies of crystal symmetry and low-temperature magnetisation.<sup>6</sup>

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**Summary**—Because vanadium sulphate solutions are very stable, they make useful analytical reagents. A solution of quinquevalent vanadium sulphate in dilute sulphuric acid can be used for the determination of  $Fe^{II}$ ,  $Ti^{III}$  and  $V^{III}$  ions present in solid oxides. A similar solution of quadrivalent vanadium can be used for the determination of  $Co^{III}$ ,  $Mn^{III}$  and  $Mn^{IV}$ . The importance of the method in studies of mixed transition-metal oxides is briefly discussed.

**Zusammenfassung**—Vanadinsulfatlösungen sind wegen ihrer Stabilität nützliche Masslösungen. Fünfwertiges Vanadin in verdünnter Schwefelsäure kann zur Bestimmung von  $Fe(II)$ ,  $Ti(III)$   $V(III)$  in festen Oxyden verwendet werden. Vierwertiges Vanadin in gleicher Lösung dient zur Bestimmung von  $Co(III)$ ,  $Mn(III)$  und  $Mn(IV)$ . Die Wichtigkeit der Verfahren zur Analyse von Mischungen von Übergangsmetalloxyden wird kurz diskutiert.

**Résumé**—Les solutions de sulfate de vanadium constituent en raison de leur grande stabilité un réactif très utile en analyse. Une solution de sulfate de vanadium(V) en milieu acide sulfurique dilué peut être utilisée pour le dosage des ions  $Fe^{II}$ ,  $Ti^{III}$  et  $V^{III}$  présents dans les oxydes solides. Une solution de vanadium(IV) peut être utilisée pour le dosage de  $Co^{III}$ ,  $Mn^{III}$  et  $Mn^{IV}$ . L'importance de la méthode pour l'étude des oxydes mixtes des métaux de transition est brièvement discutée.

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## The polarography of cerium<sup>IV</sup> in acetate buffer

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THE oxidation potential of the cerium<sup>IV</sup>-cerium<sup>III</sup> couple is so positive that the diffusion current of the reduction of cerium<sup>IV</sup> to cerium<sup>III</sup> starts at zero applied e.m.f.<sup>1</sup> in polarographic analysis in the presence of strong acids.<sup>2,3</sup> A cathodic wave ( $E_{1/2}$ -0.526 v. vs. S.C.E.) has been observed by Meites and co-workers<sup>4</sup> when a dilute solution of cerium<sup>IV</sup> is taken in 1M KCNS. Recently Dole<sup>2</sup> and Novak,<sup>5,6</sup> have observed a well defined and reversible wave of cerium in 2M K<sub>2</sub>CO<sub>3</sub>, in which they found the existence of a carbonate complex.

The authors have found that cerium<sup>IV</sup> gives a diffusion-controlled wave in acetate buffer (total acetate 1M), which is useful for determination of cerium<sup>IV</sup> in small amounts. At lower acetate concentration, the wave is often associated with a depression or is succeeded by a small second wave, possessing anomalous characteristics.

### MATERIAL AND APPARATUS

Cerium<sup>IV</sup> sulphate solution was prepared from ammonium hexanitratocerate.<sup>7</sup> All materials used were of AnalaR grade and solutions were prepared in doubly-distilled water. The mercury used in the dropping mercury electrode was first purified chemically by treatment with nitric acid and subsequently distilled twice.

A Leeds and Northrup Electro-Chemograph, Type E, was used in all the polarographic experiments. A manual set up was also used, the circuit of which was similar to that described by Lingane and Kolthoff.<sup>8</sup> All potentials were measured against a Hume and Harris<sup>9</sup> saturated calomel electrode. The characteristics of the d.m.e. capillaries used were:

- (1)  $m = 1.6 \text{ mg sec}^{-1}$ ;  $t = 4.68 \text{ sec}$ ;  $h = 50 \text{ cm}$ :  $m^{\frac{2}{3}} t^{\frac{1}{3}} = 1.769 \text{ mg}^{\frac{2}{3}} \text{ sec}^{-\frac{1}{3}}$ .  
 (2)  $m = 1.357 \text{ mg sec}^{-1}$ ;  $t = 3.37 \text{ sec}$ ;  $h = 40 \text{ cm}$ :  $m^{\frac{2}{3}} t^{\frac{1}{3}} = 1.501 \text{ mg}^{\frac{2}{3}} \text{ sec}^{-\frac{1}{3}}$ .

For pH measurements, a Leeds and Northrup pH meter was used.

### RESULTS AND DISCUSSION

Polarograms, taken in acetate buffers of different pH values and strength, have been evaluated in Table I.

#### pH 4

In 0.2M buffer two waves were observed, one already present at zero applied e.m.f., representing the reduction of cerium<sup>IV</sup> to cerium<sup>III</sup> and the other starting at -0.9 v. A depression in the first wave appeared at -0.5 v. The second wave was roughly  $\frac{1}{3}$  of the height of the first wave and was well defined at cerium<sup>IV</sup> concentrations of  $1 \times 10^{-3}M$  and above.

Linearity of the height of the first wave with the concentration of cerium<sup>IV</sup> or with the square-root of mercury pressure was poor. It is noteworthy that the height of the second wave decreased on increasing the mercury pressure.

In 1M buffer only one wave was observed with the diffusion region present at zero applied e.m.f. The wave height was proportional to the concentration of cerium<sup>IV</sup>.

#### pH 5

Only one wave was observed with the diffusion region present at zero applied e.m.f. The proportionality of wave height with cerium<sup>IV</sup> concentration was satisfactory in 1M acetate medium only. It was found that the value of  $iI/cm^{\frac{2}{3}}t^{\frac{1}{3}}$  increased with increasing acetate concentration.

#### pH 5.6

Polarograms of cerium<sup>IV</sup> in 0.2M buffer showed nearly the same characteristics as at pH 5. However, because of slow hydrolysis, the solution turned turbid after some time, and so satisfactory results could not be obtained.

The results thus show that 1M acetate buffers of pH 4 and 5 are satisfactory media for the polarographic determination of cerium<sup>IV</sup>. In Table II the average diffusion current constant ( $I_D$ ) values and diffusion coefficient of cerium<sup>IV</sup>, calculated from the Ilkovič equation, in 1M acetate buffers of pH 4 and 5 are given.

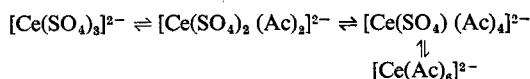
TABLE I

pH of acetate buffer	Concn. of $\text{Ce}^{IV}$ , $M \times 10^3$	Concn. of total acetate, $M$	Ionic strength	Limiting current of first wave, $\mu A$	$i_1/\text{cm}^2\text{t}$ (1st wave)	Limiting current of 2nd wave, $\mu A$	$i_2/\text{cm}^2\text{t}$ (2nd wave)	pH	Temp., $^{\circ}C$
4.0	0.50	0.2	0.061	0.62	0.7	0.06	0.068	3.65	20
	0.952	0.2	0.086	1.205	0.712	0.26	0.154	3.2	20
	1.363	0.2	0.106	1.83	0.757	0.38	0.156	2.7	20
	0.952	1.0	0.21	1.38	0.819	—	—	3.95	20
	1.818	1.0	0.23	2.66	0.825	—	—	3.9	20
	2.609	1.0	0.24	3.88	0.836	—	—	3.85	20
5.0	0.50	0.2	0.166	0.545	0.616	—	—	4.6	20
	0.952	0.2	0.190	1.00	0.593	—	—	4.2	20
	1.74	0.2	0.234	1.77	0.576	—	—	3.3	20
	0.952	1.0	0.73	1.36	0.802	—	—	4.95	24
	1.818	1.0	0.755	2.6	0.808	—	—	4.9	24
	2.609	1.0	0.775	3.78	0.816	—	—	4.8	24
5.6	0.049	4.5	3.175	0.087	1.173	—	—	5.0	35
	0.099	4.5	3.177	0.171	1.146	—	—	5.0	35
	0.196	4.5	3.18	0.327	1.107	—	—	5.0	35
	0.50	0.2	0.205	0.533	0.604	—	—	5.45	22
	0.952	0.2	0.23	1.1	0.644	—	—	5.2	22
	1.74	0.2	0.274	0.03	0.661	—	—	4.85	22

TABLE II

pH	$I_D$	$D \times 10^6$ , $cm^2 sec^{-1}$	Room temperature, $^{\circ}C$
4	0.827	1.855	20
5	0.809	1.744	24

It is known that cerium exists in solution as part of a complex anion. It is likely that acetate ions, when present in high concentration, may displace the sulphate ions in the  $[Ce(SO_4)_2]^{2-}$ . The resulting species will have different diffusion characteristics. This may explain the increase in the  $I_D$  value with increasing acetate concentration. The replacement of sulphate ions by acetate ions could occur in the following manner:



The second wave observed in acetate buffer of pH 4 (total acetate 0.2M) seems to be an anomalous wave, not corresponding to any electrochemical reduction. Such waves have often been observed.<sup>10</sup> They are observed only in the presence of some reducible substance. The height of such a wave is roughly proportional to that of the preceding diffusion-controlled wave. There is also some evidence that the anomalous wave disappeared in concentrated supporting electrolyte medium.<sup>10</sup> The second wave observed by the authors is present in 0.2M acetate buffer (pH 4) but is absent in 1M buffer (pH 4); and the height is roughly  $\frac{1}{2}$  of the height of the preceding wave.

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**Summary**—The polarographic behaviour of cerium<sup>IV</sup> has been studied in Walpole acetate buffers of different concentrations and pH values (4, 5 and 5.6). 1 M Acetate media of pH 4 and 5 have been found useful for the polarographic determination of cerium<sup>IV</sup>. At pH 4, in 0.2M acetate medium, a second wave at  $-0.9$  v. S.C.E. was observed, which had anomalous characteristics.

**Zusammenfassung**—Das polarographische Verhalten von Cer(IV) in Walpole-Puffern verschiedener Konzentration und bei pH- Werten 4, 5 und 5.6 wurde untersucht. 1 M Acetat bei pH 4-5 wurde als polarographisches Medium zur Bestimmung von Cer als geeignet gefunden. Bei pH 4 und einer Acetatkonzentration von 0.2 M tritt eine zweite Welle bei  $-0.9$  V (ges. Kalomel) auf; die Welle zeigt anomales Verhalten.

**Résumé**—Le comportement polarographique de Ce(IV) a été étudié dans des temps acétiques de Walpole de différentes concentrations et différents pH (4, 5 et 5.6). Un milieu 1 M en acétate, de pH compris entre 4 et 5, permet le dosage polarographique de Ce(IV). A pH 4 et en milieu acétate 0,2 M, on observe une deuxième vague à  $-0,9$  V. par rapport à l'électrode au calomel saturé, vague qui présente des caractéristiques anormales.

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## Spectrophotometric determination of the dissociation constant of the Woods reagent\*

(Received 11 July 1962. Accepted 6 November 1962)

THE Woods reagent, 2-hydroxymethyl-6-(2'-hydroxymethyl-5'-hydroxy-4'-pyrone-6')-pyran[3,2-b]-pyran-4,8-dione, has been employed for the spectrophotometric determination of iron<sup>1</sup>. More recently, the interaction stoichiometry of this reagent with iron has been studied<sup>2</sup>. The proposed structural formula of the Woods reagent<sup>1</sup> indicates that it contains two alcoholic hydroxyl groups which should be neutral, one phenolic hydroxyl group which should be weakly acidic, and three oxonium oxygen atoms which should be weakly basic. As expected, aqueous solutions of the Woods reagent are very weakly basic.

Because ultraviolet and visible spectral data have been applied successfully in the calculation of equilibrium constants,<sup>3,4,5,6</sup> the authors found it desirable to study spectrophotometrically the ionisation characteristics of the Woods reagent in aqueous solutions over a wide pH range. This study was undertaken to obtain spectrophotometric data in the ultraviolet region of the spectra for the purpose of ascertaining the dissociation constant corresponding to the ionisation of the hydrogen from the phenolic hydroxyl group of the Woods reagent.

### EXPERIMENTAL

#### Reagents

0.886*mM* Aqueous solution of Woods reagent: This stock solution was prepared from reagent purified by the procedure of Wilson and Daniel.<sup>1</sup>

All other chemicals used in the preparation of solutions were reagent grade chemicals.

#### Apparatus

All spectral measurements were obtained at  $25 \pm 2^\circ$  with a Bausch and Lomb Double Beam Spectronic 505 Recording Spectrophotometer using matched silica cells of 1.00-cm optical path.

All pH measurements were made with a Beckman Zeromatic pH meter which was standardised before use against a standard buffer system.

#### Spectral data and pH measurements

A series of solutions were prepared by placing 1-ml aliquots of the freshly prepared stock solution of the Woods reagent in 25-ml volumetric flasks and adding a calculated amount of acid or base to give the desired pH's, then diluting the resulting solutions to volume. The final concentration of the Woods reagent in these solutions was 3.54  $\mu$ M. The pH was measured for each solution and the spectral curve for each solution was determined over the wavelength region 200–400  $m\mu$ . Graphical presentation of the spectral-pH data for several of these solutions is shown in Fig. 1, and spectral data for some of the solutions for two selected wavelengths are given in Table I. As the pH of the series of solutions approaches 10, the absorbancies of the solutions approach a limit of minimum absorbance at 270  $m\mu$  and a limit of maximum absorbance at 315  $m\mu$  for the basic form of the Woods reagent. Similarly, as the pH of the series approaches 6, the absorbancies of the solutions approach a limit of maximum absorbance at 270  $m\mu$  and a limit of minimum absorbance at 315  $m\mu$  for the acid form of the Woods reagent. From 230  $m\mu$  to 400  $m\mu$ , the magnitude and sign of the quantity  $A(a) - A(b)$ , the difference between the absorbancies of the acidic and basic forms of the Woods reagent, corresponds to the relative amounts of the acidic and basic forms. At 240  $m\mu$  and 290  $m\mu$ ,  $A(a) - A(b)$  is zero, which corresponds to two isosbestic points.

\* This work was supported by a grant from the Robert A. Welch Foundation.

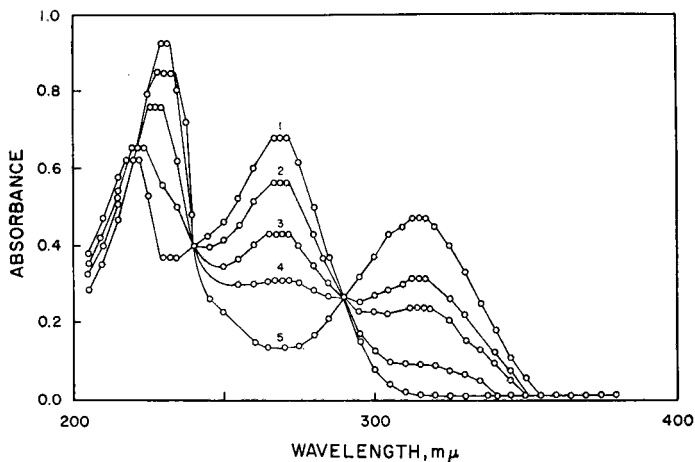


FIG. 1.—Spectral curves for a  $3.54 \mu M$  solution of the Woods reagent at different values of pH:

1. pH 2.00–6.00
2. pH 7.30
3. pH 8.05
4. pH 8.28
5. pH 10.00–12.00.

From the curves in the pH range 6–10 in Fig. 1, the law of mass equilibrium, and according to Stenstrom and Goldsmith,<sup>7</sup> the following relationship is easily obtained

$$K_i = \frac{A_m - A(a)}{A(b) - A_m} (H^+) \quad (1)$$

or 
$$\log R = \text{pH} + \log K_i \quad (2)$$

where  $A_m$  is the total molar absorbance of the mixture of the basic and acidic forms of the Woods reagent,  $R$  is the absorbance ratio, and  $K_i$  is the dissociation constant.

TABLE I.—pH-ABSORBANCE DATA FOR THE WOODS REAGENT

pH	Absorbance at 270 mμ	Absorbance at 315 mμ
2.56	0.673	0.012
3.11	0.673	0.012
4.15	0.680	0.012
6.75	0.639	0.041
7.70	0.495	0.162
7.73	0.430	0.242
8.05	0.384	0.307
8.28	0.310	0.344
8.83	0.220	0.403
10.50	0.133	0.465
11.35	0.133	0.465
11.61	0.133	0.465

By using equation (1) the dissociation constant can be calculated when  $A(a)$  and  $A(b)$  are known and a value of  $A_m$  lying between  $A(a)$  and  $A(b)$  has been determined for a certain pH. The dissociation constant for the Woods reagent was calculated from several selected points taken from the curve in Fig. 2 for which  $A_m$  was approximately the arithmetical mean of the limiting values of  $A(a)$

and A(b). These values for the dissociation constant of the Woods reagent at wavelengths 270  $m\mu$  and 315  $m\mu$  are given in Table II. To obtain the best apparent value of  $K_1$ , one should construct the entire absorbance-pH curve as shown in Fig. 2 using the experimentally determined pH-absorbance

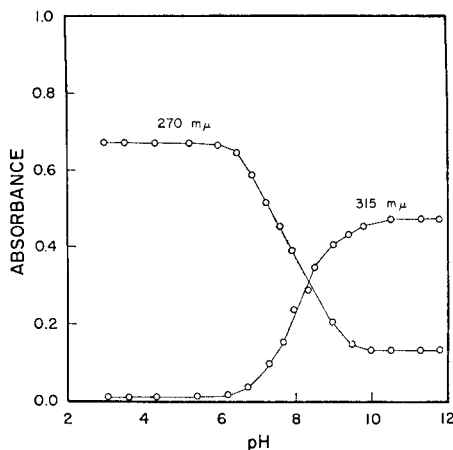


FIG. 2.—Absorbance as a function of pH for a 3.54  $\mu M$  solution of the Woods reagent.

data and therefrom determine the pH at which the second derivative for the curve is zero. According to the equilibrium principle at this point  $pK_1 = \text{pH}$ , because the ratio of the molar concentration of the basic form to the acid form of the Woods reagent is unity. The average value of the dissociation constant for the Woods reagent determined in the above manner from Fig. 2 is  $9.7 \times 10^{-9}$ . If the  $R$  values are calculated from the absorbance data shown in Table II over the pH range 7.70–8.83 and the logarithms of these  $R$  values are plotted against the corresponding pH values according to equation (2), the log  $R$  intercept at pH 0 is log  $K_1$ . The average dissociation constant for the Woods reagent determined in this manner is  $9.7 \times 10^{-9}$ .

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TABLE II—pH, ABSORBANCE, DISSOCIATION CONSTANT DATA  
FOR THE WOODS REAGENT  
 $\lambda = 315 m\mu$

pH	$(H^+) \times 10^9$	$A_m$	$A(a)$	$A(b)$	$K_1 \times 10^9$
8.83	1.48	0.403	0.012	0.465	9.81
8.45	3.55	0.344	0.012	0.465	9.73
8.28	5.25	0.307	0.012	0.465	9.87
8.05	8.91	0.242	0.012	0.465	9.17
7.70	20.00	0.162	0.012	0.465	9.90
Average $K_1$ at 315 $m\mu$ : 9.70					
$\lambda = 270 m\mu$					
pH	$(H^+) \times 10^9$	$A_m$	$A(a)$	$A(b)$	$K_1 \times 10^9$
8.83	1.48	0.220	0.673	0.133	8.60
8.45	3.55	0.285	0.673	0.133	9.05
8.28	5.25	0.310	0.673	0.133	10.76
8.05	8.91	0.384	0.673	0.133	10.24
7.70	20.00	0.495	0.673	0.133	9.84
Average $K_1$ at 270 $m\mu$ : 9.69					

(Average value of  $K_1$  at both wavelengths:  $9.70 \times 10^{-9}$ )

**Summary**—The spectrophotometric determination of the dissociation constant for the Woods reagent, 2-hydroxymethyl-6-(2'-hydroxymethyl-5'-hydroxy-4'-pyrone-6')-pyranyl[3,2-b]pyran-4,8-dione, which contains one weakly ionised phenolic hydroxyl group, is presented. The value of  $9.7 \times 10^{-9}$  is the average of the values obtained for the dissociation constant at wavelengths 270  $m\mu$  and 315  $m\mu$ . The best recommended value of the dissociation constant for the Woods reagent is  $9.7 \times 10^{-9}$ , which is obtained from the plot of log R against the corresponding pH values according to equation (2) and extrapolating to pH 0.

**Zusammenfassung**—Die photometrische Bestimmung der Dissoziationskonstante von Wood's Reagens, 2-Oxymethyl-6-(2'-oxymethyl-5'-oxy-4'-pyron-6')-pyranyl-3-2-b) pyran-4,8-dione, welches eine schwach dissoziierende phenolische Oxygruppe enthält wird beschrieben. Die Konstante beträgt  $9.7 \times 10^{-9}$ , was einen Mittelwert der Bestimmungen bei 270 und 315  $m\mu$  darstellt.

**Résumé**—Les auteurs ont déterminé par spectrophotométrie la constante de dissociation du réactif de Woods, le 2-hydroxyméthyl-6(2'-hydroxyméthyl-5'-hydroxy-4'-pyrone-6')-pyranyl 3,2-b)pyrane-4,8 dione dont le molécule présente un groupement oxhydre phénolique faiblement ionisé. La valeur de la constante de dissociation est de  $9,7 \times 10^{-9}$ , moyenne des valeurs obtenues à 270 et 315  $m\mu$ . La valeur recommandée est  $9,7 \cdot 10^{-9}$ , valeur obtenue en portant log R en fonction du pH selon l'équation (2) et en extrapolant à pH 0.

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### Interference of silicon in the determination of phosphorus by the vanadomolybdate method

(Received 5 October 1962. Accepted 17 November 1962)

Rieman and coworkers<sup>1,2</sup> have recently applied the technique of salting-out chromatography to the separation of several organophosphorus compounds. The separations were achieved on a column of low-capacity cation-exchange resin with aqueous eluents containing lithium chloride and/or hydrochloric acid. Eluted compounds were oxidised to orthophosphate with hot alkaline ammonium persulphate<sup>3</sup> prior to determination by the vanadomolybdate method.<sup>4,5,6</sup> This oxidation was carried out in the same glass test tubes used for the collection of small fractions of the effluent. The separations were excellent, but the recoveries of individual compounds varied from 84 to 108%. The aforementioned authors believed that the poor recoveries were caused by an error in the phosphorus determination rather than an incomplete separation.

The extension of the method of Rieman *et al.* to the separation of the mono and dialkyl esters of orthophosphoric acid is under investigation in this laboratory. Eluent solutions, free from any phosphorus compounds, that had been treated with alkaline ammonium persulphate and digested for 2 hr in a boiling water bath developed a characteristic yellow colour upon the addition of the vanadomolybdate reagent. The intensity of this colour increased upon standing.

It was reasoned that the strong alkali was dissolving significant amounts of silicon from the test tubes. This was confirmed by a spectrographic examination of the digestion mixture.

Harel, Tamari and Klein<sup>7</sup> developed a spectrophotometric method for the determination of silica based on the yellow colour of the silicovanadomolybdate complex. The absorbance of the complex was measured at 390  $m\mu$ . This wavelength is close to that recommended for the determination of

phosphorus by the vanadomolybdate method. However, conditions for the development of a stable and reproducible silicovanadomolybdate colour are much more rigid than those required for the corresponding determination of orthophosphate. The final acid concentration must be 0.20M. Increasing the acid concentration from 0.20 to 0.30M results in an absorbance decrease of 80%.

### EXPERIMENTAL

#### Reagents

All chemicals were of reagent grade and were used without further purification.

The vanadomolybdate reagent was prepared according to the method of Barton.<sup>6</sup>

#### Apparatus

Absorbance measurements were made with a Beckman DU spectrophotometer with 1-cm Corex cells.

The polypropylene test tubes were obtained from Van Waters and Rogers Inc., San Francisco, California, U.S.A.

#### Procedures

(1) *Development of the yellow silicovanadomolybdate complex.* Known amounts of aqueous sodium silicate solutions were transferred to a 100-ml volumetric flask. Twenty-five ml of vanadomolybdate solution were pipetted into each flask and the flasks were filled to the mark with distilled water. The absorbance at 400 m $\mu$  versus a blank was measured at 1-hr intervals.

(2) *Evaluation of various types of test tubes.* Two ml of 1M ammonium persulphate, 1 ml of 18M sodium hydroxide, and enough water to reach within 2 cm of the top were added to each type of test tube. The contents of each tube were thoroughly mixed and the tubes were placed in a boiling water bath for 2 hr. The digested mixtures were transferred to 100-ml volumetric flasks with 50 ml of 0.3M nitric acid. Twenty-five ml of vanadomolybdate reagent were added to each flask and the absorbance was measured at 400 m $\mu$ <sup>5,6</sup> after 1-hr intervals.

### RESULTS AND DISCUSSION

Fig. 1 shows that small quantities of silica will interfere with the determination of phosphorus even though the concentration of nitric acid is 0.8M. The absorbance of the silicovanadomolybdate complex increases strongly upon standing.

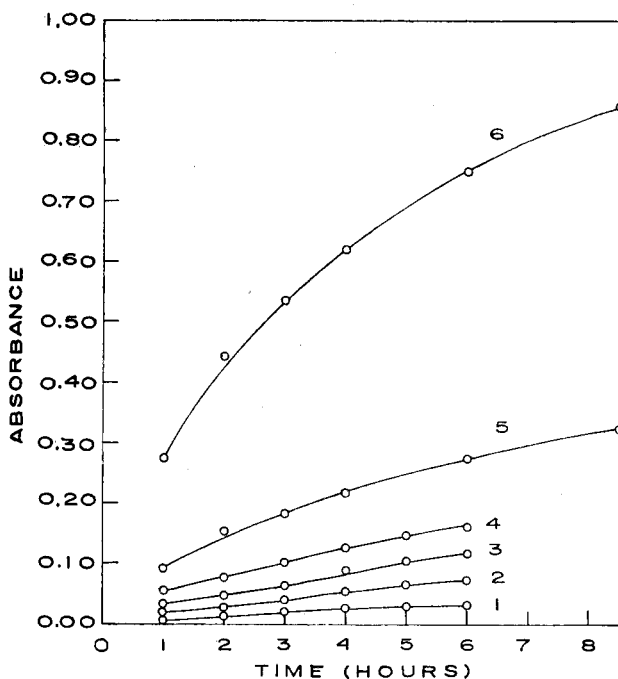


FIG. 1.—Absorbance of the silicovanadomolybdate complex in 0.8M nitric acid:  
 1. 0.20 mg of Si; 2. 0.40 mg of Si; 3. 0.60 mg of Si;  
 4. 0.80 mg of Si; 5. 1.00 mg of Si; 6. 3.00 mg of Si.

Table I indicates that significant amounts of silica are dissolved by the strongly alkaline digestion mixture. The quantity of silica that is leached out depends on the type of glass and condition of the

TABLE I—ABSORBANCE OF SILICOVANADOMOLYBDATE COMPLEXES  
AFTER ALKALINE PERSULPHATE DIGESTION

Type of test tube	Dimensions, mm	Development time	
		1 hr	2 hr
Exax glass	16 × 150	mean: 0.221 σ: 0.015	mean: 0.260 σ: 0.016
Kimax glass	16 × 150	mean: 0.287 σ: 0.018	mean: 0.348 σ: 0.021
Pyrex glass	16 × 150	mean: 0.258 σ: 0.011	mean: 0.308 σ: 0.010
Polypropylene	19 × 115	mean: 0.003 σ: 0.001	mean: 0.003 σ: 0.001

test tubes. These results explain the large variation in recoveries that were observed by Rieman and his coworkers. The interference from silicon can be eliminated by substituting polypropylene test tubes for those made of glass. Polypropylene tubes can be heated repeatedly in boiling water for many hr without any apparent change in form. These test tubes have been employed in the present studies and consistent recoveries of 98–99% have been obtained.

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**Summary**—Silicon interferes with the determination of phosphorus by the vanadomolybdate method because it forms a yellow complex that shows strong absorbance at 400 mμ. Alkaline ammonium persulphate oxidation in polypropylene test tubes, instead of glass, eliminates the interference of silicon in the determination of organophosphorus compounds.

**Zusammenfassung**—Silizium stört die Phosphorbestimmung nach der Vanadomolybdatmethode durch die Bildung eines gelben Komplexes, der bei 400 mμ stark absorbiert. Die Verwendung von Polypropylen-Probieröhren, anstatt solcher aus Glas, um die alkalische Ammonpersulfatoxydation durchzuführen, eliminiert die Störung bei der Analyse von organischen Siliziumverbindungen.

**Résumé**—Le silicium est gênant pour le dosage du phosphore dans la méthode au vanado-molybdate car il donne un complexe jaune présentant une forte absorption à 400 mμ. Une oxydation par le persulfate d'ammonium dans des tubes de propylène (ou bien de verre) supprime cet inconvénient pour le dosage du phosphore organique.

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**Quantitative treatment of exchange equilibria involving complexans—III\*:  
Chelatometric determination of calcium in presence of magnesium with EGTA**

(Received 18 June 1962. Accepted 24 November 1962)

THE great difference in stabilities of the EGTA [ethyleneglycol-bis-( $\beta$ -aminoethylether)- $N:N'$ -tetraacetic acid] chelates of calcium and magnesium enables one to titrate calcium selectively in the presence of magnesium. Thus there have been published methods of visual titration of calcium in the presence of magnesium using either the Zn-EGTA-Zincon system<sup>1,2</sup> or Calcon<sup>3</sup> as indicator. In this paper the possible use of the Zn-EGTA-PAN† system as indicator in the selective chelatometry of calcium is reported. The method seems to be better than the earlier methods.

**RESULTS AND DISCUSSION**

When the NY-HA system is used as indicator for the chelatometry of metal M, the pH and concentrations of NY and HA‡ are critical for the indicator transition. If the constants of the equilibria involved are all available, the end-point can be quantitatively accounted for by equation (27) of our previous paper,<sup>4</sup> which is reproduced below:

$$[Y]_t''/[M]_t = 1 - \frac{[NA_n]}{[A]^n} \cdot \frac{1}{K_1[NY]} + \frac{[A]^n}{[NA_n]} \cdot \frac{K_2[NY]}{[M]_t}, \quad (1)$$

where  $K_1 = K_{MY}K_{NA_n}/K_{NY}\beta_{(M)}$  and  $K_2 = K_{NA_n}\alpha_{H(Y)}/K_{NY}\S$ , and  $[M]_t$  and  $[Y]_t''$  denote the total concentration of M and of complexan used as titrant, respectively. Because Zn(PAN)<sub>2</sub> participates in the titration, equation (1) can be rewritten as:

$$[Y]_t''/[M]_t = 1 - \frac{[NA_2]}{[A]} \cdot \frac{1}{K_1[NY][A]} + \frac{[A]}{[NA_2]} \cdot \frac{K_2[NY][A]}{[M]_t}, \quad (2)$$

in which the term  $[NA_2]/[A]$  is a function of the indicator transition.

Studying the effects of pH, concentrations of Zn-EGTA, PAN and magnesium using equation (2), the results are represented as photometric curves in Figs. 1–3. Taking into account these results and the fact that the indicator transition is somewhat irreversible because of the low solubility of Zn(PAN)<sub>2</sub>, a procedure is established in which an excess of EGTA is titrated with calcium standard solution. As seen from Fig. 3, the present method allows the visual titration of calcium in a sample of which the ratio Mg:Ca does not exceed 10. For a higher proportion of magnesium, however, photometric titration is recommended.

**EXPERIMENTAL**

*Solutions*

**10<sup>-2</sup>M EGTA standard solution:** 3.8036 g of EGTA (Dojindo Co., Kumamoto, Japan) are dissolved in 20 ml of 1M sodium hydroxide solution and the whole is diluted to 1 litre. The solution is standardised chelatometrically with 10<sup>-2</sup>M zinc standard solution using Erio T as indicator.

**10<sup>-2</sup>M Calcium standard solution:** 1.0000 g of calcium carbonate is dissolved in a small amount of hydrochloric acid, of which the excess is expelled completely by evaporation to dryness on a steam bath. The residue is taken up in distilled water and diluted to 1 litre. The solution is standardised chelatometrically with EDTA standard solution.

**10<sup>-3</sup>M Zn-EGTA solution:** An equivolume mixture of 10<sup>-2</sup>M EGTA solution and 10<sup>-2</sup>M zinc solution is diluted five fold.

**10<sup>-3</sup>M PAN solution:** 25 mg of PAN (Dojindo Co., Kumamoto, Japan) are dissolved in 100 ml of methyl alcohol.

**Buffer solution (pH 8):** 1M hydrochloric acid is added to a saturated solution of borax until the pH of the solution is brought to 8.0.

*Apparatus*

Filter photometer and conventional titration cell (Hirama Co., Tokyo, Japan).

\* Part II: see reference 4.

† PAN = 1-(2-pyridylazo)-2-naphthol.

‡ If only the formation of NA has to be taken into consideration, [HA] does not influence the indicator transition as long as [HA] is sufficiently low.

§ Substituting  $\alpha_{H(Y)}$  by  $\alpha_{H, M_{II}(Y)}$ , the influence of a second metal (M<sub>II</sub>) can be accounted for by means of the concept of "ligand buffer".<sup>5</sup>

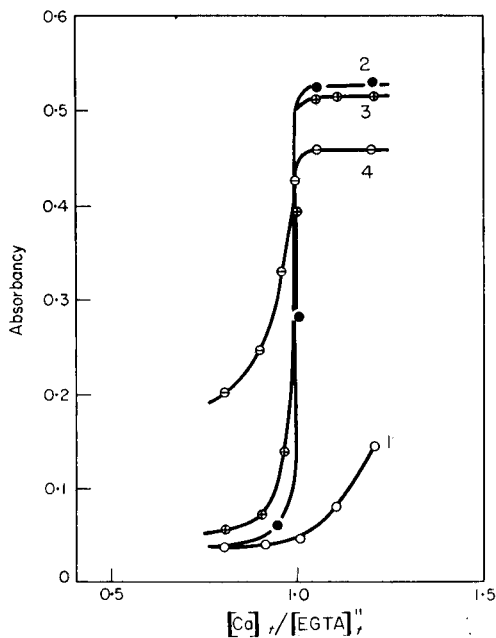


FIG. 1—Effect of pH on the titration of EGTA with calcium standard solution:

1. pH 7.0,
2. pH 8.0,
3. pH 9.0,
4. pH 10.0.

([EGTA]<sub>i</sub>:  $10^{-3}M$ ; [PAN]:  $2 \times 10^{-5}M$ ; [Zn-EGTA]:  $4 \times 10^{-5}M$ ; 562 m $\mu$ )

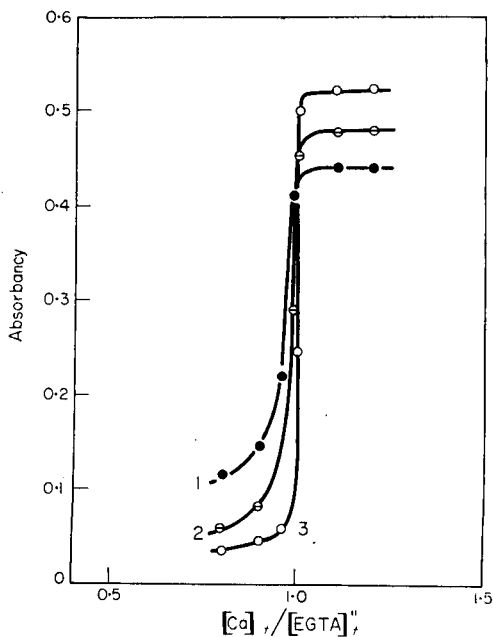


FIG. 2—Effect of concentration of Zn-EGTA:

1. [Zn-EGTA]:  $4 \times 10^{-4}M$ ,
2. [Zn-EGTA]:  $8 \times 10^{-5}M$ ,
3. [Zn-EGTA]:  $2.5-5 \times 10^{-5}M$ .

([EGTA]<sub>i</sub>:  $10^{-3}M$ ; [PAN]:  $2 \times 10^{-5}M$ ; pH: 8.0; 562 m $\mu$ )



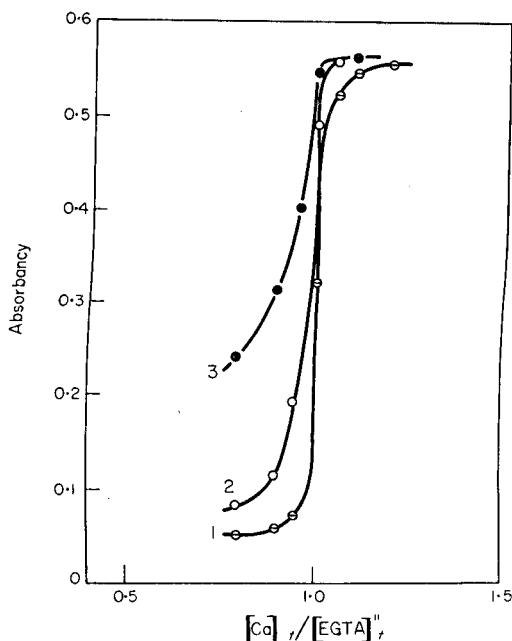


FIG. 3—Effect of concentration of magnesium:

1.  $[\text{Mg}^{2+}]$ : None,
2.  $[\text{Mg}^{2+}]$ :  $10^{-3}M$ ,
3.  $[\text{Mg}^{2+}]$ :  $10^{-2}M$ .

( $[\text{EGTA}]_0$ :  $10^{-3}M$ ;  $[\text{PAN}]$ :  $2 \times 10^{-5}M$ ;  $[\text{Zn-EGTA}] = 2.5 \times 10^{-5}M$ ; pH: 8.0; 562  $m\mu$ )

#### Recommended procedure

50 ml of buffer solution (pH 8) and 5–20 ml of  $10^{-2}M$  EGTA solution\* are added to 25 ml of neutral sample solution containing 1–4 mg of calcium and less than 10 mg of magnesium.† After the addition of 2.5–3 ml of  $10^{-3}M$  Zn-EGTA solution and 2 ml of  $10^{-3}M$  PAN solution, the excess EGTA is titrated with  $10^{-2}M$  calcium standard solution. Near the end-point, the solution is heated to about 50–60° and the titration is continued drop by drop under vigorous stirring. A colour change from pale yellow to pink is observed at the end-point. Titrate to a pink with no yellowish shade.

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**Summary**—A method of selective chelatometry of calcium in the presence of magnesium is established using the Zn-EGTA-PAN system as indicator. Effects of pH and concentrations of Zn-EGTA, PAN and magnesium are studied by means of photometric titration curves. The method allows the visual titration of calcium in a sample of which the ratio Mg:Ca does not exceed 10.

\* Total concentration of EGTA to be added is preferably more than 1.5 times calcium or 0.5 magnesium in the sample solution.

† By means of the photometric titration, the presence of about 100 mg of magnesium is tolerable.

**Zusammenfassung**—Eine Methode zur selektiven Bestimmung von Calcium in Gegenwart von Magnesium wurde ausgearbeitet. Das System Zink-AeGTE-PAN dient zur Anzeige des Endpunktes. Der Einfluss von pH, und der Konzentrationen des Indicatorsystems sowie des Magnesiums wurde mittels photometrischer Titrationskurven studiert. Die Methode gestattet die visuelle Bestimmung von Calcium in Proben, in denen das Verhältnis Mg:Ca den Wert 10 nicht überschreitet.

**Résumé**—On établit une méthode de dosage chélatométrique sélective du calcium en présence du magnésium employant le système Zn-EGTA-PAN comme indicateur. On étudie les effets de pH et des concentrations de Zn-EGTA, PAN et de magnésium au moyen des courbes de titrage photométrique. Cette méthode permet le titrage visuel du calcium contenu dans un échantillon dont Mg/Ca n'excède pas 10.

#### REFERENCES

- <sup>1</sup> A. Ringbom, G. Pensar and E. Wänninen, *Analyt. Chim. Acta*, 1958, **19**, 525.
- <sup>2</sup> F. S. Sadek, R. W. Schmid and C. N. Reilley, *Talanta*, 1959, **2**, 38.
- <sup>3</sup> R. A. Burg and H. F. Conaghan, *Chemist-Analyst*, 1959, **48**, 13.
- <sup>4</sup> G. Nakagawa and M. Tanaka, *Talanta*, 1962, **9**, 917.
- <sup>5</sup> M. Tanaka, *Analyt. Chim. Acta*, submitted for publication.

## NOTICES

(Material for this section should be sent directly to the Associate Editor)

### FRANCE

30 avril 1963: **Les peroxydes organiques: Applications Industrielles et determination analytique:** M. V. KARNOJITZKY. Faculté de Pharmacie, Paris.

### GERMANY

Wednesday-Saturday 24-27 April 1963: Meeting of *Analytical Chemistry Division, Society of German Chemists with German Committee for Spectrochemistry and Division of Mass Spectroscopy, German Physical Society.* Erlangen.

### HUNGARY

Wednesday-Saturday 24-27 April 1963: **Winkler Centenary Symposium.** Budapest.

The programme outline is as follows:

Wednesday afternoon, 24 April: *Winkler Memorial Session*

Thursday morning, 25 April: *Winkler Memorial Session*

Friday morning, 26 April: *Pharmaceutical Scientific Session*

The Plenary Lectures of the Winkler Memorial Sessions are:

L. W. Winkler: *Scientist and Teacher*

L. W. Winkler's Contribution to Gravimetry

L. W. Winkler's Contribution to Physical Chemistry

L. W. Winkler's Contribution to Titrimetry

L. W. Winkler's Contribution to Pharmaceutical Chemistry

E. SCHULEK

L. ERDEY

Z. SZABÓ

P. SZARVAS

A. VÉGH

The Pharmaceutical Scientific Session will consist of original papers from the following branches of the pharmaceutical sciences: pharmaceutical analysis, pharmaceutical technology, drug research and medicinal plant research.

### UNITED KINGDOM

Wednesday-Friday 3-5 April 1963: **Symposium on Soil Analysis and Its Relation to Plant Composition and Growth:** *Society of Chemical Industry, Agriculture Group.* Bristol (see *Talanta*, 1963, 10, No. 2, i).

Friday 5 April 1963: **Pharmacological Studies of Habituation:** Dr. E. M. GLASER: *Society for Analytical Chemistry, North of England Section and Biological Methods Group.* Evans Medical Research Laboratories, Speke, Liverpool. 6.00 p.m.

Tuesday 9 April 1963: Contributions from Research Workers in Universities and Colleges of Advanced Technology: *Society for Analytical Chemistry.* Chelsea College of Science and Technology, Manresa Road, London, S.W.3.

Wednesday-Thursday 17-18 April 1963: **First International Meeting in Questioned Documents.** London School of Pharmacy, Brunswick Square, W.C.1 (see *Talanta*, 1962, 9, 1073).

Thursday-Friday 18-19 April 1963: **Symposium on Analysis of Calcareous Materials:** *Society of Chemical Industry, Road and Building Materials Group.* Imperial College, London S.W.7 (see *Talanta*, 1962, 9, 94).

Wednesday 24 April 1963: **Examination of Questioned Documents,** Professor C. L. WILSON: *Society for Analytical Chemistry, Midlands Section and Royal Institute of Chemistry, Lea Valley Section.* Luton. 6.30 p.m.

Friday 10 May 1963: **Symposium on Modern Aspects of Electro-analytical Chemistry:** *Society for Analytical Chemistry, Scottish Section and Physical Methods Group.* Education Centre, I.C.I. Ltd., Nobel Division, Stevenston, Ayrshire.

Subjects will include:

*Automatic Analysis.*

*Differential Electrolytic Potentiometry.*

*Polarographic Determination of Oxygen.*

*Controlled-Potential Coulometry.*

*Chromatopolarography.*

G. MATTOCK

E. BISHOP

G. KNOWLES

G. W. C. MILNER

G. F. REYNOLDS

Further information may be obtained from Mr. A. F. WILLIAMS, I.C.I. Ltd., Nobel Division, Stevenston, Ayrshire.

*Wednesday–Friday 17–19 July 1963: Microchemical Meeting: Society for Analytical Chemistry, Microchemistry Group.* School of Pharmacy, London W.C.1.

This meeting will follow the XIX I.U.P.A.C. Congress, and it will consist of lectures and discussions on microchemical topics, visits to microchemical laboratories and a social programme. Among the lectures will be:

*Future Possibilities in Microanalysis.*

*Methods of Organic Microanalysis: A Comparative and Critical Study.*

*Mass Spectrometry and Microanalysis.*

*Infrared and Microchemistry.*

*Some Recent Developments in Functional Group Analysis on the Micro Scale.*

*The Status of Microgram Analysis.*

A. J. P. MARTIN

R. LEVY

A. QUAYLE

D. M. W. ANDERSON

S. VEIBEL

R. BELCHER

Introductory speakers in the discussions will include: H. MALISSA, W. SIMON, W. R. NALL and G. INGRAM.

Further information may be obtained from Mr. D. W. WILSON, Sir John Cass College, Jewry Street, Aldgate, London, E.C.3.

At the **Eighth Annual General Meeting** of the *Western Section* of the *Society for Analytical Chemistry*, Thursday, 10 January, 1963, the following Officers of the Section were elected for the coming year:

*Chairman:* Dr. F. H. POLLARD

*Vice-Chairman:* Mr. E. A. HONTOIR

*Secretary/Treasurer:* Dr. T. G. MORRIS, Brockleigh, Clevedon Avenue, Sully, Glamorgan.

At the **Twenty-Eighth Annual General Meeting** of the *Scottish Section* of the *Society for Analytical Chemistry*, Friday, 25 January, 1963, the following Officers of the Section were elected for the forthcoming year:

*Chairman:* Dr. R. A. CHALMERS

*Vice-Chairman:* Mr. J. K. McLELLAN

*Secretary/Treasurer:* Mr. J. W. MURFIN, Standards Department, Boots Pure Drug Co. Ltd., Motherwell Street, Airdrie, Lanarkshire.

At the **Thirty-Eighth Annual General Meeting** of the *North of England Section* of the *Society for Analytical Chemistry*, Saturday, 26 January, 1963, the following Officers of the Section were elected for the forthcoming year:

*Chairman:* Mr. C. J. HONSE

*Vice-Chairman:* Mr. J. F. CLARK

*Secretary/Treasurer:* Mr. G. F. LONGMAN, Unilever Research Laboratory, Port Sunlight, Cheshire.

**British Standards Institution** announces the following *New British Standards*:

*B.S. 1673: Methods of testing raw rubber and unvulcanised compounded rubber: Part 5/5.1: 1963: Analysis of styrene butadiene copolymers (SBR): Bound styrene content.* This covers determination of bound styrene and gives details of apparatus and materials, procedure and calculation of result. (Price 3s.)

*B.S. 3582: 1963: Method for the determination of oils, fats and waxes in wool.* This provides a method for the determination of oils, fats and waxes in wool by dichloromethane treatment. It applies to wool in any processed form but not to unscoured raw wool. (Price 3s.)

The following *Revised British Standards* are announced:

*B.S. 1756: Methods for the sampling and testing of flue gases: Part 1: 1963: Methods of sampling.* This deals with the general principles to be adopted in order to obtain a representative flue gas sample for analysis. (Price 7s.6d.) *Part 2: 1963: Analysis by the Orsat apparatus.* This deals with the analysis of a flue gas sample with the Orsat apparatus. (Price 4s.6d.)

*B.S. 2073: 1962: Methods of testing essential oils.* This describes (1) the preparation of the oil for examination, the methods of test for: (2) specific gravity, (3) apparent density, (4) optical rotation, (5) refractive index, (6) freezing point, (7) solubility in ethanol, (8) residue on evaporation, (9) acid value, (10) ester value, (11) ester value after acetylation, (12) apparent cineole content, (13) carbonyl value and (14) phenols. In some of the methods the details of the procedure are varied slightly according to the oil being analysed, and for details of these variations reference is required to the British Standard specifications for the individual oils concerned. (Price 7s.6d.)

The following *Amendment Slips* are announced:

*B.S. 1672: Methods of testing rubber latex: Part 2: 1954: Chemical and physical tests. Amendment No. 6: PD 4755.*

*B.S. 3477: 1962: Determination of oils, fats and waxes in cotton. Amendment No. 1: PD 4768.*

## UNITED STATES OF AMERICA

Sunday 31 March–Friday 5 April 1963: 144th National Meeting: American Chemical Society.  
Los Angeles, California.

The programme for the Division of Analytical Chemistry is:

## Monday Morning, 1 April

- Section A—Fluorescence and Phosphorescence Symposium*
- Fluorescence of Mono- and Diprotonated 1,10-Phenanthroline in Aqueous Solution.* W. W. BRANDT, B. E. JONES and M. E. LANGMUIR
- Phosphorescence of o-Phenanthroline and Related Nitrogen Heterocycles.* J. S. BRINEN, D. D. ROSEBROOK and R. C. HIRT
- Spectral Characteristics of Fluorescent Chelates.* R. ARGAUER and C. E. WHITE
- Solvent Effects on the Fluorescence of Aminophenols and Related Compounds.* D. W. ELLIS and L. B. ROGERS
- Organic Molecules and Optical Masers.* M. W. WINDSOR
- Studies on the Fluorescence of 9-Anthranol.* J. P. PARIS and D. M. HERCULES
- Total Luminescence of Organic Molecules of Petrochemical Interest.* S. P. MCGLYNN, B. T. NEELY and C. NEELY

## Monday Afternoon, 1 April

- Section A—Fluorescence and Phosphorescence Symposium*
- Double Beam Fluorescence Spectroscopy.* W. KAYE
- Comparison of Spectrophotometric and Spectrofluorometric Methods for the Determination of Malonaldehyde.* E. SAWICKI, T. W. STANLEY and H. JOHNSON
- Photoreduction of Carbonyl Compounds—I: Fluorescent Intermediates of Quinones.* J. D. GORSUCH, J. P. PARIS and D. M. HERCULES
- Fluorescent Ion-Exchange Resins.* A. H. HEIMBUCH, H. GEE and H. BOULD
- Mechanisms of Fluorescence Quenching.* A. WELLER
- A Study of the Triplet States of Some Aromatic Hydrocarbons.* R. M. HOCHSTRASSER and S. K. LOWER
- On the Origin of the Phosphorescence Radiation in Aromatic Hydrocarbons.* M. A. EL-SAYED
- Section B*
- Current Research in Analytical Chemistry.* Informal Discussion

## Tuesday Morning, 2 April

- Section A—Fisher Award Symposium honouring D. N. Hume*
- Polarographic and Chronopotentiometric Behaviour of o-Phthalic Acid in Acidic Solutions.* R. P. BUCK
- Qualitative Gas Chromatographic Analysis.* C. MERRITT, JR.
- Separation and Quantitative Analysis of Brominated Salicylanilides using an Automated Anion-Exchange Procedure with UV-Column Monitoring.* H. J. KEILY, A. L. GARCIA and R. N. PETERSON
- Introduction of D. N. Hume.* I. M. KOLTHOFF and H. A. LAITINEN
- The Analysis of a Profession (Fisher Award Address).* D. N. HUME
- Section B*
- Determination of Nitrogen, Oxygen and Hydrogen in Metals by Inert Gas Fusion.* B. D. HOLT and H. T. GOODSPEED
- A Simple Method for Microdetermination of Boron, either Alone or Simultaneously with Nitrogen and/or Phosphorus in Organoboranes.* R. C. RITTNER and R. CULMO
- The Acidity of Tetraphosphoric Acid.* J. I. WATTERS, P. E. STUURCK and R. E. SIMONAITIS
- The Formation of Lead Chloride Fluoride at Lower pH Values for Gravimetric Purposes.* R. A. BOURNIQUE and L. H. DAHMER
- An Approach to the Standardisation of pH Measurements in Alcohol–Water Solvents.* R. G. BATES, M. PAABO and R. A. ROBINSON
- Anion-Exchange Separation of Magnesium and Calcium with Alcohol–Nitric Acid.* J. S. FRITZ and H. WAKI
- Separation of Technetium from Mixed Fission Products by Solvent Extraction with Tributyl Phosphate.* M. H. CAMPBELL
- A Redetermination of the Half-life of Uranium-232* J. M. CHILTON, R. A. GILBERT, R. E. LEUZE and W. S. LYON

- Rapid Radiochemical Separations and Activation Analysis of Rare Earth Elements.* K. RENGAN and W. W. MEINKE
- Activation Analysis for Sodium in Sodium Tungsten Bronzes.* R. J. REULAND and A. F. VOIGT
- Radiochemical Determination of Caesium-137 in Soils using Ammonium Phosphomolybdate and Sodium Tetraphenylboron.* W. R. COLLINS, JR., D. C. SUTTON and M. J. SOLAZZI
- A Selective Spectrophotometric Method for the Determination of p-Aminophenol.* G. G. GUILBAULT

Tuesday Afternoon, 2 April

- Section A—Fisher Award Symposium honouring D. N. Hume*
- Column Fractional Precipitation.* W. W. SCHULTZ and W. C. PURDY
- The Analytical Chemist in the Aerospace Industry.* E. A. BURNS
- Application of Cyclic Voltammetry and Polarography to a Study of the Reduction Paths of Several Tertiary Aliphatic Nitro Compounds.* D. L. MARICLE, W. H. JURA, A. K. HOFFMAN and W. G. HODGSON
- The Current Crisis in Education in Analytical Chemistry.* D. D. DEFORD

Wednesday Morning, 3 April

- Section A—Symposium on New Instrumental Methods and Techniques*
- Push-Button Analyses.* H. V. MALMSTADT
- An Automatic Reaction Rate Method for Ultramicro Determination of Iodine.* T. P. HADJIOANNOU
- Thermal Analysis: New Methods from a Classical Technique.* D. R. JOHNSON and J. CHIU
- A New Automatic End-point Detector for Constant Current Coulometric Titrations.* C. B. ROBERTS
- Analytical Applications of  $\beta$ -Excited X-rays.* R. H. MÜLLER
- Automation of Analytical Procedures based on Enzyme Catalysed Reactions.* G. P. HICKS and W. J. BLAEDEL
- Section B*
- Gas Chromatography with Mixed-Bed Packing.* C. N. REILLEY, G. P. HILDEBRAND, L. J. PAPA and W. E. NORTEMAN, JR.
- Gas Chromatographic Analysis of Lead Alkyls with Electron Affinity Detectors.* E. M. BARRALL and P. BALLINGER
- Temperature Programmed Columns in Gas Chromatography: Comparison of Packed and Capillary Columns for Analysis of Dilute Hydrocarbon Gas Mixtures.* D. J. MCEWEN
- Determination of Residual Monomer in Polymer Emulsions by Rapid Distillation and Gas Chromatography.* O. TWEET and W. K. MILLER
- Computer Optimisation of Mixed Liquid Phases for Gas Chromatography.* R. S. PORTER, R. L. HINKINS, L. TORNHEIM and J. F. JOHNSON
- Rapid Method for Nitrogen Analysis in Organic Compounds and Associated Materials by Gas Chromatography.* M. L. PARSONS, S. N. PENNINGTON and J. M. WALKER
- Gas Analysis by Geiger Pulse Attenuation.* A. F. FINDEIS and F. W. WILLIAMS
- Analysis of Tars and Pyrolysates by Gas Chromatography Programmed at Moderate Temperatures.* W. LIJINSKY, I. I. DOMSKY and G. MASON
- Gas Chromatographic Analysis of Helium at Reduced Pressures.* J. E. ATTRILL, C. M. BOYD and A. S. MEYER, JR.

Wednesday Afternoon, 3 April

- Section B*
- Electrochemical Determination of Glucose Oxidase using Diphenylamine Sulphonic Acid as a Potential Poiser.* G. G. GUILBAULT, B. C. TYSON, JR., D. N. KRAMER and P. L. CANNON, JR.
- Base-Catalysed Acetylation of Hydroxyl Groups: Method and Mechanisms.* G. H. SCHENK and P. WINES
- Leucofluorescent Substances as Substrates for Enzymatic Analytical Methods.* A. S. KESTON, C. H. WOO and R. BRANDT
- Burning of Large Samples using the Flowing Oxygen Combustion-in-a-Bottle Technique.* L. L. FARLEY and R. A. WINKLER
- Determination of Primary Alcohol Groups in Polyglycols using Trityl Chloride.* J. G. HENDRICKSON

- Elution Properties of Organic Substances in Solution-Adsorption Chromatography.* H. D. FRAME, H. H. STRAIN, D. STEFFENSON and C. K. ROFER
- Kinetic Analysis of Binary Mixtures by the Method of Proportional Equations: Case where  $\Sigma$  [Reactants]  $\gg$  [Reagent].* H. B. MARK, JR. and L. J. PAPA
- Micro Method for Measuring Lipid Tolerance.* L. M. BERGQUIST and R. L. SEARCY
- Characterisation of Alkyl and Aryl Halogen Compounds by 2,4-Dinitrophenylhydrazones of Aldehydes formed from Reaction of Their Grignard Reagents with Dimethylformamide.* J. G. SHAREFKIN and A. FORSCHIM
- A Nuclear Magnetic Resonance Spectra-Structure Correlation for Chlorinated Propanes.* H. F. WHITE
- Characterisation of Aromatic Iodine Compounds by Formation of Polyvalent Iodine Derivatives with Peracetic Acid.* J. G. SHAREFKIN and H. SALTZMAN
- Method for Determining Carboxyl Content of Insoluble Carbonaceous Materials.* J. I. FESTER and W. E. ROBINSON
- Evaluation of the Automatic Analysis of Urea in Biological Fluids.* R. L. SEARCY and J. A. FOREMAN

Thursday Morning, 4 April

Section A—Symposium on Thermal Methods

- Review of Thermal Analysis.* P. D. GARN
- Differential Thermal Analysis of Crude Oil Oxidation.* D. W. PEACOCK
- Approximate Heats of Explosion using Differential Thermal Analysis.* R. L. BOHON
- Simultaneous Thermal Analysis using the Open Pan Type of Sample Holder.* H. G. MCADEIE
- Kinetics of the Thermal Dehydration of Hydrous Silicates.* J. B. HOLT, I. B. CUTLER and M. E. WADSWORTH

Section B

- Polarography of 2-Aminoethanethiosulphuric Acid and 2-Aminoethaneselenosulphuric Acid.* W. STRICKS and R. G. MUELLER
- Determination of Reactant Adsorption and Oxide Film Reduction at Platinum Electrodes by Integration of Single-Sweep Oscillopolarograms.* R. A. OSTERYOUNG, G. LAUER and F. C. ANSON
- The Pyrolytic Carbon Electrode: A New Electrode for Electroanalytical Studies.* A. L. BEILBY and W. BROOKS, JR.
- Polarographic Determination of Certain Medicinal Compounds containing Dichloroacetamido Groups.* C. A. KELLY and M. E. AUERBACH
- Heterogeneous Reaction Rate Constants and Transfer Coefficients for Nitrobenzenes at Elevated Temperatures.* T. DeVRIES and J. T. BURR
- An Automated Polarographic Analyser for Continuous Analysis* R. A. HAGSTRON and A. F. KRIVIS
- Effect of Adsorption and Electrode Oxidation on the Oxidation of Oxalic Acid at Platinum Electrodes.* F. A. SCHULTZ and F. C. ANSON
- Ligand Bridging in the Oxidation of Chromium<sup>III</sup> at Mercury Electrodes.* J. G. JONES and F. C. ANSON
- Use of the Pyrolytic Graphite Indicating Electrode in Voltammetry.* F. J. MILLER and H. E. ZITTEL
- A.C. Polarography of Electrode Processes with Coupled Homogeneous Chemical Reactions.* D. E. SMITH

Thursday Afternoon, 4 April

Section A—Symposium on Thermal Methods

- Dynamic Diffuse Reflectance Spectroscopy.* W. W. WENDLANDT
- New Studies on Calcium Oxalate Monohydrate.* E. L. SIMONS and A. E. NEWKIRK
- Differential Thermal Analysis Apparatus.* E. M. BARRALL, J. F. GERNERT, R. S. PORTER and J. F. JOHNSON
- Detection of Organic Polymer Transitions by Differential Thermoanalytical Techniques.* A. W. HAY
- Class Transitions in Polypropylene.* D. L. BECK, A. A. HILTZ and J. R. KNOX

- Investigation of Comonomer Distribution in Ethylene-Acrylate Copolymers with Thermal Methods.* K. J. BOMBAUGH, C. E. COOK and B. H. CLAMPITT

### Section B

- Electrochemical Analysers for Air Pollution and Environmental Monitoring.* G. A. ROST and D. J. SWARTZ
- Galvanic Determination of Carbon Dioxide.* P. A. HERSCH and C. J. SAMBUCETTI
- Coulometric Determination of Bromine Numbers: A Constant-Current Potentiometer End-point System.* F. BAUMANN and D. D. GILBERT
- Conductimetric Titration of Metal Naphthenates.* M. C. MOHRHOFF and G. E. F. BREWER
- Chronopotentiometric Determination of Hammett Substituent Constants using Substituted Phenylferrocenes.* J. D. JOHNSON, W. F. LITTLE, C. N. REILLEY and A. P. SAUNDERS
- Properties of Tubular Platinum Electrodes applied to Continuous Analysis.* W. J. BLAEDEL and C. OLSON
- Controlled Potential Coulometry of Metals in Fused Lithium Chloride-Potassium Chloride Eutectic.* R. D. CATON, JR. and H. FREUND
- Determination of Technetium by Controlled-Potential Coulometric Titration in Buffered Sodium Tripolyphosphate Medium.* A. A. TERRY and H. E. ZITTEL
- Amperometric Titration of Zirconium with Cupferron.* H. KUBOTA and J. C. SURAK
- Electro-Oxidation of p-Phenylenediamine and Related Compounds in Concentrated Acid Solutions.* H. B. MARK, JR. and F. C. ANSON

### Friday Morning, 5 April

- Section A—Symposium on Operational Amplifiers in Analytical Instrumentation Basic Characteristics of Operational Amplifiers as Instrumentation Components.* D. D. DEFORD
- The Stabilised Operational Amplifier.* C. G. ENKE
- The Heath Analog Computer as a Versatile Analytical Instrument.* G. W. EWING and T. E. BRAYDON
- Characteristics and Applications of an Educational Operational Amplifier System.* H. V. MALMSTADT and C. G. ENKE
- A Practical Instrument Synthesiser.* C. F. MORRISON
- A Multipurpose Operational Amplifier Instrument for Electroanalytical Studies.* W. L. UNDERKOFFLER and I. SHAIN
- A Multipurpose Electrochemical Instrument for Current and Potential Control: Integration of Currents with Application of Linear Potential Sweep.* G. LAUER, H. SCHLEIN and R. A. OSTERYOUNG

### Friday Afternoon, 5 April

- Section A—Symposium on Operational Amplifiers in Analytical Instrumentation Applications of Commercial Operational Amplifiers in Instrumentation for Chemical Analysis.* M. T. KELLEY, D. J. FISHER, H. C. JONES, W. L. MADDOX and R. W. STELZNER
- Instrumentation for Cyclic Voltammetry Using Operational Amplifier Switching Modules* R. P. BUCK
- Operational Amplifiers in Instrumentation for A.C. Polarography.* D. E. SMITH
- Chronopotentiometric Power-of-time and Exponential Current Functions.* R. W. MURRAY
- Some Novel Operational Amplifier Circuits for Modular Instrumentation* E. C. TOREN, JR., C. P. DRISCOLL and J. W. YARBROUGH
- Electroanalytical Controlled-Potential Instrumentation.* G. L. BOOMAN and W. B. HOLBROOK
- A Square Wave Polarograph employing Operational Amplifiers.* D. D. DEFORD and E. H. NAGEL

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**Tuesday 2 April 1963: Application of the Microprobe to Mineralogical and Biological Problems:**  
 DR. I. ADLER: *Society for Applied Spectroscopy, New York Section.* Hotel Manhattan, 44 Street and 8 Avenue, New York. 8.00 p.m.



*Monday–Wednesday 1–3 April 1963: Oak Ridge Radioisotope Conference—Applications to Physical Science and Engineering: Oak Ridge Institute of Nuclear Studies, ORNL and Isotopes and Radiation Division of American Nuclear Society. Gatlinburg, Tenn.*

*Tuesday–Wednesday 16–17 April 1963: Ohio Valley Instrument-Automation-Electronics Exhibit and Symposium. Cincinnati Garden, Cincinnati, Ohio.*

*Sunday–Wednesday 21–24 April 1963: Third Rare Earth Conference. Grand Bahama Hotel, Grand Bahama Island nr. Miami, Fla.*

*Wednesday–Friday 7–9 August 1963: Twelfth Annual Conference on Applications of X-ray Analysis. Albany Hotel, Denver, Colorado.*

Papers are invited, the titles and abstracts of which should be submitted in duplicate (200 words) by 15 April to: William M. MUELLER, Head of Metallurgy Division, Denver Research Institute, University of Denver, Denver 10, Colorado. Final manuscripts should be sent by 15 July with consent to publish in copyrighted proceedings. The conference will have sessions devoted to: diffraction, emission spectrography, absorption and microscopy, instrumentation.

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## ERRATA — VOLUME 10

Page 208, reference 5: this should read *Talanta*, 1963, **10**, 209.

Page 214, reference 4: this should read *Talanta*, 1963, **10**, 205.

## PAPERS RECEIVED

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- Die Bestimmung kleiner Fluormengen—III. Bestimmung von Fluoridionen im Bariumtitanat mittels Zr—Xylenol-Orange in Anwesenheit von Kieselsäure:** JOSEF NOVAK and ROMAN VALACH. (1 January 1963)
- Electrolytic generation of sulphate for precipitation studies:** DAVID H. KLEIN and BERNARDO FONTAL. (4 January 1963)
- Spectrophotometric determination of decaborane by the  $\beta$ -naphthoquinoline complex:** ROBERT S. BRAMAN and THOMAS N. JOHNSTON. (4 January 1963)
- A tentative method in radioactivation analysis:** TOSHI KAWASHIMA. (7 January 1963)
- Selective spot test for europium in the presence of other rare earths:** ERVIN JUNGREIS and EZRA LEVY. (8 January 1963)
- Spectrophotometric determination of hexanitrodiphenylamine in microgram quantities:** R. D. TIWARI and J. P. SHARMA. (8 January 1963)
- Estimation of mucopolysaccharide sulphate in connective tissue:** GERALDINE ZDYBEK, D. S. McCANN and A. J. BOYLE. (9 January 1963)
- Studies of volumetric and spectrophotometric methods for the determination of gold:** A. CHOW and F. E. BEAMISH. (9 January 1963)
- 8-Acetoxyquinoline as an analytical reagent:** E. J. BILLO, B. E. ROBERTSON and R. P. GRAHAM. (11 January 1963)
- Gravimetric determination of vanadium-V with  $\alpha$ -nitroso- $\beta$ -naphthol:** S. V. PATIL. (11 January 1963)
- Ion exchange in mixed solvents: Adsorption behaviour of the rare earths and some other elements on strong-base anion-exchange resin from nitric acid-alcohol media: Methods for separation and spectrophotometric determination:** J. KORKISCH and I. HAZAN. (12 January 1963)
- The application of some hydrazine derivatives as reductimetric agents:** J. VULTERIN and J. ZYKA. (15 January 1963)
- The precipitation of uranium  $\alpha$ -nitroso- $\beta$ -naphtholate from homogeneous solution:** S. V. PATIL, (15 January 1963)
- The determination of tertiary amines in the presence of primary and secondary amines:** M. MILLER and D. A. KEYWORTH. (21 January 1963)
- The recovery of rhodium, iridium, palladium and platinum from ores and concentrates by wet assay and a comparison with recovery by fire assays:** G. G. TERTIPIS and F. E. BEAMISH. (21 January 1963)
- Infrared determination of chlorate in the presence of other oxyhalogen anions:** MICHAEL W. MILLER, ROBERT H. PHILP, JR. and A. L. UNDERWOOD. (21 January 1963)
- The improved preparation of ammonium nitrocerate and routine analytical testing procedure to prove primary reference-standard purity:** G. FREDERICK SMITH. (22 January 1963)
- Studies on the complex compounds of titanium-III and -IV—Part I: Spectrophotometric studies on the titanium-III chloride-cacotheline complex and the chemical analysis of the solid product:** S. M. S. AKHTAR, NASEER-AHMAD and S. M. F. RAHMAN. (22 January 1963)
- Studies on the complex compounds of titanium-III and -IV—Part II: Spectrophotometric studies on the titanium-III complexes with alizarin and dithizone and chemical analysis of titanium-III alizarin complex:** S. M. S. AKHTAR, NASEER-AHMAD and S. M. FAZLUR RAHMAN. (22 January 1963)
- Oxidation of carbohydrate osatriazoles with vanadium-V:** K. S. PANWAR and J. N. GAUR. (22 January 1963)
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