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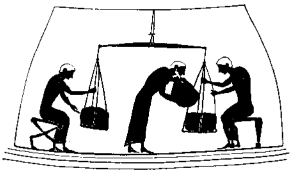

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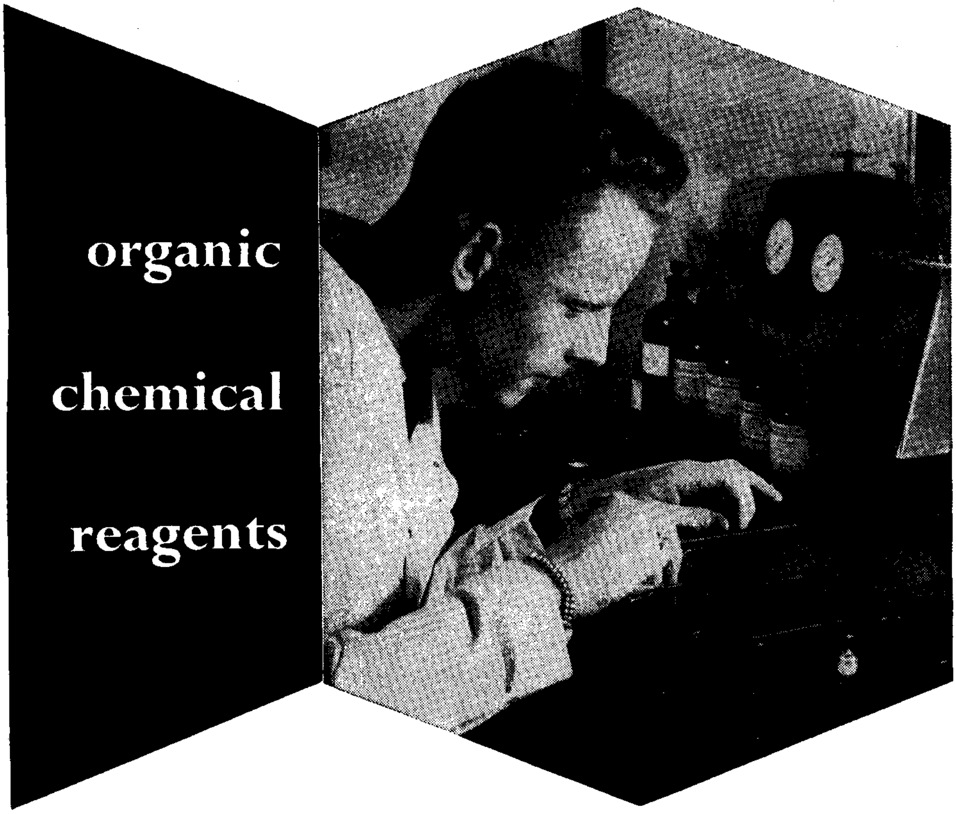
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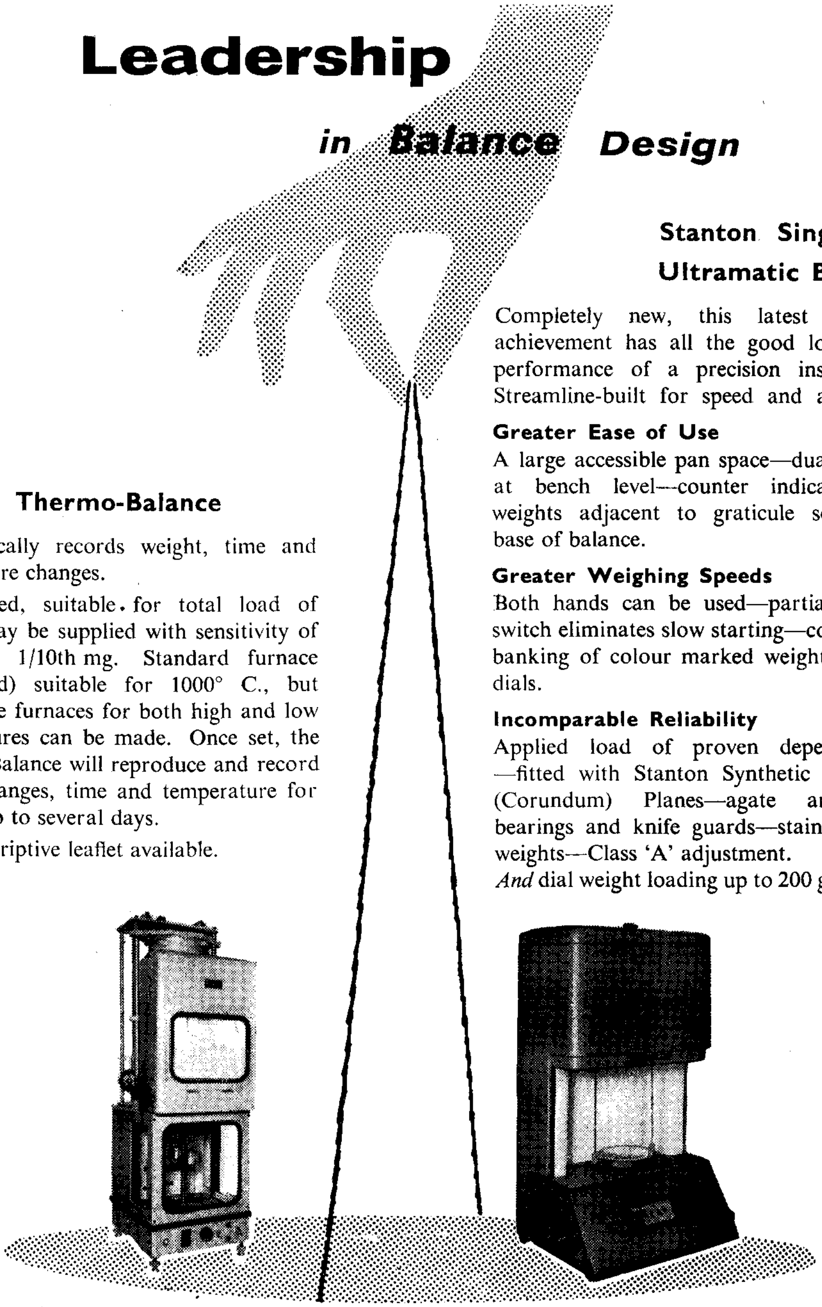

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BENZIDINE AND ITS DERIVATIVES IN ANALYTICAL CHEMISTRY

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Summary—A survey has been made of the analytical applications of benzidine and diphenylamine and their derivatives, as precipitants, in the detection and colorimetric determination of oxidants and as indicators in titrimetric analysis. The period covered is from the beginning of 1946 to the end of 1958.

Benzidine (4:4′-diamino-1:1′-diphenyl) is the parent of an important group of organic reagents used in chemical analysis. It includes nuclear-substituted and N-substituted benzidines and the diphenylamines since diphenylamine has been shown[1,2] to oxidise to N:N′-diphenylbenzidine (probably through N:N′-tetraphenylhydrazine) and then to diphenylbenzidine violet.

The analytical applications of this class of compound have been surveyed by Welcher[3] up to 1946. This review discusses new applications of the reagents covered by Welcher; it also deals with new reagents, structurally related to benzidine, which have been developed and reported in the literature between 1946 and the end of 1958.

Benzidine owes its versatility as an organic reagent to the amino groups and their arrangement in the molecule. These groups confer on it the properties of complex formation with metal cations and of salt formation from acid solution; in addition, the arrangement of the groups in the diphenyl nucleus is responsible for the formation of highly coloured products on oxidation and at least partially responsible for the insolubility of certain salts and complexes.

Benzidine is not now used in the gravimetric analysis of metals because of the availability of more selective precipitants, giving better defined products, and the increased use of titrimetric and instrumental methods of analysis. Considerable interest has been shown in the salt-forming properties of this class of compound, particularly for sulphate precipitation and for the precipitation and fractionation of mixtures of polyphosphates and polythionates. However, reactions involving the oxidation of benzidine type compounds have received most attention and have been applied mainly in spot test reactions, and in colorimetric, absorptiometric, and titrimetric methods of analyses.

PROCEDURES DEPENDING ON PRECIPITATION

Sulphate

A few indirect methods for analysis of sulphate, based on precipitation with benzidine, have been proposed. Andersen[4] has determined sulphate by precipitating as the benzidine salt, dissolving the precipitate in a measured volume of dilute hydrochloric acid and measuring the absorbance at 250 mμ with a spectrophotometer.

In this way sulphate is determined in samples containing as little as 1 to 25 μg sulphur. The benzidine precipitate with sulphate has been digested with lead nitrate, the resulting lead sulphate being dissolved in an acetate buffer and the lead determined by amperometric titration. The working time and accuracy of this method is claimed to be comparable with that of the gravimetric procedure.[5] Sulphate can also be determined by direct conductometric titration with standard benzidine dihydrochloride using a 30% ethanol-aqueous solution and working in the pH range 4 to 7. Errors of about 1% may be expected in the 1-mg to 40-mg sulphur range, but the method has the advantage of being rapid.[6] Phosphate if present must be removed. Benzidine sulphate is stable between 70 and 156° and is best dried between 72 and 130° in the gravimetric determination.[7] *o*-Tolidine (3:3′-dimethylbenzidine) is not recommended for sulphate determination.

Two serious disadvantages of benzidine as a reagent for sulphate are the appreciable solubility of the sulphate and the non-selective nature of the precipitant. The solubility of the sulphate is 0·098 g per litre at 25° in neutral solution and rises to almost 10 times this value in 0·5*N* hydrochloric acid. Phosphate, molybdate, tungstate, iodate, ferricyanides and ferrocyanides and many cations are also precipitated by benzidine. However, it has the advantage over barium of not being affected by moderate amounts of chloride or nitrate.

Within the last ten years, efforts have been made to find other amines possessing advantages over benzidine as sulphate precipitants. A study of the solubility of the sulphate salts of substituted benzidines and related compounds by Belcher and Nutten[8] led to an investigation[9] of the effect of replacement of one amino group in benzidine by halogen. The sulphate solubilities of the four possible 4-amino-4′-halogenodiphenyls indicated that all of these amines would be superior to benzidine in removing sulphate from solution. Of these potential reagents, 4-amino-4′-chloro-1:1′-diphenyl is most suitable for sulphate determination as it has the highest hydrochloride solubility in water (*ca.* 0·35%) and the greatest sensitivity. Sulphate has been precipitated with this reagent at pH 1 to pH 2 with a twofold excess of reagent and a standing time of 20 to 30 minutes.[9,10] The sulphate in the precipitate is determined by suspending in water and titrating with standard caustic alkali. Oxidising agents, except hydrogen peroxide interfere, but halide, nitrate, acetate, citrate and tartrate do not interfere. Phosphate, tellurite, selenate and oxalate interfere through formation of insoluble salts. Oxalate and phosphate are removed by calcium. Zinc, copper and magnesium ions tend to form soluble complexes with the reagent but can be tolerated in tenfold amounts. Ferric, chromic, calcium and alkali metal ions do not interfere but aluminium tends to form an insoluble complex containing sulphate unless tartaric acid is present. The sensitivity of the reagents toward sulphate is superior to that of the barium ion but later work has shown that the solubility of the precipitate is higher (*ca.* 10 times) than had been reported initially. It is well known that the solubility of a substance is not a constant and it seems likely that the method of precipitating and drying the sulphate salt used by Belcher, Nutten and Stephen would lead to a lower observed solubility than that found for the sulphate precipitated from an aqueous solution under the conditions employed in an actual determination. This work[10] also indicates the necessity for care in the use of the reagent, in particular in adjusting the acid concentration of the test and reagent solutions before precipitation, and in the addition of the optimum excess of reagent (*cf.* Bengtsson[11]).* The addition of a little paper-pulp to the test solution before precipitation is advantageous and care is necessary in preparing the pulp-pad and in its actual use in filtering off the precipitate. Another disadvantage of the reagent is the low solubility of the amine hydrochloride in water, necessitating the use of large volumes of reagent solution. The possible use of other salts of this amine as reagents has been examined but none show any advantage over the hydrochloride.[10]

The reagent, which is undoubtedly the best of its class, is suitable for the micro determination of sulphur in organic compounds containing nitrogen,[12] in coal[13] and in rubber.[14] In each method the sulphate is determined titrimetrically. Jones and Letham[15] have determined 20 μg to 50 μg quantities of sulphate resulting from nucleic acid degradation, by precipitating the sulphate with a measured excess of this reagent and determining the excess in the solution spectrophotometrically. Absorbance measurements are made at 254 mμ. An essentially similar method has been applied to the determination of milligram amounts of sulphur in coal with good results.[16]

From a study of the sulphate solubilities of a range of substituted benzidines and other diamines, Belcher, Kapel and Nutten[17] concluded that co-planarity of the aromatic nucleii in diphenyls and linking of the amino and phenyl groups to each other in the *p*-positions are essential structural characteristics for low sulphate solubility. Electron microscopic studies of the sulphate salt of benzidine led Fischer and Sprague[18] to suggest that incompleteness of sulphate precipitation with benzidine is probably due to imperfect crystal formation and growth caused by a very tight surface adsorption of foreign ions on the growing crystallites.

Molybdate and tungstate

Benzidine hydrochloride will precipitate tungstate completely from neutral solution. The precipitate is insoluble in a solution of the reagent but will pass through a filter if washed with water. Precipitation from hot solution gives a coarser precipitate which is somewhat soluble in hot water and should not be filtered until the solution is cold. Von Knorre[19] showed that precipitation from the cold in the presence of a little sulphuric acid, resulted in good recovery of tungsten. The mixed benzidine tungstate and sulphate is ignited to tungsten trioxide at 800°. Phosphate, except in very small amounts, will interfere, as will molybdate unless the solution is about 0·5*N* to hydrochloric acid. At this acid concentration the tungstate becomes appreciably soluble so that benzidine and also diphenyline (2:4′-diamino-1:1′-diphenyl) is unsatisfactory for tungstate determination in the presence of molybdate.

Belcher and Nutten[20] have examined benzidine, diphenyline and several substituted benzidines and other aromatic amines as precipitants for tungstate in the presence of molybdate. Of the other amines investigated only 4:4′-diaminostilbene and 1-amino-4-*p*-aminophenylnapthalene give virtually quantitative precipitation of tungstate from 1*N* hydrochloric acid. Both molybdate and tungstate are quantitatively precipitated from neutral solution by these two reagents but tungstate is precipitated completely enough for most practical purposes from 0·7*N* hydrochloric acid while molybdate remains in solution. Oxidising agents interfere but ferric iron

* Since the period which this review is intended to cover ended, a short communication (R. Belcher and W. I. Stephen, *Analyt. Chim. Acta*, 1959, **20**, 197) has appeared refuting Bengtsson's main criticisms.

has no effect on diaminostilbene. However, the diaminophenylnaphthalene reagent is preferable as it is more readily obtained. Iron^{III}, chromium^{III}, copper^{II}, cadmium, aluminium, nickel, zinc, calcium, magnesium, sodium and potassium ions do not interfere.

The tungstate content of the precipitate formed with these reagents is variable. For benzidine, the tungstate content increases with decreasing pH and this has been attributed to *iso*-polytungstate formation.[21]

The tungstate of *o*-dianisidine (3:3′-dimethoxybenzidine), precipitated from diluted acetic acid solution contains 50·2% tungsten and 4·01% nitrogen.[22] The tungsten content of the precipitate is more reliably determined by ignition to tungsten trioxide before weighing. Molybate is completely removed from solutions neutral to methyl orange with *o*-dianisidine. Analyses of the precipitate dried at 80° suggests that it contains 1·792% molybdenum trioxide.[23] Since the solubilities of the sulphate and tungstate of all the 3:3′-disubstituted benzidines investigated are higher than those of the corresponding benzidine compounds, *o*-dianisidine would appear to be less attractive as a precipitant for tungstate or molybdate than benzidine, which itself is unsuitable for the separation of these anions. In view of the indeterminate nature of such tungstates or molybdates it is hardly advisable to weigh the precipitates and apply a factor except perhaps in a "rough" analysis.

Nardelli[24] has investigated the use of benzidine to precipitate the silicododecatungstate ion from hydrochloric or nitric acid solution. Pyrolysis of the white precipitate at 850° gives a composition ratio for the residue of silica to tungsten trioxide of 1 : 12·08.

Phosphates and polyphosphates

Orthophosphate is quantitatively precipitated from neutral or acetic acid solution by benzidine. Phosphate in the precipitate is best determined by titration with standard caustic alkali as in the sulphate determination. If the precipitate is to be weighed it can be washed free from excess benzidine with aqueous acetic acid or ethanol. Oxidants will interfere in the precipitation as will other anions forming insoluble salts under the conditions used for phosphate precipitation. Interference from sulphate can be overcome by dissolving out the benzidine phosphate from the mixed sulphate and phosphate precipitate with 0·1*N* hydrochloric acid. The phosphate salt with benzidine is reprecipitated by making the filtrate alkaline with aqueous ammonia. However, sulphate is more conveniently removed with barium chloride. Ferric iron must be reduced to the ferrous state and in the presence of aluminium, phosphate must be precipitated from acetic acid solution. Dimethyl hydrogen phosphate reacts quantitatively with benzidine dihydrochloride in solutions neutral to phenolphthalein. Trimethylphosphate is also precipitated but the precipitate is of indefinite composition and contains free benzidine.[25]

Hecht[26] has investigated the precipitation of trimetaphosphates and tetrametaphosphates with benzidine. With neither is precipitation quantitative nor can a separation be effected under the conditions he employed; but over 90% of the trimetaphosphate is precipitated at pH 5 while tetrametaphosphate is precipitated in somewhat better yield over a less restricted pH range (*ca.* 3–5). Graham's salt is precipitated by benzidine dihydrochloride from solutions of pH < 1 and can be separated from mono-, di-, tri- and tetrametaphosphates in this way. The use of various amines including benzidine, *o*-tolidine, *o*-dianisidine and 3:3′-diaminobenzidine as precipitants for straight chain polyphosphates and polymetaphosphates has been examined by Ebel *et al.*[27,28] By using acetic or hydrochloric acid solutions of the reagents and controlling the pH of precipitation, various separations and fractionations are possible. With the most suitable reagents over 90%, but never quantitative precipitation, is obtained from aqueous solutions. Trimetaphosphates and tetrametaphosphates can be separated. Quantitative but non-selective precipitation with benzidine is possible by the addition of alcohol to the reaction mixture.

Polythionates

Benzidine and *o*-tolidine have received attention as precipitants in the fractionation of complex mixtures of polythionic acids. Singer *et al.*[29] have discussed the formation and fractionation of such mixtures. They consider that mixtures of thiosulphate and arsenic^{III} in concentrated hydrochloric acid solution give polythionic acids containing from five up to at least ten sulphur atoms. The mixture is partially separated by fractional precipitation with benzidine (Bnz) or *o*-tolidine. In the highest fraction, Bnz $H_2S_nO_6$, n approaches 12 but in the main portion n has values from 6 to 9. The lowest sulphur-containing fraction ($n \leq 6$) and the highest fraction ($n > 10$) do not yield highly crystalline salts with benzidine as does the middle fraction. By fractional precipitation with benzidine they found that the method advanced by Goehring and Feldmann[30] for the preparation of hexathionic acid from thiosulphate and sulphur monochloride in the presence of concentrated hydrochloric acid, assumed to proceed as follows,

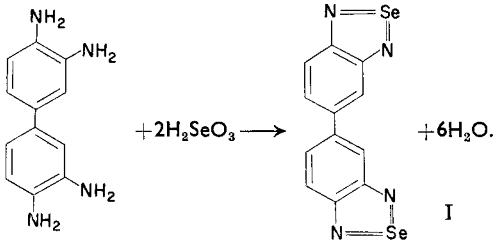
$$S_2Cl_2 + 2H_2O \rightarrow S_2O_2H_2 + 2HCl$$

$$S_2O_2H_2 + 2H_2S_2O_3 \rightarrow H_2S_6O_6 + 2H_2O,$$

actually gives a mixture of polythionates containing from 5 to 15 sulphur atoms. The overall composition of the mixture corresponds to that of hexathionic acid but this acid cannot be freed from other thionic acids by fractional precipitation with benzidine. Yanitskii and Patsauskas[31] found that precipitation of polythionates by benzidine from a reaction mixture similar to that above but using sulphur dichloride in place of the monochloride gave a fraction containing the salts of hepta-, octa-, and nonathionic acids. The preparation of a pure crystalline benzidine salt of octathionic acid has also been claimed.[32]

Miscellaneous salts

Gillis[33] has shown that the reaction between 3:3′-diaminobenzidine and selenite can be made the basis of a sensitive test for selenium. The final precipitate formed, however, is not a simple selenite but a dipiazselenole (I) formed by the following condensation reaction.



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Tellurium does not interfere but sulphurous acid and 1:2-diketones will interfere through formation of condensation products. Cheng[34] has determined selenium in the 50 μg region by extracting I into toluene and measuring the absorbance of the extract at 420 mμ. Oxidising agents, vanadate, iron^{III}, and copper^{II} ions interfere. The last two mentioned are masked by tartaric or oxalic acid. The method has been applied to the determination of selenium in sulphuric acid.[35]

Shiraeff[36] has used benzidine in the analysis of an ionic detergent, "Igepon T" (the sodium salt of N-methyl oleyl tauride). The salt of this sulphonic acid with benzidine may be weighed or dissolved in alcohol and titrated with standard alkali to phenolphthalein. Suggestions have been made for the extension of the method to other detergents containing sulphonic acid groups and giving insoluble salts with benzidine.[37] Anionic surface active agents are sometimes marketed as salts of nitrogen bases and precipitation of the insoluble benzidine salts of the anionic material leads to a convenient way of distinguishing between nitrogen in the anion and in the associated cation.[38] The benzidine salt is converted to the soluble sodium salt of the anion, leaving free benzidine suspended in the solution. Filtration and evaporation of the filtrate gives the sodium salt of the anionic part of the sample, on which a Kjeldahl nitrogen determination is made. Results suggest that nitrogen contents below 0·5% should be ignored by this method. Such nitrogen possibly arises from small amounts of cation carried down by the benzidine salt in the initial precipitation and from nitrogen in the benzidine dissolved in the final filtrate to be evaporated.

According to Duval,[39] the ferrocyanide and ferricyanide salts with benzidine should be ignited at temperatures exceeding 944° and 975°, respectively, if ferric oxide is to be used as the weighing form. $H_4Fe(CN)_6 \cdot 3Bnz$ would require drying below 52°. Iodate cannot be determined gravimetrically by precipitating with benzidine because of the thermal instability of the salt. Tellurate is removed from solution by benzidine and ignition of the precipitate gives the trioxide.[40]

PROCEDURES DEPENDING ON COLOUR REACTIONS

Many applications of the coloured products resulting from the oxidation of benzidine and related compounds have been recorded in recent years and progress has been made in the inprovememt of the colour stability on oxidation, and in the reversibility and sensitivity of some of the reactions. Improved tests in qualitative analysis and improved procedures in colorimetric and titrimetric analysis have resulted in some instances.

Qualitative tests

It is well known that haematin catalyses the oxidation of benzidine by hydrogen peroxide. Malowan[41] has discussed the effect of salts (Table I) on the reaction as used in clinical and forensic tests for blood. Excess hydrogen peroxide or the presence of ascorbic acid destroys the colour.

Tests carried out with diphenylamine, diphenylbenzidine and nitrodiphenylamine for the detection of the nitrate ion and nitramine explosives in sulphuric acid solution indicate that careful control of the acid concentration is essential.[42] These reagents do not distinguish between nitrate and nitramines, but a difference in rate of colour development is observed when diphenylamine is used to test for *cyclo*-trimethylenetrinitramine and *cyclo*-tetramethylenetetranitramine.

Robinson and West[44] have described a very sensitive test for orthophosphate. It is precipitated as the insoluble *o*-dianisidine phosphomolybdate which is then reduced to a "molybdenum blue" with hydrazine hydrate. In this way, 0·05 μg, at a concentration limit of 1 in 1,000,000, is detected. Apart from sulphide, which interferes through formation of a blue colour after the phosphomolybdate precipitation, the test is almost free from interference from other ions.

TABLE I. THE EFFECT OF SALTS ON THE HAEMATIN CATALYSED HYDROGEN PEROXIDE OXIDATION OF BENZIDINE.

None	Retarding	Intensifying
KCl, NaCl, NH_4Cl, $AlCl_3$, $HgCl_2$, K_2SO_4, $CaSO_4$, $Al_2(SO_4)_3$, $HgSO_4$ $Pb(OAc)_2$	$MgCl_2$, $CaCl_2$ $ZnCl_2$, $(NH_4)_2SO_4$, $MgSO_4$, $ZnSO_4$.	$AcONH_4$ $(NH_4)_2HPO_4$.

N-Phenylanthranilic acid has been recommended in place of benzidine in the detection of chlorate.[44] In the macro test, 1 ml of test solution is mixed with 0·1 ml of a 0·1 % reagent solution in alkali and 0·1 to 2 ml of concentrated sulphuric or hydrochloric acid is added. A violent raspberry colour at the interface in sulphuric or a pink colour in hydrochloric acid indicates chlorate in the absence of other oxidants. In the micro test, the test drop, taken to dryness, is treated with one drop of reagent solution and one drop of acid. In sulphuric acid, amounts of chlorate down to 1 μg at a dilution limit of 1 part in 1,000,000 and 0·016 μg at 1 in 1,250,000 are detected by the macro and micro methods respectively. In hydrochloric acid, 1·5 μg at a dilution limit of 1 in 670,000 by the macro method, and 0·08 μg at 1 in 250,000 by the micro method, are detected. There are few interferences from anions and cations apart from oxidants. Bismuth^{V} and nitrate interfere in sulphuric acid but not in hydrochloric acid. Perchlorate does not interfere.

A micro test for thallium in alkaline solution with benzidine and ferricyanide has been proposed by Feigl and Goldstein.[45] The test solution is treated with one drop of a 1 % ferricyanide solution and, after standing 30 minutes, with one drop of an acetic acid solution of benzidine. A blue colour indicates thallium. The least amount detected is 1·2 μg at a dilution limit of 1 in 100,000. Lead, if present must first be precipitated with ammonia. Lead in oils and varnishes may be detected with benzidine, after precipitation with alkali and oxidation with bromine water.

Naphthidine and 3:3′-dimethylnaphthidine, in the presence of ferricyanide, have been examined as reagents for the detection of zinc.[46] The latter amine is ten times as sensitive as the former and is less affected by changes in acid concentration. The reagent consists of one part of a 5 % solution of potassium ferricyanide mixed with two parts of a saturated solution of naphthidine or dimethylnaphthidine dihydrochlorides. The identification limits on a spot tile for one drop each of test and reagent solutions are 1 μg and 0·1 μg at dilution limits of 1 in 50,000 and 1 in 500,000 respectively. Metal ions giving sufficiently insoluble ferrocyanides will interfere with this test.

Dimethylnaphthidine gives sensitive colour reactions with other oxidants such as dichromate, permanganate, and vanadate. A 1% solution of this amine in acetic acid provides a sensitive test for vanadate.[47] On a spot tile the limit of identification is 0·1 μg at a concentration limit of 1 in 500,000. Other oxidising agents must be absent. Of other benzidine-type reagents examined only 2:7-diaminofluorene is as sensitive towards vanadate, but the colour produced by this reagent, unlike that with dimethylnaphthidine, fades rapidly after development.

The 3′-sulphonic and 3:3′-disulphonic acids of benzidine have been examined in their reactions with oxidants.[48] The disulphonic acid only reacts with more powerful oxidants like cerium^{IV} and dichromate and is less sensitive than the monosulphonic acid. A specific test of moderate sensitivity for copper^{II} in the presence of thiocyanate has been described using the monosulphonic acid.[49]

Cullinane and Chard[50] have investigated the reactions of 2:7-diaminodiphenylene oxide as a spot test reagent and conclude that it may replace benzidine in several spot tests. The sensitivity is generally higher than for the corresponding benzidine reaction and as it is subject to the same interferences, these are overcome as in the benzidine tests. This conclusion has been confirmed by Belcher and Nutten[51] who compared the sensitivities of benzidine and various substituted benzidines including diaminodiphenylene oxide in neutral and in 0·05*N* hydrochloric acid solutions. They found that for most of the oxidants tested, the last mentioned reagent is about ten times as sensitive as benzidine or the other substituted derivatives examined.

Some new 3:3′-disubstituted naphthidines have been prepared[52] and properties of analytical interest, examined.[53] Replacement of methyl groups in 3:3′-dimethylnaphthidine by ethyl, *n*-propyl or *iso*propyl groups does not alter the sensitivity or colour reaction of the amine with oxidants. On replacement by sulphonic acid groups none of the common oxidants used except iron^{III} give sensitive colour reactions in solutions lower than 2*M* in sulphuric or hydrochloric acid, but a red–violet colour the stability of which increases with increase in acid concentration is obtained in stronger acid solutions. Phenyl groups result in a slight decrease in sensitivity and a colour change to violet instead of purple-red. Substitution by nitro groups gives a yellow product unaffected by oxidants, while by contrast the diaminonaphthidine gives only transient colours with oxidants and is unstable in air. Dimethoxynaphthidine gives a greenish-blue colour of stability intermediate between naphthidine and 3:3′-dialkylnaphthidines but more comparable to the latter in sensitivity towards oxidants.

Feigl and Jungreis[54] have devised a test of micro sensitivity for the detection of mono- and di-N-alkylanilines. The Duff formylation reaction is used to convert the substituted aniline to the corresponding *p*-benzaldehyde. If certain phenols are present they will also be formylated and so must be removed before the test is applied.

Colorimetric methods

The high sensitivities of benzidine and some nuclear-substituted and N-substituted derivatives have resulted in their application in colorimetric and absorptiometric methods of analysis. One of the major drawbacks to most of these reagents is colour instability. This has stimulated interest in the search for derivatives giving more stable colours on oxidation and for improved procedures for the reagents more commonly employed. Substitution *o*- to the amino groups or substitution of the hydrogens on the amino groups results in more stable colours on oxidation but this can be associated with a decrease in rate of colour development and sensitivity suggesting that a balance must be sought between increased colour stability through substitution and decreased rate of reaction, in the most favourable reagents. The effect of N-methyl substitution in benzidine and *o*-tolidine on the sensitivity of the resulting reagents to oxidants has been attributed to steric factors.[55] Compared with the unsubstituted compounds, methyl, ortho to an N-methyl group reduces the sensitivity whereas in the same position to an unsubstituted amino-group, it raises the sensitivity. Suitable N- or *o*- substituents may shield the sensitive oxidised groups increasing colour stability in favourable cases, but when present together may result in "over-crowding" around the nitrogen with adverse effects on the reaction with oxidants.

Benzidine and *o*-tolidine have achieved widespread use in the colorimetric determination of chlorine in water. *o*-Tolidine gives a more stable colour than benzidine but it is customary to employ artificial colour standards because of the colour instability of both reagents, and strict working conditions are necessary. A mixture, in tablet form, containing *o*-tolidine has been patented for this determination.[56]

Kul'berg and Borzova[57] have investigated the use of N:N'-tetramethylbenzidine as an alternative reagent in the determination of chlorine in water. This reagent gives a clear yellow to orange colour on oxidation and the improved colour stability permits more accurate determination of chlorine. The water sample (100 ml) is treated with a 1% solution of the reagent (0·1 ml) in 5% hydrochloric acid and set aside for 10 minutes. The absorbance is read at 470 mμ. Belcher, Nutten and Stephen[58] have made a comparison between the sensitivities of the reactions of several nuclear and N:N'-substituted benzidines including N:N'-tetramethylbenzidine, naphthidine and 3:3'-dimethylnaphthidine, with chlorine in water. Dimethylnaphthidine is more sensitive than any of the other reagents tested and can be used in the absorptiometric determination of chlorine in water. Beer's law is obeyed over a satisfactory concentration range, the colour develops quickly (5 minutes) and is stable for at least 15 to 20 minutes. Acetate ions and mineral acids interfere.

N:N'-diphenylbenzidine finds new applications in the determination of vanadium. Eeckhout and Weynants[59] have made the yellow colour produced by orthovanadate with this reagent the basis of a spectrophotometric method for vanadium. Beer's law is obeyed in the concentration range 1 to 10 μg per ml. The colour intensity depends on pH, amount of reagent, time of colour development, temperature and the presence of other ions, suggesting that considerable experience with such a method would be necessary for satisfactory results. Wrightson[60] has shown that vanadium in petroleum oils, oxidised to vanadate with bromine water, is determined with this reagent in samples containing 0·01 to 0·08 mg V_2O_5. The colour is developed in an aqueous solution containing 50% phosphoric acid (s.g. 1·71) and the absorbance is measured 15 minutes later at 575 mμ. A method based on the colour produced by diphenylamine-4-sulphonic acid on oxidation by vanadate is used for the analysis of vanadium in steel. An attempt is made to correct for excess reagent by measuring the absorbance of the oxidised reagent at 562 mμ and again after reduction of the coloured form with ferrous iron; the difference in the absorbances is proportional to the vanadium content.[61] Milner and Nall[62] have used 3:3′-dimethylnaphthidine for the micro determination of vanadium in ferrous alloys. It is superior to diphenylamine in this determination. Scholes[63] found in his investigation of the possible use of dimethylnaphthidine for the macro colorimetric determination of vanadium in steel, that Beer's Law is obeyed in the concentration range 12·5 to 250 μg vanadium per 50 ml, and that maximum colour intensity is reached in 5 to 10 minutes, remaining constant for about 20 minutes. A mixture consisting of 1 part each of sulphuric and phosphoric acids and 8 parts of water is the most suitable medium for colour development and stability. In the presence of small amounts of chromium, special precautions are necessary in using these reagents.

Iridium is determined photometrically by making use of the deep purple colour resulting from the reaction of *o*-dianisidine with the chloroiridate anion.[64] Other platinum metals and oxidants must be removed before the colour is developed in a strongly acid solution containing acetic acid and sodium acetate.

A detailed study of the use of *o*-tolidine in the absorptiometric determination of gold^{III}, and hence the thickness of electrodeposited gold, has been made.[65] Commercial *o*-tolidine is recrystallised three times from 2*N* sulphuric acid and the reagent is used in strong sulphuric acid solution. Maximum colour development takes 1 to 3 minutes and the colour is stable for 10 to 30 minutes. The absorbance is measured at 437 mμ.

Jones and Pridham[66] have shown that the orange–yellow colour produced by heating a sugar in glacial acetic acid with benzidine can be used to determine the sugar. In this way many monosaccharides and methylated derivatives and a few disaccharides, *e.g.* sucrose, are determined.

The acceleration of the oxidation of benzidine and other amines giving colour reactions by peroxides, in the presence of various organophosphorus compounds including some nerve gases and insecticides, and of certain carboxylic acid anhydrides, *e.g.* phthalic acid anhydride, has been used in the determination of such organic compounds colorimetrically.[67] The organic substance is thought to oxidise to a peroxide which then oxidises the benzidine.

The oxidation potential of a cobaltic complex ion depends to some extent on the ligand. This makes possible the indirect determination of certain ligands colorimetrically by measuring the colour intensity on addition of a redox indicator such as benzidine or a substituted benzidine.[68] 1:2-Bis(methylthio)ethane, dibutylamine, and N:N-diethylethan-2-ol are determined in this way, but not ethylene-1:2-diamine and cyanide. The method could probably be extended to other ligands and, where the oxidation potentials of the complex ions were sufficiently far apart, selective methods devised for mixtures of two or more ligands.

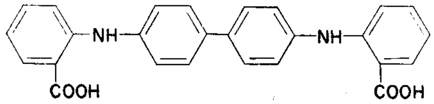
Titrimetric analysis

The period under review has produced improved procedures, new uses for existing indicators and several new indicators in redox titrimetry. Several short reviews[69,70,71] have appeared dealing with some of these developments. Various attempts have been made to study the redox properties of some indicators.

Eggertsen and Weiss[72] carried out a polarographic study of the relative oxidation potentials of benzidine and a number of substituted benzidines at pH 9·4 using a 1 : 1 water-acetone solvent mixture and a stationary platinum indicating electrode. In conjunction with absorbance measurements, they found that the amines with the lowest half-wave potentials give the highest colour intensity on oxidation and that the potentials are increased by substituents in the ring, particularly if they are electron attracting groups. Compounds with substituents ortho to the linkage between the two aromatic rings have relatively high potentials and only give slight oxidation to coloured products.[73]

Crawford and Bishop[74] studied the oxidation of *o*-dianisidine by direct potentiometric titration with cerium^{IV} and obtained formal potentials under certain experimental conditions. They discussed some of the difficulties associated with such work, the most important being the instability of the oxidised form of the reagent leading to indeterminate side reactions. Earlier, Kolthoff and Sarver[2] had commented similarly in their study of the oxidation of diphenylamine and diphenylbenzidine. The low solubility of most benzidine type compounds in aqueous systems is also a drawback, since it may delay attainment of equilibrium, which, coupled with the instability of the oxidised substance can upset the measurement of potentials.

From a study of the oxidation of N-phenyl-, and N-*o*-, N-*m*-, and N-*p*-tolylanthranilic acids, Lederer and Ward[75] showed that only the first two mentioned were of use as reversible indicators. The N-*m*-tolyl compound gives only a transient colour change and the N-*p*-compound no colour change, thus indicating that oxidation proceeds through the phenyl or tolyl nucleus *e.g.* to N:N′-di-(*o*-carboxyphenyl)-benzidine (II) from N-phenylanthranilic acid. From potentiometric studies in molar sulphuric acid, they obtained a formal oxidation potential of 1·09 *V* for N-phenylanthranilic acid, in good agreement with the value (1·08 *V*) obtained by Syrokomski and Stiepin;[76] and 1·11 *V* for N-*o*-tolylanthranilic acids. However, the actual colour changes were estimated to lie between 0·94 and 1·00 *V* and 0·81 and 1·01 *V* respectively, *i.e.* below the formal potential values in both cases.



II

It is evident from the work discussed that at present formal potentials of indicators of the benzidine and diphenylamine type are not always satisfactory, and may be of little value in the chemical systems of interest to the analyst. This will be particularly true if the indicator solubility is low and the oxidised form unstable. Efforts have been made to surmount this difficulty through the determination of the potential at which an indicator first begins to change colour visually as the oxidation potential is increased (lower transition potential) and less frequently the potential at which the colour is fully developed (upper transition potential). Such potential measurements are entirely empirical and are carried out in the redox systems in which the indicator is or might be of use. The values obtained give some indication of trends in redox potentials with change of environment *e.g.* varying acid concentration, and also give a fairly narrow potential range (*ca.* 0·15*V*) or transition interval within which the formal potential associated with the colour change of the indicator would be found under suitable experimental conditions.

Stockdale[77] compared the transition potentials of diphenylamine, N:N′-diphenylbenzidine and diphenylamine-4-sulphonic acid in the ferrous iron titration with dichromate in molar sulphuric acid. Diphenylamine and N:N′-diphenylbenzidine are considered to have the formal oxidation potential (0·76*V*) which would be expected, but Stockdale found that while the lower transition potentials are the same, the upper potentials are 0·86*V* and 0·94*V* respectively. He suggested that the higher value and hence the greater transition interval of the latter is due to its low solubility. In support, the transition intervals of a series of 3:3′-disubstituted naphthidines suggest that the lower the solubility the greater the transition interval.[52] This interval is 0·14*V* for 3:3′-dimethylnaphthidine in molar sulphuric acid but only 0·05*V* in a soluble medium consisting of equal parts by volume, of acetic and 4*M* sulphuric acids. Such results suggest that an indicator having an oxidation potential lower than required by the potential at the equivalence point in a titration may still function satisfactorily if its solubility is sufficiently low. Transition potentials for a number of indicators are recorded in Table II.

When dichromate is titrated with iron^{II} in molar sulphuric acid the equivalence point lies between 1·22*V* and 0·85*V* and in the reverse titration between 0·85*V* and 1·0*V*,[78] so that N-phenylanthranilic acid should be a satisfactory indicator in either titration, contrary to what would be expected from its formal potential, which is higher than that of ferroïn (1·06*V*). (The oxidation potential of ferroïn is generally considered to be too high for its use in the titration of iron^{II} with dichromate in molar acid). The transition interval which may be compared with the colour change pH range of an acid base indicator, could be of considerable practical value if known for redox indicators under different titration conditions.

Stockdale concluded from his study of the three indicators referred to above, that it does not make any difference to the numerical results which indicator is used, or whether phosphoric acid is present or not, in the titration of 0·1*N* solutions of iron^{II} with dichromate. The end-point, taken when maximum colour of the indicator has developed, must be reached quickly, probably to prevent irreversible oxidation and to reduce coagulation of the less soluble indicators. Irreversible oxidation of the indicator is more important in the reverse titration in which it is advisable to complete the titration without delay after addition of the indicator, particularly if diphenylamine sulphonic acid is used, as it is more susceptible than either diphenylamine or diphenylbenzidine to decomposition under such conditions.

Adams and Hammaker[79] recommended N:N′-tetramethylbenzidine and its 3-sulphonic acid derivative as indicators in the titration of iron^{II} with cerium^{IV}. Development of colour is slow, even at temperatures approaching 100° at which the oxidised forms are stable, thus promoting a tendency towards over-titration.[80] N:N′-tetraethylbenzidine is even less satisfactory for the same reason.

Uranium^{IV} is determined by titration with cerium^{IV} at room temperature using diphenylamine, diphenylbenzidine, diphenylamine-4-sulphonic acid or N-phenylanthranilic acid as internal indicator.[81] For every 50 ml of solution 3 to 5 ml of 85% orthophosphoric acid are added. By adding a large excess of phosphoric acid to complex uranium^{IV}, iron^{II} is titrated in the same solution with cerium^{IV} using

TABLE II. TRANSITION POTENTIALS (IN VOLTS VERSUS THE NORMAL HYDROGEN ELECTRODE AT 18 OR 20°) OF VARIOUS INDICATORS IN MOLAR SULPHURIC ACID.

Indicator	Transition potential, *V*		Redox system	Ref.
	Lower	Upper		
diphenylamine	0·76	0·86	A	77
diphenylamine-4-sulphonic acid	0·83	0·91	A	77,113
N:N′-diphenylbenzidine	0·76	0·94	A	77
N:N′-tetramethylbenzidine	0·86	—	B	79
N:N′-tetramethylbenzidine-3-sulphonic acid	0·88	—	B	79
naphthidine	0·79	0·83	A, B	53,113
3:3′-dimethylnaphthidine	0·71	0·85	A, B	53,113
3:3′-diethylnaphthidine	0·72	0·90	A, B	53
3:3′-di-*n*-propylnaphthidine	0·72	0·90	A, B	53
3:3′-di-*iso*-propylnaphthidine	0·75	0·91	A, B	53
3:3′-diphenylnaphthidine	0·76	0·94	A, B	53
3:3′-dimethoxynaphthidine	0·74	0·88	B	53
naphthidine-3 : 3′-disulphonic acid	0·83(a) 0·86(b)	0·91	A, B	53
3-bromobenzidine	0·90	—	A	114
3:3′-dibromobenzidine	0·94	—	A	114
N-phenylanthranilic acid	0·94	1·00	B	75
N-*o*-tolylanthranilic acid	0·81	0·11	B	75

A: Fe^{2+}–Fe^{3+} and $Cr_2O_7^{2-}$–Cr^{3+} system;
B: Fe^{2+}–Fe^{3+} and Ce^{4+}–Ce^{3+} system.
(a) $Cr_2O_7^{2-}$ as oxidant
(b) Ce^{4+} as oxidant.

diphenylamine as indicator.[82] Molybdenum^{V} and titanium^{III} are determined in the same way and will interfere in the determination of iron if present.

Gopala Rao and Sastri[83] have found that interference from oxalic acid in the determination of hydroquinone by titration with cerium^{IV} is prevented by sodium fluoride. Diphenylbenzidine and N-phenylanthranilic acid are suitable indicators. Replacement of cerium by dichromate is unsatisfactory.

Unlike most indicators of its class, N-phenylanthranilic acid is satisfactory in strong acid redox systems. As a result it has been used successfully in titrations involving vanadate as oxidant in sulphuric acid solution *e.g.* in the titration of uranium^{IV},[84] hypophosphite and phosphite.[85] Naphthidine-3:3′-disulphonic acid and probably also α-naphthylamine-β-sulphonic acid could replace phenylanthranilic acid in such titrations.

The use of a redox indicator of the benzidine type in the ferrocyanide-ferricyanide system depends on the formation of an insoluble metal ferrocyanide. Removal of the ferrocyanide from the solution raises the oxidation potential of the system. Above the transition potential the indicator will be oxidised, or reduced if the reverse procedure is used. Thus, if ferrocyanide in the presence of a little ferricyanide and a suitable redox indicator is titrated with zinc, sparingly soluble $K_2Zn_3[Fe(CN)_6]_2$ is precipitated and at the end-point all the ferrocyanide, except the small amount resulting from dissociation of the zinc salt is removed from the solution. At this point, the oxidation potential of the system increases sharply and the indicator will change colour. *o*-Dianisidine was shown to be a satisfactory indicator in this titration by Frost[86] and later by Crawford and Bishop.[73] Belcher and Nutten[87] compared naphthidine, *o*-dianisidine and *p*-ethoxychrysoïdine recommended by Tyler,[88] in this titration. They consider that naphthidine is superior to the others giving a more distinct colour change. Benzidine, 3-methylbenzidine and 3:3′-diethylbenzidine give better end-points than *p*-ethoxychrysoïdine or diphenylbenzidine, the first internal indicator used in this redox system, but inferior to *o*-dianisidine. The zinc solution to be titrated is best treated with an excess of standard ferrocyanide and the excess titrated with standard zinc solution in the presence of the indicator and a little ferricyanide. Milner[89] has shown that with naphthidine as internal indicator, suitable procedures for the determination of zinc in various non ferrous alloys and rubber ashes, can be devised. Zinc in aluminium alloys, aluminium bronzes, and white metals is separated from interfering elements by hydrogen sulphide. With tin bronzes, separation is best effected with 8-hydroxyquinoline. Zinc is separated from rubber ashes by digesting with hydrochloric acid, then making ammoniacal and filtering. Later, Belcher, Nutten and Stephen[90] found that 3:3′-dimethylnaphthidine was a more sensitive indicator and the colour more stable than the naphthidine or *o*-dianisidine colour. As good colour changes are obtained in titrations with 0·001*M* zinc solutions using this indicator as can be obtained with 0·01*M* zinc solutions using naphthidine. It is the best indicator available for the titration of very dilute solutions of metal ions with ferrocyanide. Cadmium, gallium and calcium can be titrated directly with ferrocyanide and indium by the back titration used in the zinc determination.[91] Naphthidine, *o*-dianisidine and N:N′-diphenylbenzidine are less satisfactory than 3:3′-dimethylnaphthidine in these titrations.

Brown and Hayes[92] have extended the use of 3:3′-dimethylnaphthidine by employing it with ferrocyanide and ferricyanide as the indicator system in the complexometric titration of zinc. Titration of the system containing zinc ferrocyanide and ferricyanide and indicator removes zinc from the zinc ferrocyanide precipitate, thus lowering the oxidation potential and causing the indicator colour to fade and finally discharge at the end-point. One disadvantage is that the titrant must be added very slowly near the end-point. For this reason Flaschka and Franschitz[93] recommend the addition of excess ethylenediamine-N:N′-tetra-acetic acid and back titration with zinc. In this way manganese^{II},[94] zinc, cadmium, iron^{III}, lead^{II},[93] nickel and copper[95] are determined. The titration of tin in copper alloys,[96] the rare earths,[97] and the micro titration of aluminium,[98] and gallium[99] is also possible. Benzidine has been used in such complexometric titrations[95] and it is likely that *o*-dianisidine, *o*-tolidine, naphthidine and other such indicators could also be employed.

Benzidine has been recommended as indicator in the titration of silver with iodide[100] and with bromide.[101] More recently a number of papers have appeared in which benzidine and substituted benzidines have been used in titrations of a similar nature. The indicator reaction is thought to involve both oxidation and absorption on the precipitated halide. In the methods referred to above, benzidine acetate with copper acetate and benzidine sulphate with copper nitrate were used in the titrations with bromide and iodide respectively. The colour changes are from yellow to green (bromide) and from greenish-yellow to greyish-blue (iodide). The reaction may proceed as follows (X = halide):

$$2KX + 2Cu(NO_3)_2 + BnzH_2SO_4 \rightarrow 2CuBnzX_2 + 2K_2SO_4 + 2HNO_3$$

$$2KX + 2Cu(NO_3)_2 \rightarrow CuX_2 + 2KNO_3$$

$$2CuX_2 \rightarrow Cu_2X_2 + X_2$$

The halogen produced oxidises the indicator. When precipitation is complete both the metal benzidine complex and the oxidised indicator are absorbed on the precipitate. Chloride, as expected from the reaction scheme, cannot be determined in this way, nor is this titration reversible; but with iron^{III} in place of copper^{II} it may be determined by titration with silver or used in the titration of silver in conjunction with benzidine, *o*-tolidine or *o*-dianisidine.[102] In such a system the iron^{III} may well act directly as indicator oxidant. The oxidised indicator is then adsorbed on or desorbed from the precipitate at the end-point as in the method of Lang and Messinger[103] in which chlorides and bromides are successfully titrated in 0·5*N* to 5*N* sulphuric acid solutions using diphenylbenzidine violet (oxidised diphenylamine) as adsorption indicator. Silver is titrated with iodide using gold^{III} and *o*-dianisidine as indicator in solutions up to 5·5*N* in nitric acid[104] or with iodide or bromide in the presence of a little acid using iron^{III} instead of gold^{III}.[105] The latter titration is reversible and iodide or bromide is titrated with silver ions in strong nitric acid solution.[106] The copper^{II}-*o*-tolidine system is said to be more sensitive and to give more reproducible results than copper^{II}-benzidine in the determination of silver with iodide and bromide.[107] Mercury^{I} is determined reversibly with bromide in slightly acid solution using iron^{III} and benzidine, *o*-tolidine or *o*-dianisidine as indicator.[108] For the titration of chloride or bromide with mercury^{I}, Matsuo[109] claims that the iron^{III}-*o*-dianisidine system is preferable. When a mixture of iodide and bromide is titrated with silver there are two colour changes; the first corresponds to complete precipitation of iodide and the second to bromide in 0·001*N* to 0·01*N* nitric acid solutions containing the iron^{III}-benzidine indicator system.[110] Benzidine, 3-methylbenzidine and 3:3′-diethylbenzidine have been compared in the titration of silver with bromide and iodide in the presence of copper^{II}.[111] All three indicators give sharp end-points which are superior to those obtained when conventional adsorption indicators are used as originally claimed by Sierra and Burriel. The resistance of the iron^{III}-benzidine, iron^{III}-*o*-tolidine or iron^{III}-*o*-dianisidine systems to nitric acid is greater than that of phenosafranine on silver chloride.[102] Careful control of the amount of indicator used in these titrations is necessary. Halogen and silver determinations using such oxidation-adsorption systems have been discussed by Cañavate.[106] Further comparison of these newer titrimetric procedures with established methods of analysis seems desirable in order to be able to assess them properly.

Willard and Manalo,[112] from a study of derivatives of diphenylamine as indicators in direct titrations with hypobromite, found that satisfactory end-points could be obtained with diphenylamine sulphonic acid and with 2-aminodiphenylamine-4-sulphonic acid. The former behaves reversibly but the latter which is destroyed at the end-point gives a more distinct colour change and a smaller blank value.

CONCLUSION

There may still be room for improvement of reagents of the benzidine class as precipitants and as colorimetric reagents. As a precipitant for anions, in the benzidine type molecule, a balance is necessary between the solubility of the reagent and the insolubility of the salt of the reagent to be precipitated. So far there are no data available to enable the analytical chemist to ascertain whether the best balance has already been achieved or whether further improvements are possible in the design of the most suitable reagent. Studies of a more fundamental nature on the physical and chemical phenomena involved in such precipitation reactions with available reagents, and investigation of the structure of the precipitates might assist towards this end. Benzidines and diphenylamines at present available are nearly all subject to the influence of many variables; and the colour on oxidation is either slow in developing or is insufficiently stable when developed to allow the use of these reagents in precise macro determinations. The effect of *o*- and N-methyl groups on the rate of colour development and on the stability has been studied qualitatively but little attention has been given to other groups which might be used.

In discussing indicators, several points which require investigation or re-investigation, notably in connection with the determination of oxidation potentials, have been mentioned.

Zusammenfassung—Es wird ein Überblick über die analytischen Anwendungen des Benzidins und des Diphenylamins sowie ihrer Derivate als Fällungsmittel, Nachweisreagenzien, zur kolorimetrischen Bestimmung von Oxydanzien und als Indikatoren in der Massanalyse gegeben. Es ist die Zeit von 1946 bis 1958 berücksichtigt.

Résumé—L'auteur a fait une étude des applications analytiques de la benzidine, de la diphenylamine et de leurs dérivés, comme précipitants, pour déceler et doser colorimétriquement des oxydants, et comme indicateurs dans l'analyse titrimétrique. Cette étude couvre la période: début 1946-fin 1958.

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DIREKTE KOMPLEXOMETRISCHE EISENBESTIMMUNG MIT XYLENOLORANGE ALS INDIKATOR

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Zusammenfassung—Es wurde eine komplexometrische Eisen(III)-Bestimmung ausgearbeitet, die auf einem neuen Indikationsprinzip beruht. Als Indikator wurde Xylenolorange benützt, das mit Eisen(III) einen violettblau gefärbten jedoch robusten Komplex bildet. Durch Zugabe von Eisen(II) zu der titrierten Lösung wird die übliche Verdrängungsreaktion im Endpunkte der Titration durch Redox-Vorgang ersetzt und dadurch eine sehr scharfe Indikation erzielt. Das ausgearbeitete Verfahren ermöglicht eine genaue und sehr selektive Eisen(III)-Bestimmung. Nur Wismuth, dreiwertiges Thallium und grössere Mengen von Kupfer müssen vor der Titration beseitigt werden.

Die theoretische Grundlage der komplexometrischen Eisen(III)-Bestimmung ist durch die aussergewöhnlich hohe Stabilitätskonstante des Eisen(III)-Aethylendiamintetraacetates $K_{(\mathrm{FeY})^-} = 10^{25,1}$; vgl.[1]) gegeben. Dieser hohe Wert kann allerdings nicht voll ausgenützt werden, weil die Titration wegen der leichten Hydrolyse der Eisen(III)-Salze einerseits und der Bildung viel weniger fester Hydroxo-Komplexonate anderseits, nur auf das saure Gebiet beschränkt ist. Die untere Grenze der praktischen Anwendbarkeit der Bestimmung möge theoretisch bei pH = 1 liegen, wo die pH-abhängige Bildungskonstante $(\mathrm{K}_{(\mathrm{FeY})^-} \cdot \alpha_{\mathrm{H}}^{-1} = 10^{7,9})$,[2] etwa mit der Konstante des Bariumkomplexonates $(\mathrm{K}_{(\mathrm{BaY})^{2-}} = 10^{7,8})$ gerade noch vergleichbar ist. Für die selektive Eisenbestimmung liegen die Verhältnisse auch günstig vor, denn die Bildungskonstanten der meisten in Frage kommenden Begleitmetalle sind genügend niedriger als die des Eisens. Das gilt besonders auch für Aluminium. Obwohl jedoch die theoretischen Voraussetzungen erfüllt sind und eine ganze Reihe von komplexometrischen Verfahren für die Eisenbestimmung auch beschrieben wurde (vgl.[3]), kann dieses Problem immer noch nicht als endgültig gelöst betrachtet werden.[4] Der Grund dafür liegt in den Indikatoren.

Wie wir schon früher gezeigt haben,[2] ist die passende Empfindlichkeit des Indikators ganz allgemein nicht nur für das Gelingen der Titration, sondern auch für die Ausschaltung der Interferenz anderer Metallionen von ausschlaggebender Bedeutung. Beim Eisen ist die Situation soweit paradox, dass es kaum ein anderes Metallion gibt, das so viel Farbreaktionen wie dieses zeigt und es sehr schwer ist, unter diesen eine für die Komplexometrie in aller Hinsichtem geeignete zu finden. Einmal stimmt es mit den Farbeigenschaften oder mit der Empfindlichkeit nicht, das andere Mal sind die Komplexe des Indikators, in der Uebereinstimmung mit der ganz allgemeinen Neigung des Eisen(III) zu robust, so dass die Titration erst in der Hitze oder überhaupt nicht möglich ist. Manchmal treten noch andere Störerscheinungen zum Vorschein, wie z.B. die Oxydation des Indikators, die zu den Verlusten an Eisen(III) und dadurch zu fehlerhaften Resultaten führt. Den letztgenannten Nachteil haben ganz allgemein die o-Diphenole, bzw. Chromotropsäure und ihre Derivate, die sehr häufig und gewöhnlich in verhältnissmässig hohen Konzentrationen als Indikatoren Verwendung finden. Wie ersichtlich, ist es wünschenswert, neue und bessere Indikatoren für die komplexometrische Eisenbestimmung zu sauchen.

Wir haben schon in den ersten Mitteilungen über Xylenolorange die schöne Reaktion mit Eisen(III) teilweise beschrieben.[5,6] Die gelbe Farbe des Indikators geht in eine intensiv blauviolette über. Die Empfindlichkeit ist bei pH 1–3 in 10 ml Volumen (Makroreagenzglas) und bei der Zimmertemperatur durch das pD = 4,6 gegeben, ist also sehr hoch. Bei der erhöhten Temperatur wird sie noch gesteigert; bei 60–70°C besteht sogar in $0{,}5N\text{-}HNO_3$ immer noch das pD = 4. Bei dem Versuch, Eisen mit Hilfe dieses Indikators zu bestimmen, stellte es sich jedoch heraus, dass der Indikatorkomplex zu robust ist. Die Titration erschien selbst in der Hitze unerträglich schleppend. Deswegen wurde bisher nur die indirekte komplexometrische Eisenbestimmung mit Xylenolorange als Indikator beschrieben.[7]

Vor kurzer Zeit haben wir unserer Meinung nach eine sehr interessante Erscheinung beobachtet: Wird zu einer sauren Lösung, die Eisen(III) und Xylenolorange enthält, etwas Eisen(II)-Salz (z.B. Ferrosulfat) zugegeben, so geht die Titration mit dem Aethylendiamintetraacetat schon bei der Zimmertemperatur überraschend glatt, mit scharfem Umschlag vonstatten. Benützt man noch eine inerte Atmosphäre im Titrationskolben, werden die Ergebnisse für Eisen(III) sehr genau. Selbst ein sehr grosser Ueberschuss an Eisen(II) (z.B. 10 g Ferrosulfat in 100 ml) stört die Titration nicht. Die Bildungskonstante des Eisen(II)-Komplexonates ($K_{(\mathrm{FeY})^{2-}} = 10^{14,3}$) ist nämlich viel niedriger als die des Eisen(III), ferner reagiert der Indikator unter den erwähnten Bedingungen mit Eisen(II) nicht und seine Empfinlichkeit zu Eisen(III) passt offensichtlich gerade (vgl.[2]). Die „katalytische" Beschleunigung der Farbumschlagsreaktion durch Eisen(II) kann wie folgt verstanden werden:

Bei der Titration reiner Eisen(III)-Lösung, setzt, nachdem alles freie Eisen(III) durch Komplexon gebunden wurde (1):

$$\mathrm{Fe^{III} + Y = Fe^{III}Y} \tag{1}$$

die übliche Verdrängungsreaktion (2) ein:

$$\underset{\text{blau}}{\mathrm{Fe^{III}Xo}} + \mathrm{Y} = \mathrm{Fe^{III}Y} + \underset{\text{gelb}}{\mathrm{Xo}} \tag{2}$$

(Die elektrischen Ladungen und die Verschiedenheit der Dissoziationsformen sind hier und auch im Weiteren vernachlässigt). Wie schon erwähnt, verläuft diese Reaktion (2) zu langsam, so dass sie für die komplexometrische Eisenbestimmung unbrauchbar ist. Im Gemisch reagiert mit Komplexon sowohl Eisen(III), als auch Eisen(II) (3):

$$\mathrm{Fe^{II} + Y = Fe^{II}Y} \tag{3}$$

Doch sind die Verhältnisse in jedem Augenblick der Titration durch die Gleichung (4)

$$[\mathrm{Fe^{III}Y}] : [\mathrm{Fe^{II}Y}] = [\mathrm{Fe^{III}}] \cdot K_{(\mathrm{Fe^{III}Y})} : [\mathrm{Fe^{II}}] \cdot K_{(\mathrm{Fe^{II}Y})} \quad \text{gegeben} \tag{4}$$

Hieraus folgt, dass erst, dann wenn alles freie Eisen(III) gebunden ist ($[\mathrm{Fe^{III}}] \rightarrow 0$, also praktisch im Endpunkte der Eisen(III)-Titration, die Konzentration des $\mathrm{Fe^{II}Y}$ beträchtlicher ansteigen kann. Infolgedessen tritt nun die Reaktion (5) ein:

$$^{*}\underset{\text{blau}}{\mathrm{Fe^{III}}}\,\mathrm{Xo} + \mathrm{Fe^{II}Y} = {}^{*}\mathrm{Fe^{II}Xo} + \mathrm{Fe^{III}Y} \tag{5}$$

Es handelt sich um eine Redox-Reaktion. Ihr Verlauf muss schnell sein, da es dabei nur zu einem Elektronenübergang kommt (die Sternchen bedeuten dasselbe Eisenatom) Der Komplex des Eisen(II) mit Xylenolorange ($Fe^{II}Xo$) ist erst um etwa pH 5 stabil. Bei niedrigerem pH, also in unserem Fall, wird er im Augenblicke seiner Entstehung gleich zersetzt (6):

$$Fe^{II}Xo = Fe^{II} + \underset{\text{gelb}}{Xo}. \qquad (6)$$

Die Indikation wird also durch die Gleichungen (5) und (6) gegeben. Zusammenfassend kann man sagen, dass durch Zugabe von Eisen(II) die langsame Verdrängungsreaktion (2) am Endpunkte der Eisen(III)-Titration durch die schnelle Redox-Reaktion (5) ersetzt wird.

Im Einklang mit unseren Vorstellungen muss die nötige Eisen(II)-Menge eine Funktion des pH sein. Tatsächlich je niedriger das pH der Lösung ist, um so mehr Eisen(II) muss benützt werden, um dieselbe Konzentration des Eisen(II)-Komplexonates und dadurch dieselbe „katalytische" Wirkung zu erzielen. Aehnliche Rolle spielt dabei die Temperatur. Bei der Titration von etwa 20 mg Eisen(III) bei pH 1,5 und bei Zimmertemperatur, ist für die Erreichung eines scharfen Farbumschlages die Menge von cca 2 g Ferrosulfat notwendig, während bei pH 3 und 60°C nur wenige mg genügen. Die Frage der Umschlagsqualität ist jedoch soweit subjektiv, dass wir uns nicht bestrebt haben, die optimale Eisen(II)-Sulfatmenge als Funktion des pH und der Temperatur wiederzugeben.

Durch Verwendung des neuen Indikationsrinzips wurde eine hochselektive Eisen(III)-Bestimmung ausgearbeitet. Von den zweiwertigen Kationen stört nur eine grössere Menge von Cu^{2+}. Von den üblichen dreiwertigen Kationen stören Bi^{3+} und Tl^{3+}; Al^{3+} stört selbst in hohen Konzentrationen bei Zimmertemperatur nicht, bei erhöhter Temperatur interferiert es hauptsächlich wegen der Reaktion mit dem Indikator (mit Komplexon verbindet es sich nur langsam), kann jedoch unter den erwähnten Bedingungen schon durch die äquimolekulare Fluoridmenge ohne Niederschlagbildung getarnt werden. Von den in Frage kommenden vierwertigen Kationen stört Ti^{4+} überhaupt nicht, die Interferenz von Zr^{4+} kann wieder mit Fluorid beseitigt werden (wenigstens dreifach molarer Ueberschuss). Das Th^{4+} wird bei pH 1–1,5 durch die aus dem Ferrosulfat stammenden Sulfatione maskiert.

EXPERIMENTELLER TEIL

Reagenzien

0,05*M* *Dinatriumsalz der Aethylendiamintetraessigsäure* (Chelaton 3; Chemapol–Prag). Die Lösung wurde gegen Bleinitrat als primärer Standard[8] eingestellt.

0,05*M*-$Fe(NO_3)_3$. Sein Titer wurde gravimetrisch emittelt.

$FeSO_4 \cdot 7H_2O$ in der Qualität „für Analyse". In Zeitabständen wurde die Eisen(III)-Verunreinigung mit Hilfe der unten beschriebenen Methode bestimmt.

Die Lösungen verschiedener Salze wurden aus den „für Analyse" Präparaten dargestellt und der Inhalt vorwiegend komplexometrisch kontrolliert.

Xylenolorange (Chemapol–Prag). Eine 0,5% Lösung (Haltbarkeit etwa 1 Monat).

Komplexometrische Eisenbestimmung in Gegenwart einer Reihe anderer Metalle

Die abgemessene und mit Hilfe der Salpetersäure zu pH 1–1·5 angesäuerte Probelösung wird in den Titrationskolben der Einrichtung für die Titration in inerte Atmosphäre eingegossen und einige Tropfen Xylenolorange-Lösung zugegeben, Danach wird einige Minuten ein Strom des inerten Gases (N_2, CO_2) durchgeleitet. Nachdem Sauerstoff aus dem System verdrängt wurde, werden etwa 2 g Ferrosulfat des bekannten Eisen(II)-Gehaltes zugegeben und unter ständigem Durchleiten des inerten Gases mit 0,05*M* Aethylendiamintetraacetat titriert. Die ursprünglich blauviolette Farbe der Lösung geht im Umschlagspunkte in reingelb über. Bei einer grossen Eisen (III)-Konzentration wird infolge der Eigenfarbe des Eisen(III)-Komplexonates die Lösung kurz vor dem Endpunkte orangegefärbt. Bei erhöhter Temperatur (ca 60°C) ist der Umschlag unter Verwendung der gleichen Eisen(II)-Sulfatmenge schärfer als bei der Zimmertemperatur.

Bei der Anwesenheit von Zirkonium, oder bei erhöhter Temperatur auch von Aluminium, wird vor der Titration eine genügende Menge von Ammoniumfluorid zugegeben. Dabei muss man für das richtige pH der Lösung sorgen. Dreiwertiges Thallium, Wismuth oder grössere als 10 mg-Menge von Kupfer müssen vor der Titration beseitigt werden.

Nach der Titration der ersten Probe können bei Serien-analyse die weiteren unmittelbar in die austitrierte Lösung pipettiert werden-soweit der Eisengehalt nicht allzu gross ist-und die Titrationen so lange nacheinander wiederholt werden sofern es der Inhalt des Kolbens erlaubt.

Mit Hilfe des beschriebenen Verfahrens wurde eine Reihe Eisenbestimmungen sowie in reinen Lösungen (bis 60 mg Eisen(III) in 100 ml), als auch in Gemischen mit anderen Ionen durchgeführt. In der letztgenannten Versuchsreihe wurde immer mit 20 mg Eisen(II) (in 100 ml) gearbeitet. Unter den angegebenen Bedingungen stören 10 mg Cu gerade noch nicht. Auch die Titration in Gegenwart von 40 mg Cr, 150 mg Ni, 120 mg Co, 200 mg Th, 500 mg Al 100 mg Ti, 30 mg Zr, oder 1000 mg NaH_2PO_4 (grössere Mengen wurden nicht geprüft) verlief störungsfrei. Statistische Verarbeitung der Resultate ergab die gleiche Standardabweichung ($\sigma = \pm 0{,}07$ mg Fe) für reine Lösungen wie für die Titration in Gemischen.

Summary—The complexometric determination of iron^{III}, based on a new end-point procedure, has been developed. Xylenol orange was used as the indicator. This forms a stable violet-blue complex. By the addition of iron^{II} to the titrated solution the usual displacement reaction at the end-point of the titration is replaced by a redox process which gives a very sharp end-point. The new procedure makes possible an accurate and very selective determination of iron^{III}. Only bismuth, thallium^{III} and large amounts of copper require to be removed before the titration.

Résumé—L'auteur décrit un dosage par complexométrie du fer(III), basé sur un nouveau procédé de détermination du point équivalent. On utilise comme indicateur l'orangé de xylénol qui forme un complexe violet-bleu stable. En ajoutant du fer(II) à la solution à titrer, la réaction de déplacement usuelle au point équivalent du titrage est remplacée par un processus d'oxydoréduction qui donne un point équivalent très net. Ce nouveau procédé rend possible un dosage du fer(III) précis et très sélectif. Seuls le bismuth, le thallium(III) et de grandes quantités de cuivre doivent être séparés avant le titrage.

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THE EFFECT OF ABSORBANCY UPON RAMAN INTENSITIES IN SOLUTIONS

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Summary—Reasonable agreement is obtained in the relationship between intensities of Raman lines as measured experimentally and as calculated from an equation derived on the basis of absorbancy laws. A direct relationship between Raman intensity and concentration exists with excitation outside an absorption band, and an inverse relationship over some or all concentration ranges is found with excitation within an absorption band.

THE Raman effect was predicted in 1923 and first observed in 1928. Research in Raman spectroscopy has proved very valuable in the calculation of thermodynamic data and in the interpretation of molecular structure. Raman spectra are also of considerable potential use in analytical chemistry, but the development of analytical applications has proceeded quite slowly.[1,2] Experimental difficulties have seriously limited the widespread development of analytical applications, although much has recently been accomplished in the design and construction of instruments for analytical use.

Quantitative analytical applications must be based upon the intensities of Raman lines. However, the relationship between line intensity and concentration of the Raman-active component is not necessarily linear, and this relationship may even differ from one Raman line to another for the same component. Placzek has predicted that the Raman intensity is greater if excitation occurs within an absorption band than if excitation is not within an absorption band.[3] Others have considered some of the implications of this effect.[4–6] The purpose of the present study is twofold: to investigate experimentally the influence of absorption properties upon the relationship between Raman intensity and concentration; to offer an interpretation thereof in terms of usual absorbancy laws.

EXPERIMENTAL

Raman spectra of aqueous solutions of sulphuric and phosphoric acids were obtained with specially designed apparatus[7] consisting of a helical quartz lamp with predominant 2537 Å output, a quartz sample tube placed within the helical lamp, a specially constructed mercury vapour resonance filter operated at 120°C, and an A.R.L. 1.5-meter concave grating monochromator with photographic recording of spectra. Intensity values were obtained with the aid of a Leeds and Northrup recording densitometer by conventional procedures. A Rayleigh line close to the Raman line was used as the standard in a modified internal-standard method.

Results are tabulated in terms of concentration vs. ratio of Raman to Rayleigh intensities in Table 1 for several Raman lines of sulphuric acid and in Table II for two Raman lines of phosphoric acid. For sulphuric acid it is evident that the intensity ratio rises with increasing concentration for every Raman line listed. Similar relationships were found for the Raman intensities alone, which were used in calculating the intensity ratios of Table I. For phosphoric acid the same "normal"

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relationship exists between intensity and concentration for 3131 Å excitation except for the lowest concentration listed, but with 2537 Å excitation there is a decrease in Raman intensity with increasing concentration throughout the entire concentration range.

In order to ascertain experimentally the influence of absorption properties upon the relationship between Raman intensity and concentration, it was also necessary to obtain absorbancy data on the same systems. This was done with a Beckman DU quartz prism spectrophotometer by conventional procedures. The absorbancy of sulphuric acid was very slight and was uniform throughout the spectral region of interest. The absorbancy of phosphoric acid was slight in the region involved in Raman spectra with 3131 Å excitation but was considerable in the region used with Raman excitation at 2537 Å.

Therefore the direct relationship between Raman intensity and concentration occurs outside an absorption band, as observed for sulphuric acid with all Raman lines measured, and for phosphoric acid with 3131 Å excitation; and an inverse relationship is found when excitation and emission occur within an absorption band, as for phosphoric acid with 2537 Å excitation.

TABLE I. INTENSITIES OBSERVED FOR SULPHURIC ACID WITH 2537 Å EXCITATION

Concentration, volume %	$I_{\text{Raman}} \div I_{\text{Rayleigh}}$ for stated Raman line					
	455 cm^{-1}	600 cm^{-1}	890 cm^{-1}	980 cm^{-1}	1030 cm^{-1}	1160 cm^{-1}
3	.104	.216	.117	.203	.591	.122
6	.167	.265	.219	.308	.670	.180
12	.247	.303	.346	.533	.854	.311
25	.361	.501	.499	.808	1.103	.385
50	.572	.741	.720	.854	1.360	.489
75	.845	.950	1.116	—	1.632	.802

TABLE II. INTENSITIES OBSERVED FOR PHOSPHORIC ACID

Concentration, Volume %	$I_{\text{Raman}} \div I_{\text{Rayleigh}}$ with stated conditions	
	2537 Å Excitation 880 cm^{-1} Raman line 2652 Å Rayleigh line	3131 Å Excitation 880 cm^{-1} Raman line 3341 Å Rayleigh line
12	.0998	.00760
25	.0383	.00280
51	.0209	.00482
85	.0136	.0107

INTERPRETATION

Raman excitation of a liquid can be visualised as consisting of three steps: incident light traversing the solution; interaction with the solution producing the Raman light; Raman light traversing the solution to the monochromator entrance slit. Absorbancy phenomena are of significance in the first and third steps, so these steps may be treated mathematically by means of the Lambert-Beer law along with consideration of the geometrical arrangement of the light source and the sample. Rayleigh scattering can be visualised similarly but, for binary mixtures such as sulphuric or phosphoric acid in water, both components may participate in the second step. For peripheral excitation along the sample tube within a helical type lamp, the following equations may be derived for the Raman intensity, the Rayleigh intensity and the ratio of Raman to Rayleigh intensities (the derivations are included in reference 7).

$$\frac{I_{\text{Raman}}}{I_0} = \frac{4\pi}{{a_1}^2{C_1}^2}\left[e^{-a_1C_1D} + 1 - 2e^{-a_1C_1D/2}\right] K_1C_2 \left[\frac{1}{a_2C_1}\left(1 - e^{-a_2LC_1}\right)\right] \tag{1}$$

$$\frac{I_{\text{Rayleigh}}}{I_0} = \frac{4\pi}{{a_3}^2{C_1}^2}\left[e^{-a_3CD} + 1 - 2e^{-a_3CD/2}\right] \left[K_2C_1 + K_3(100 - C_1)\right]\left[\frac{1}{a_3C_1}\left(1 - e^{-a_3LC_1}\right)\right] \tag{2}$$

$$\frac{I_{\text{Raman}}}{I_{\text{Rayleigh}}} = \frac{{a_3}^3}{{a_1}^2a_2}\left[\frac{K_1C_2}{K_2C_1 + K_3(100 - C_1)}\right] \left[\frac{1 + e^{-a_1C_1D} - 2e^{-a_1C_1D/2}}{1 + e^{-a_3C_1D} - 2e^{-a_3C_1D/2}}\right]\left[\frac{1 - e^{-a_2LC_1}}{1 - e^{-a_3LC_1}}\right] \tag{3}$$

in which a_1 = absorbancy coefficient for Raman excitation line

a_2 = absorbancy coefficient for Raman line

a_3 = absorbancy coefficient for Rayleigh line

K_1 = constant for transition probability for Raman excitation of solute

K_2 = constant for transition probability for Rayleigh excitation of solute

K_3 = constant for transition probability for Rayleigh excitation of solvent

C_1 = concentration of solute (expressed in volume %, so that concentration of solvent = $100 - C$)

C_2 = concentration of the ionic or molecular form of the solute which gives rise to the Raman line (C_2 may or may not equal C_1)

D = diameter of sample tube

L = length of sample tube.

It is not feasible at the present time to make a complete experimental test of these equations which have been derived to show the influence of absorbancy phenomena upon the relationship between concentration and intensity. It is possible, however, by assuming reasonable values of the transition probabilities and using the measured values of the absorbancy coefficients for sulphuric and phosphoric acids, to determine whether the equations result in a direct or an inverse relationship between concentration and intensity for comparison to the trends of the experimental data of Tables I and II. This has been done (full details are included in reference 7), and close correlation is obtained. The direct relationship between concentration of sulphuric acid and intensity ratio is predicted from the equation. The inverse relation is predicted for 2537 Å excitation of phosphoric acid, and the inflection point in the Rayleigh intensity ratio at a concentration of about 30% is predicted for 3131 Å excitation of phosphoric acid. This seems to account for the peculiarities in the intensity relations found.

CONCLUSIONS

Experimental data have been obtained on the intensities of Raman lines for aqueous phosphoric and sulphuric acids. A general equation for the intensity has been derived on the basis of absorbancy laws. Reasonable agreement is obtained between calculated and experimental data. A direct relationship between Raman intensity and concentration exists with excitation outside an absorption band, and an inverse relationship over some or all concentration ranges is found with excitation within an absorption band. Thus absorbancy is a very significant factor in the relationship between concentration and Raman intensity. For straight-forward quantitative analytical applications of Raman spectroscopy, spectral regions in which the sample exhibits appreciable absorption should preferably be avoided.

Acknowledgement—This work was supported by the Office of the Surgeon General, Research and Development Division, U.S. Department of Defense, under contract DA-49-007-MD-769.

Zusammenfassung—Eine Formel zur Berechnung der Intensität von Ramanlinien aufgrund der Absorptionsgesetze wurde abgeleitet. Übereinstimmung der berechneten und gefundenen Intensitäten ist gut. Intensität und Konzentration sind proportional wenn die Anregung ausserhalb einer Absorptionsbande erfolgt, umgekehrt proportional bei Anregung innerhalb einer Absorptionsbande.

Résumé—On obtient pour la relation entre les intensités des raies Raman une concordance satisfaisante, que celles-ci soient mesurées expérimentalement ou calculées à partir d'une équation déduite des lois d'absorption. Il existe une relation directe entre intensité Raman et concentration lorsque l'excitation est extérieure à la bande d'absorption, et on observe une relation inverse pour tout ou partie du domaine de concentration lorsque l'excitation correspond à la bande d'absorption.

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A TRANSISTORIZED DROP COUNTER FOR CHROMATOGRAPHIC USE

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Summary—A completely transistorized drop counter for use in chromatography is described. The instrument is compact and reliable, and offers high versatility.

CORYN, Speecke and Hoste[1] recently described an electronic drop counter for use in ion exchange chromatography. As highly sensitive miniature photo-diodes are now currently available, a completely transistorized drop counter has been developed, offering compactness, reliability and versatility.

The wiring diagram, an exploded view of the photodiode housing and the transistor assembly are represented in Figs. 1, 2 and 3.

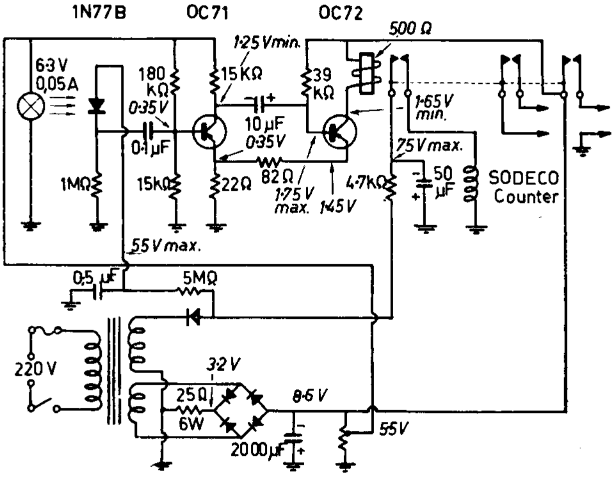

FIG. 1.

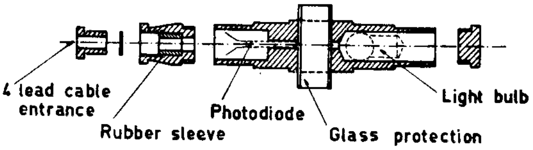

FIG. 2.

The power section of the drop counter includes the 75-volt DC high voltage, supplying the photodiode and the counter, and 8·6 volt DC for the transistors, the light source and the output pulse. The high voltage supply of the photo-diode and 5·5 volt DC of the light source are connected to

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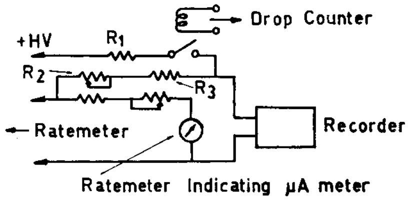
* Member of the Institut Interuniversitaire des Sciences Nucléaires.

the housing by means of a 4-lead cable, the fourth one carrying the signal. The use of ripple-fre DC for the light source is required to achieve reliable operation of the counter.

When an incident light beam on the junction diode IN77B is interrupted by a falling drop, positive 4-volt pulse is produced over the 1-Megohm load resistor and triggers the univibrator circui (transistors OC71 and OC72). A 500-ohm relay with triple contacts is incorporated in the collecto



R_1 : 270 KΩ 10 % 1 Watt
R_2 : 20 KΩ pot. wirewound
R_3 : 10 KΩ 5 % 1 Watt
Recorder : 5 mA 800 Ω

FIG. 4.

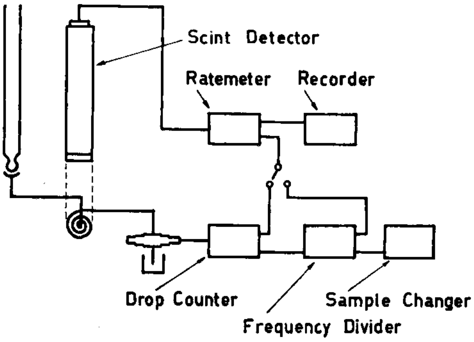


FIG. 5.

circuit of the OC72. One contact operates the Sodeco counter (type TCeZEc25), the second contac provides a negative 8·6-volt pulse to an output, whereas the third contact is connected to a secon output.

The use of a univibrator between photo-diode and counter insures high stability in operatio and makes drop velocity uncritical. The counting rate however is limited by the pulse length, whic is of the order of 100 milliseconds but this is adequate in most cases. No light shielding of the photo diode assembly is needed under normally occurring illuminating conditions.

In chromatography of radioactive species, the separation can be controlled by continuous monitoring of the effluent with a suitable detector coupled to a rate-meter and a recorder. The pulses o the first output from the relay are fed to the rate-meter and give a pulse for each eluted drop on th registered curve. An adequate coupling circuit for the Tracerlab Precision Rate-meter is represente in Fig. 4.

For short columns and/or species with a low value of the distribution coefficient this procedur will involve the counting of only a relatively small number of pulses on the curve to locate the elute species. For large columns and/or species with large distribution coefficients however, this countin becomes very time consuming. Moreover the length of the paper strip becomes large, as the spee of the recorder must be high enough to distinguish between two successive pulses. This can b avoided by using the second output from the relay together with a multi-decade predetermine counter. The circuit proposed by Philips N.V.[2] with EIT tubes is adequate if preceded by a puls shaper to trigger the multi-decade counter.

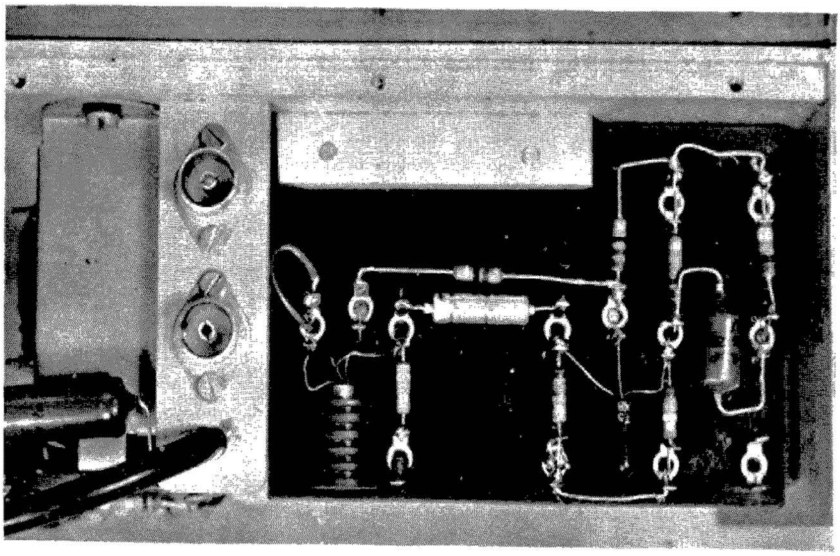


FIG. 3.—Transistor assembly

If a three-decade counter is used, any pre-set number of drops between 1 and 1000 will give rise to one pulse on the registered curve. Provision can also be made to connect the output of the decade counter to a sample changer. This allows separate collection of a preset number of drops.

A possible and highly versatile setup is represented schematically in Fig. 5.

Acknowledgement—This work is part of the research sponsored by the Institut Interuniversitaire des Sciences Nucléaires. Acknowledgements are due to L. Van de Keer for technical assistance.

Zusammenfassung—Ein zuverlässiger und vielseitig anwendbarer transistorischer Tropfenzähler für die Chromatographie wird beschrieben.

Résumé—Les auteurs décrivent un compteur de gouttes à transistors utilisable en chromatographie. L'instrument est peu volumineux, fidèle et à usages multiples.

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NEW CONTRIBUTIONS TO THE STUDY OF THE HALOGENATING EFFECT OF IODINE BROMIDE

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Summary—It was found that iodine bromide has exclusively an iodinating effect in an aqueous solution, in the presence of elementary iodine (of non interhalogen nature).

The small homolytic dissociation of iodine bromide is suppressed by iodine. In this way the formation of elementary bromine is inhibited. Consequently, in suitable conditions the brominating effect of iodine bromide is suspended.

The degree of homolytic dissociation of solutions of iodine bromide of various composition at room temperature was established.

ACCORDING to the literature,[1,2,3] iodine bromide in its substitution reactions exhibits a partial brominating effect. As part of a study of the chemistry of interhalogen compounds, a series of aromatic substitution reactions of iodine bromide was examined. It was pointed out[4] that *in an aqueous solution* (i.e. in a solvent of high dielectric constant) iodine bromide mainly behaves as an iodinating agent, and possesses brominating effect only to a subordinate extent. In the same solvent, the iodinating effect is promoted by raising the dipole character of the molecule of iodine bromide. The differences in the behaviour of iodine bromide and iodine chloride in aromatic substitution reactions were interpreted by assuming that, in addition to the heterolytic dissociation into I^+ and Br^- which predominates in an aqueous solution, a homolytic dissociation of iodine bromide into I_2 and Br_2 also takes place, owing to the appreciably weaker dipole character of its molecule. The brominating effect of iodine bromide is ascribed to elementary bromine formed during homolytic dissociation.

On studying the chemistry of bromine chloride, homolytic dissociation of a similar type was observed.[5] However, it could be suppressed by small amounts of elementary bromine or chlorine.

We believed also that the homolytic dissociation of iodine bromide can be suppressed in a similar way, by adding elementary iodine. For this purpose, solutions of iodine bromide of different iodine content were prepared and the halogenating effect of the solutions examined. Antipyrine was chosen as a reaction partner because it is known that antipyrine does not react with elementary iodine in an acid solution whilst with iodine bromide a reaction actually takes place. By suitable isolation of the reaction product, and mineralising it by fluxing with alkali, the contents of iodide and of bromide were determined.

According to our investigations, the iodine-containing solution of iodine bromide (with a content of approximately 30% of iodine) possesses exclusively an iodinating effect.

The present investigations also proved that the anomalous behaviour of iodine bromide is due to the homolytic dissociation of small extent, caused by the decreased dipole character of the molecule, and that this dissociation can be suppressed by excess iodine (or bromine).

The principle of the analytical method evolved by us[5] for the determination of the content of elementary bromine in bromine chloride could also be utilised for the determination of the content of elementary iodine in iodine bromide.

In essence, the method is as follows. The solution of iodine bromide containing elementary iodine is treated with cyanide. The reaction of iodine bromide with cyanide yields iodine cyanide and bromide ions, whilst elementary iodine reacts with cyanide during the formation of iodine cyanide and iodide ions. The iodine cyanide formed and excess cyanide are removed from the slightly acidic solution by slowly passing an inert gas (or by boiling). A quantity of iodide ions equivalent to the amount of the content of elementary iodine of non interhalogen nature* remains in the solution. This quantity can be determined by iodometry in the presence of bromide.

By this method, we determined the content of iodine of non interhalogen nature formed in the course of the homolytic dissociation, and the degree of homolytic dissociation in various solutions of iodine bromide.

According to our earlier investigations mentioned in the introduction,[4] when antipyrine reacts with a solution of iodine bromide containing bromide, 80·5% of the reaction products are iodine derivatives. On using a stoichiometric solution of iodine bromide, the amount of iodine derivatives rises to 91·3% of the halogenated products, whereas in the case of solutions of iodine bromide containing chloride, the ratio of iodine derivatives is as high as 93·7%. The various strengths in iodinating activity of the solutions mentioned were interpreted by the various degrees of the homolytic dissociation of iodine bromide.

By use of the recently evolved method, we determined the quantity of elementary iodine formed in the course of homolytic dissociation, and in this way also the degree of dissociation, in the various types of iodine bromide solutions and in a solution of iodine bromide containing elementary iodine, *i.e.* iodine of non interhalogen type (Table 1).

TABLE 1

Number	Composition of solution	Degree of homolytic dissociation %
1	$0·1N$ IBr in $0·5N$ HBr	2·8
2	$0·1N$ IBr	1·0
3	$0·1N$ IBr in $0·5N$ HCl	0·5
4	$0·001N$ IBr + $0·001N$ elementary I	0·0
5	$0·01N$ IBr + $0·01N$ elementary Br	0·0

The figures in Table 1 confirm the results of our earlier investigations. In other words the decrease of the degree of homolytic dissociation promotes the iodinating effect of iodine bromide. In the case of a total suppression of homolytic dissociation, in the presence of excess iodine, only the halogenating effect of I^+ formed during

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* This is equal to half of the amount of elementary iodine of non interhalogen nature.

heterolytic dissociation dominates. Consequently, iodine bromide solely iodinates in this case.

EXPERIMENTAL

(1) *Iodine bromide solution;* This was prepared by the reaction

$$IO_3^- + 2I^- + 3Br^- + 6H^+ = 3IBr + 3H_2O \qquad (1)$$

For a detailed description, see our earlier communications.[4,6] The hydrogen ions in equation (1) were contributed by HBr, HCl, $HClO_4$ and H_2SO_4.

(2) *Iodine bromide containing elementary iodine of non-interhalogen nature;* 10 ml of a 0·05*M* solution of iodine bromide prepared as above were made up with distilled water to about 1000 ml and mixed with 2·50 ml of a 0·1*M* solution of potassium iodide. A quantity of iodine bromide equivalent to that of iodide was reduced to elementary iodine according to the equation

$$IBr + I^- = I_2 + Br^-$$

A dilution of this order of magnitude was necessary, owing to the poor solubility of iodine. (The solution of iodine bromide prepared in this way contains 50% of elementary iodine.)

Reaction of the iodine-containing solution of iodine bromide with antipyrine

1000 ml of the solution prepared as under (2) were mixed with about 4 ml of a 1% solution of antipyrine. The reaction mixture was vigorously shaken several times, allowed to stand for 10 minutes and adjusted with sodium acetate to about pH 3. The content of iodine of the solution was back-titrated with 0·1*N* sodium thiosulphate. Then, a piece of litmus paper was put in the reaction mixture and it was made alkaline with 2*N* sodium hydroxide and shaken with 3 × 50 ml of chloroform. The chloroform solution was filtered through cotton coated with anhydrous sodium sulphate, in order to remove traces of water; the bulk of solvent was distilled off, and the residue was evaporated at room temperature. On recrystallising the product from hot water, snow-white needles resulted, m.p. 165-167°. After fluxing with potassium hydroxide, the content of both iodine and bromine were determined.

The determination of elementary iodine formed during the homolytic dissociation of iodine bromide

This was carried out similarly to the determination of elementary bromine in bromine chloride. The precise description of the technique is in our earlier communications.[5,7] In essence, excess halogen cyanide and hydrogen cyanide are removed, the solution of about 50-ml volume is acidified to pH 2 and mixed with freshly saturated chlorine water completely free of bromine, until the brownish colour caused by liberated iodine and bromine disappears and the solution turns straw-yellow (the odour of chlorine must be perceptible). On allowing the solution to stand for 10 minutes, the liquid is made alkaline by adding without any delay 10 ml of 2*N* sodium hydroxide and 2 ml of a 5% solution of potassium cyanide. After 15 minutes (this period is satisfactory for the complete hydrolysis of the formed halogen cyanides) the quantity of iodate developed during the oxidation by chlorine is measured by iodometry in the conventional way.

Zusammenfassung—Verfasser haben bewiesen, dass das Jodbrom in Gegenwart von elementarem Jod in wässriger Lösung (also in Lösung von hoher Dielektrizitätskonstante) ausschliesslich jodiert. Als Modell wurde die Reaktion Antipyrin-Jodbrom gewählt. Durch freies Jod konnte die homolytische Dissociation des Jodbroms, welche als Ursache des teilweisen Bromierungseffektes anzusehen ist vollständig zurückgedrängt werden. Es wurde ein analytisches Verfahren angegeben, mittels dessen der Grad der homolytischen Dissociation einwandfrei bestimmt werden kann.

Résumé—On a trouvé que le bromure d'iode a exclusivement un effet iodant en solution aqueuse et en présence d'iode élémentaire (de nature non "interhalogène"). La petite dissociation homolytique du bromure d'iode est supprimée par l'iode. La formation de brome élémentaire est ainsi empêchée. En conséquence, on peut supprimer, dans des conditions appropriées, l'effet bromant du bromure d'iode.

On a établi le degré de dissociation homolytique, à la température ambiante, de solutions de bromure d'iode de compositions variées.

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PRECIPITATION OF BARIUM CHROMATE FROM HOMOGENEOUS SOLUTION USING COMPLEXATION AND REPLACEMENT

A SEPARATION OF BARIUM FROM RELATIVELY LARGE AMOUNTS OF STRONTIUM AND LEAD

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Summary—A new procedure is presented that efficiently separates barium from relatively large amounts of strontium and lead. The barium is precipitated as the chromate from a solution in which the multivalent cations are complexed with EDTA. The barium ions are homogeneously released in solution when magnesium ions are slowly introduced into the solution. The magnesium ions gradually replace the barium ions from their EDTA complexes, bringing about a precipitation of barium chromate from homogeneous solution.

This slow formation of barium chromate crystals holds co-precipitation to a minimum and produces crystals that are easily filtered and washed. More than 99.7% of the barium can be precipitated as the chromate, with less than 0.6% of the strontium, when the two ions are in equal molar concentration.

THE separation of barium as the chromate in the presence of strontium has been troublesome and tedious.[1–3] Usually a double precipitation is necessary if appreciable amounts of strontium are present. Small amounts of lead interfere in all these methods. Recently Ballczo and Doppler[4] used EDTA to improve the separation. This modification has the disadvantages inherent in a conventional precipitation process.

The method described here provides an excellent separation of barium from relatively large amounts of strontium and lead using a recently developed technique involving precipitation from homogeneous solution.[5,6] This general method is based on the different stabilities of cation complexes. When insufficient complexing agent is present one cation is able to replace or "squeeze out" another cation that forms a less stable complex. By slowly introducing the cation that forms a more stable complex, the cation with the less stable complex is slowly and homogeneously released in solution.

In the case of EDTA, the barium complex is less stable than the strontium, magnesium, or the lead complex. The logarithm of the formation constants for these EDTA complexes[7] are as follows: Ba = 7.76, Sr = 8.63, Mg = 8.69, Pb = 18.0. When an excess of EDTA is added to a solution containing these four cations, they are complexed according to their respective formation constants. When chromate ions are added to the solution, a precipitate does not form because of the low concentration of free cations. A dilute solution of magnesium chloride is then slowly added to the stirred solution. Because magnesium chromate is very soluble, it does not precipitate. Instead, the magnesium ion is complexed by the excess EDTA until the excess EDTA is exhausted. At this point the magnesium ion slowly replaces or "squeezes out" the barium ion from its complex. The concentration of barium ion slowly increases until the solubility product of barium chromate is exceeded. Then precipitation of barium chromate occurs and continues slowly, for the barium ion is being released in solution at almost the same rate at which it is being removed by precipitation. The change is gradual and practically uniform, i.e. a precipitation from homogeneous solution. The crystalline barium chromate produced by this method is readily filtered, easily washed, and shows negligible co-precipitation.

EXPERIMENTAL

Procedure

Add a sample containing about 0.5 millimole of barium (about 70 milligrams) to a 600 ml beaker. Dissolve the sample in 200 ml of distilled water and add an excess of EDTA. (This must be sufficient to complex all the barium and all the cations in the solution that form an EDTA complex more stable than the barium EDTA complex. One hundred and ninety milligrams of reagent grade disodium ethylenediaminetetra-acetate dihydrate will complex 70 milligrams of barium.) Make the solution distinctly alkaline with ammonium hydroxide and add about 1.0 millimole of potassium chromate. Then adjust the solution to about pH 10 with ammonium hydroxide and the volume to about 400 ml.

Place the beaker on a hot plate and heat to about 90° to 95°. Stir the solution gently with some mechanical device and slowly add a magnesium chloride solution (about $0.02M$) by introducing one drop every 4 to 6 seconds. The amount of magnesium chloride added must be sufficient to exhaust all the free EDTA and also to replace all the barium from its EDTA complex. This means that more than 0.6 millimole of magnesium must be added. The amount of magnesium chloride can vary widely depending on the sample. (See Tables II and III). The time required to add slowly the magnesium chloride solution will be about one hour.

After all the magnesium chloride has been added, filter the hot solution through a tared Selas crucible. Wash the precipitate into the crucible using a $0.001M$ potassium dichromate solution made just alkaline with ammonium hydroxide. Finally, wash with three small portions of distilled water. Dry the precipitate of barium chromate at 110° to 120° for two hours before weighing.

Notes on procedure. The procedure followed in this experimental work is fairly flexible but in attempting to apply this technique to any specific separation problem several general conditions must be met.

The EDTA must always be in excess before the addition of chromate, otherwise barium chromate will immediately precipitate when chromate ions are added.

Enough chromate ion must be added to assure quantitative precipitation. About twice the theoretical amount of chromate is needed but four times as much has no appreciable effect on the separation. (See Table II)

Enough magnesium ion must be added to take up all the excess EDTA and also to replace all the barium from its EDTA complex. An excess of magnesium ions will not noticeably affect the results, but insufficient magnesium ions will not bring about the complete precipitation of the barium. (See Table II)

Reagents

Approximately $0.1M$ solutions of $BaCl_2$, $SrCl_2$, $MgCl_2$, $K_2Cr_2O_7$, $Pb(NO_3)_2$, $Ca(NO_3)_2$, $Fe(NO_3)_3$, and EDTA were prepared by dissolving 0.20 mole of the reagent-grade salt in distilled water and making the volume up to two litres.

Five millicuries of radioactive 140-barium, (as $BaCl_2$), and two millicuries of 90-strontium, (as $SrCl_2$), were obtained from Oak Ridge National Laboratory and diluted up to 100 ml.

Aliquots of these solutions were taken as needed.

Radiochemical measurements

Only radiochemical methods for determining traces of barium in large quantities of strontium and traces of strontium in large quantities of barium are satisfactory. Therefore the use of radioactive tracers was necessary in order to establish the efficiency of the described procedure.

About 2 to 4 microcuries of 140-barium, plus the daughter 140-lanthanum, were added to the starting solution used in each radio-chemical determination of barium in the filtrate. The 140-lanthanum presents a slight complication because it remains in the filtrate when the barium chromate is precipitated. This means that an immediate count of the filtrate would yield false results unless a complicated set of time data and formulas were used. Instead, a suitable waiting period to allow for decay of the 140-lanthanum was used.

The half-life of 140-barium is 12.8 days and the half-life of 140-lanthanum is 40 hours.[8] In 10 half-lives, or 400 hours, the 140-lanthanum in the filtrate would decay to an almost insignificant amount. Meanwhile, the 140-lanthanum in the precipitate would increase and reach radiochemical equilibrium with the parent 140-barium. A waiting period of at least two and one half weeks was required before any counting of the filtrate to precipitate ratio of "tagged" barium was done. Each sample was counted again at a later date to confirm the validity of the first ratio determination.

The same general procedure was used with the 90-strontium and its daughter 90-yttrium. About two microcuries of the mixed radioisotopes were added to each starting solution. 90-Yttrium does not precipitate with the barium chromate but remains in the filtrate.

The half-life of 90-strontium is about 20 years and the half-life of 90-yttrium is about 64 hours.[8] In about 6 half-lives the 90-yttrium will grow in the precipitate and approach a constant level. A waiting period of at least two and one half weeks was used before any counting of the filtrate to precipitate ratio of "tagged" strontium was done. Each sample was counted again at a later date to confirm the validity of the first ratio determination.

Results

The results obtained when 140-barium was used as a radioactive tracer are given in Table 1. The use of 140-barium has shown that the barium is quantitatively precipitated under varying conditions, and that the presence of strontium and lead have no appreciable effect on the quantitative precipitation of the barium.

TABLE I.—PRECIPITATION OF BARIUM CHROMATE USING 140-BARIUM AS TRACER

Barium taken is 0.5 millimole or 71.1 milligrams, 0.75 millimole of magnesium added to each solution.

K_2CrO_4, *millimoles*	EDTA, *millimoles*	Sr^{2+} or Pb^{2+}, *millimole*	*mg* of Ba found, gravimetric	*mg* difference, gravimetric	*mg* Ba in filtrate, radiometric
1.0	0.6	0	71.0	−0.1	0.08
1.0	0.6	0	71.1	0.0	0.19
1.0	1.1	0.5 Sr^{2+}	71.3	+0.2	0.11
1.0	1.1	0.5 Pb^{2+}	71.0[a]	−0.1	0.04
1.5	0.6	0	71.1	0.0	0.17
2.0	0.6	0	71.9	+0.8	0.06
2.0	1.1	0.5 Sr^{2+}	71.9	+0.8	0.06
3.0	0.6	0	71.2	+0.1	0.02
5.0	0.6	0	70.6	−0.5	0.05

[a] 0.80 millimole of magnesium added.

The 140-barium has made it possible to determine accurately how much barium stays unprecipitated. This was accomplished by determining the ratio of 140-barium in the filtrate and in the dissolved precipitate. The vexing uncertainties of small gravimetric errors were by-passed and an accurate measure of the small quantity of barium present in a large quantity of strontium was made.

The data in Table I show that a five-fold change in the chromate ion concentration does not markedly change the amount of barium left in the filtrate.

The use of 140-barium also made it possible to determine the quantity of barium that is solubilized during the washing operation. This was measured by counting the 140-barium activity of the washings. Radiochemical determinations of three different washings showed that 13, 2, and 9 micrograms of barium were solubilized during the washing operation.

The results obtained using 90-strontium as a radioactive tracer are given in Table II. The use of 90-strontium has made it possible to determine accurately the small quantities of strontium that are co-precipitated with the barium chromate. These results clearly show that this method provides an excellent separation of barium from strontium. The quantities of EDTA, potassium chromate, and magnesium chloride are not critical and can be varied quite widely with no appreciable effect on the strontium co-precipitated.

TABLE II.—PRECIPITATION OF BARIUM CHROMATE IN THE PRESENCE OF STRONTIUM USING 90-STRONTIUM AS TRACER.

Barium taken is 0.5 millimole or 71.1 milligrams

K_2CrO_4, *millimoles*	EDTA, *millimoles*	$SrCl_2$, *millimoles*	$MgCl_2$, *millimoles*	Ba found gravimetric *mg*	difference gravimetric *mg*	Sr in precipitate radiometric *mg*
1.0	0.8	0.2	0.75	70.5	−0.6	0.15
1.0	1.1	0.5	0.5	56.6[a]	−14.5	0.09
1.0	1.1	0.5	0.75	71.2	+0.1	0.17
1.0	1.1	0.5	0.75	71.1	0.0	0.25
1.0	1.1	0.5	0.75	71.2	+0.1	0.16
1.0	1.6	1.0	1.5	71.0	−0.1	0.31
1.0	2.7	2.0	1.0	71.3	+0.2	0.28
1.0	6.0	5.0	1.6	69.7[b]	−1.4	0.75
2.0	0.8	0.2	0.75	71.4	+0.3	0.18
2.0	1.1	0.5	0.75	71.1	0.0	0.16
2.0	1.1	0.5	0.75	71.4	+0.3	0.23
2.0	1.1	0.5	1.1	71.0	−0.1	0.21

[a] Insufficient magnesium chloride added.

[b] Supersaturation condition in the filtrate.

TABLE III.—PRECIPITATION OF BARIUM CHROMATE IN THE PRESENCE OF CALCIUM, LEAD, OR IRON

Barium taken is 0.5 millimole or 71.1 milligrams
Potassium chromate taken is 1.0 millimole

EDTA, *millimoles*	$Ca^{2+}Pb^{2+}$ or Fe^{3+}, *millimoles*	$MgCl_2$, *millimoles*	Ba found gravimetric *mg*	Difference gravimetric *mg*
1.1	0.5 Ca^{2+}	0.75	71.0	−0.1
1.7	1.0 Ca^{2+}	1.0	71.2	+0.1
1.1	0.5 Pb^{2+}	0.75	71.1	0.0
1.1	0.5 Pb^{2+}	0.75	71.0	−0.1
1.7	1.0 Pb^{2+}	1.0	71.1	0.0
1.1	0.5 Fe^{3+}	0.75	70.7	−0.4
1.7	1.0 Fe^{3+}	1.0	71.0	−0.1

The results obtained when equal molar and double molar quantities of calcium, lead, and iron are present are given in Table III. These data clearly show that an excellect separation of barium from calcium, lead, and iron is possible using this method. Qualitative tests were made on the barium chromate precipitates formed in solutions containing lead ions and iron ions. Neither lead nor iron were detected in these precipitates.

DISCUSSION

Precipitation is performed in basic solution for several reasons. In acid solution the oxidation of the EDTA by chromate caused discoloration of the solution and the precipitate. Furthermore, the stability of the EDTA complexes decreases with increasing acidity. At a fairly high pH, about 8 to 10, the EDTA complexes are stable and no problem of hydroxide precipitation occurs either with iron or lead. The final pH of the filtrate was still fairly high, usually between pH 8.5 and 9.0.

The heating of the solution is necessary for the production of an easily filtered precipitate. In cold solution the precipitate is powdery and also tends to stick tenaciously to the walls of the beaker.

The concentration of magnesium chloride and the drop rate were selected in order to give a reasonable time for the determination. A suitable time is needed for crystal growth, and cannot be shortened to any appreciable extent.

The experimental evidence indicates the precipitation is occurring from a homogeneous solution, even though the addition of magnesium chloride solution to the original solution automatically indicates heterogeneity. The precipitate forms in a homogeneous manner throughout the solution. Microscopic examination of the barium chromate precipitates formed using this procedure showed a uniform size and shape for the crystals. Excessive co-precipitation, characteristic of a heterogeneous precipitation, is not taking place.

An interpretation of solution conditions during the precipitation process proves interesting. The solution, just before the addition of magnesium ions, is uniform with respect to all constituents. When a drop of magnesium chloride solution is added to this original solution, the uniformity is disturbed. Compared to the solution, the portion of the liquid in the vicinity of the added drop is high in magnesium ion concentration but low in chromate ion and barium EDTA complex concentration. This decreases the chances for the immediate formation of a precipitate.

The reactions that lead to the formation of a precipitate are as follows:

$$\mathrm{BaEDTA^{2-} + Mg^{2+} = MgEDTA^{2-} + Ba^{2+}}$$

$$\mathrm{Ba^{2+} + CrO_4{}^{2-} = BaCrO_4}$$

The reactants are present in the solution in low concentration. Therefore, a definite time interval is needed for these reactions to occur. This time interval is apparently of the same order of magnitude, or greater than, the time interval needed for mixing the introduced drop. This means that conditions closely approaching uniform concentration of all constituents are reached before precipitation actually occurs.

There is no drastic fluctuation in the barium ion concentration throughout the precipitation. The barium ion concentration gradually increases as the precipitation continues, being at a maximum when the precipitation is complete.

Once the barium EDTA complex is depleted some strontium ions are released by the introduced magnesium ions. However, at this point entrapment of strontium can no longer take place, for the barium has already been precipitated.

When the magnesium ions have all been added, the strontium ion concentration is fairly high but the solubility product of strontium chromate has not been exceeded. So strontium does not precipitate.

In the solutions containing lead ions complexed by EDTA, the lead EDTA complex is not significantly affected by the addition of magnesium ions because of the great difference in stability between the lead and magnesium complexes. The magnesium complex is considerably less stable than the lead complex, and at no time during the course of the precipitation is there a significant concentration of lead ions in solution. The lead chromate solubility product constant is not exceeded at any time during the procedure and no co-precipitation of lead results even though lead chromate is more insoluble than barium chromate.

Theoretically, this method should provide a separation of barium from any cation more strongly complexed with EDTA than magnesium ion. Tables II and III show that this is true for the ions of calcium and iron as well as those of strontium and lead.

Zusammenfassung—Eine neue Methode zur Trennung von Barium von relativ grossen Mengen Strontium und Blei ist beschrieben. Das Barium wird als Chromat niedergeschlagen während die anderen multivalenten Ionen mit ÄDTA komplex gebunden sind. Das Barium wird aus dem ÄDTA-Komplex "homogen" befreit wenn man zur Testlösung Magnesiumionen zufügt. Das Magnesium verdrängt Barium langsam aus dem ADTA-Komplex.

Die langsame Bildung des Bariumchromates hält Mitfällung sehr klein und erzeugt Kristalle, die leicht zu filtrieren und waschen sind. Mehr als 99.7% barium wird gefällt unter Mitfällung von weniger als 0.6% Strontium wenn beide Ionen in äquimolarer Konzentration anwesend sind.

Résumé—L'auteur expose un nouveau procédé qui sépare avec efficacité le baryum de quantités relativement grandes de strontium et de plomb. On précipite le baryum à l'état de chromate à partir d'une solution dans laquelle les cations polyvalents sont complexés par l'EDTA. Quand on ajoute lentement des ions magnésium dans la solution, les ions baryum sont libérés d'une manière homogène. Les ions magnésium (remplacent graduellement les ions baryum dans leurs complexes avec l'EDTA, provoquant une précipitation de chromate de baryum dans la solution homogène.

Cette formation lente de cristaux de chromate de baryum maintient la précipitation à un minimum et produit des cristaux qui sont facilement filtrés et lavés. On peut précipiter plus de 99,7% de baryum à l'état de chromate avec moins de 0,6% de strontium, quand ces deux ions sont à la même concentration molaire.

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LA SEPARATION NIOBIUM-TANTALE EN MILIEU CHLORO-OXALIQUE SUR ECHANGEUR D'ANIONS

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Résumé—L'étude systématique des constantes de distribution du niobium et du tantale a permis de trouver deux éluants donnant une séparation satisfaisante sur colonne en milieu chlorooxalique sur échangeur d'anion du type Dowex 1 et 2. Le premier éluant, $0{\cdot}01M\ H_2Ox + 2M\ HCl$, élue d'abord le tantale tandis qu'avec le second, $0{\cdot}5M\ H_2Ox + 1M\ HCl$, l'ordre d'élution est inverse, ce qui est particulièrement important pour la détermination de traces de tantale dans le niobium et vice versa.

Les auteurs ont étudié en détail l'influence de la température, de la charge et du degré de "cross-linking" de l'échangeur.

L'expérience a démontré que la meilleure séparation est obtenue à une température de 25° pour l'éluant rapide et de 45° pour l'éluant lent. Parmis toutes les résines étudiées le Dowex 1–X8 donne lieu à la séparation la plus favorable pour les deux éluants.

INTRODUCTION

DIFFÉRENTS auteurs[1–14] ont appliqué des méthodes chromatographiques à la séparation quantitative niobium-tantale. Cette séparation est en effet très laborieuse par les méthodes classiques, due à la grande analogie des propriétés chimiques de ces éléments.

Nous nous sommes proposés d'étudier cette séparation sur échangeur d'anions en milieu chlore-oxalique afin d'éviter l'emploi de l'acide fluorhydrique[1,5–7] qui peut donner lieu à des inconvénients pratiques. L'emploi de l'acide chlorhydrique seul, tel que l'ont proposé Huffman, Iddings et Lilly,[2] semble peu indiqué, vu l'instabilité des solutions chlorhydriques de ces éléments. J. Gillis[3] c.s. avait déjà démontré que la séparation en milieu chloro-oxalique est praticable.

Cette étude a été entreprise à l'aide des traceurs radio-actifs ^{95}Nb (produit de fission) et ^{182}Ta. Seul l'emploi de traceurs radioactifs offrait en effet la possibilité d'étudier cette séparation, les méthodes classiques de la chimie analytique ne permettant pas simultanément le dosage de traces de niobium et de tantale en solution chloro-oxalique.

DETERMINATION DES CONSTANTES DE DISTRIBUTION

Les constantes de distribution K_D, telles que définies par Kraus et Moore,[15] ont été déterminées par équilibrage des traceurs radioactifs du ^{95}Nb et du ^{182}Ta dans 10 ml de solution en présence de 100 mg de Dowex 2 (50-100 mesh) à 25° ± 0·1°. La concentration en Ta était de $4 \,.\, 10^{-6}M$ tandis que le Nb était carrier free. Les traceurs sont conservés en solution d'acide oxalique à 5% afin d'éviter la formation de radio-colloides. L'expérience montre que l'équilibre entre les deux phases est très lent à s'établir et requiert au moins 6 heures.

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* Chercheur agréé de l'I.I.S.N.

Après équilibrage et filtration de la résine, l'activité de la solution est déterminée dans un échantillon de 4 ml à l'aide d'un compteur à scintillation équipé d'un cristal creux NaI(Tl). La constante de distribution se calcule d'après l'équation (1):

$$K_D = \frac{\text{Activité par g de résine}}{\text{Activité par ml de solution}} = \frac{(A_T - 10\,A)10}{A} \qquad (1)$$

A_T = activité totale introduite

A = activité par ml après équilibrage.

SEPARATION SUR COLONNE

La Fig. 1 démontre que deux éluants conviennent pour effectuer une séparation quantitative sur colonne, notamment $0{\cdot}01M$ $H_2Ox + 2M$ HCl (éluant rapide) et $0{\cdot}5M$ $H_2Ox + 1M$ HCl (éluant lent), le rapport des constantes de distribution β étant supérieur à 2. Quoique les éluants avec une teneur en HCl de $0{\cdot}5M$ et de $0{\cdot}25M$ HCl, donnent aussi lieu à un rapport β favorable, ils sont peu indiqués pour l'emploi sur colonne, les valeurs absolues des K_D étant trop élevées.

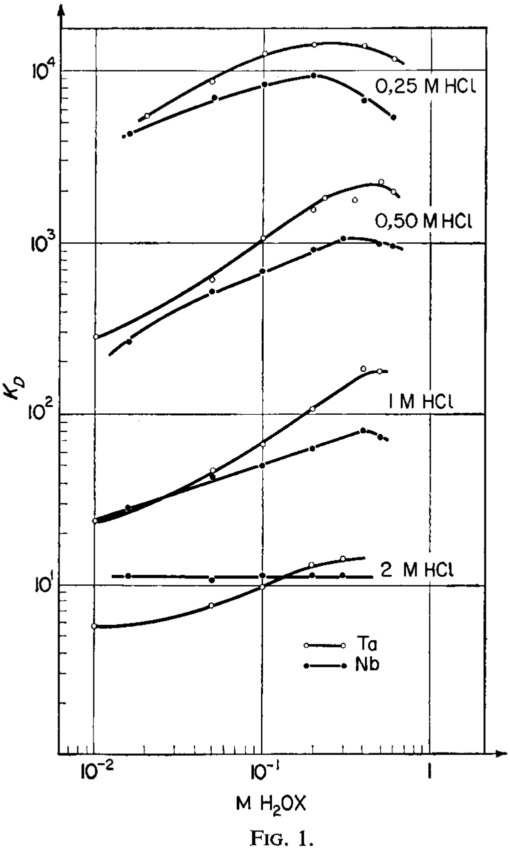

FIG. 1.

A l'aide des éluants proposés il apparait d'autre part qu'il est possible d'inverser l'ordre d'élution des deux éléments. Ceci semble particulièrement important pour la séparation de traces de tantale dans le niobium et vice versa.

Appareillage

Le schéma de l'appareillage pour contrôler la séparation sur colonne est representé dans la Fig. 2. Il consiste essentiellement d'un tube en verre à double paroi contenant la résine, et pouvant être raccordé à un thermostat. Un rodage sphérique relie la colonne à une spirale capillaire au dessus de laquelle se place le détecteur à scintillation, raccordé à un débit-mètre et à un enregistreur.

Le volume de l'eluant est mesuré par comptage électronique des gouttes. Chaque goutte donne en outre une impulsion sur la courbe enregistrée. Pour des volumes d'élution relativement grands, le compteur permet de ne donner qu'une impulsion par 50 gouttes, ce qui facilite la détermination des volumes d'élution et permet une vitesse d'enregistrement plus faible. Le compteur de gouttes a été décrit en détail ailleurs.[16] La résine employée était le Dowex 2, 100–200 mesh, conditionné par l'éluant. La vitesse d'élution était de 0·2 ml par minute. Pour l'éluant rapide, la section de la colonne était de 0·185 cm^2 tandis que la hauteur était environ 40 cm. Pour l'éluant lent la section était de 0·255 cm^2 et la hauteur environ 7·5 cm. Pour la détermination des constantes d'élution les volumes furent corrigés pour le volume mort entre la colonne et le détecteur.

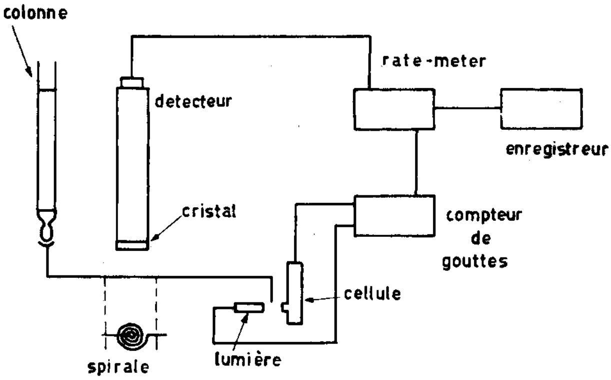

FIG. 2.

Calcul des constantes d'élution

Les constantes d'élution furent calculées d'après Kraus et Moore[1]:

$$E = \frac{dA}{V_{\max}}$$

$$E = \frac{1}{D + i}$$

$$K_D = \rho D \tag{2}$$

E = constante d'élution
d = longueur de la colonne en cm
A = section de la colonne en cm^2
$V_{\max}$ = volume où la concentration maximale est éluée
D = constante de distribution sur colonne
i = fraction de la colonne non occupée par la résine
ρ = volume de la colonne occupé par 1 g de résine.

Les constantes de distribution calculées à partir des expériences sur colonne furent trouvées en parfait accord avec les constantes de distribution déterminées par équilibrage:

éluant rapide	$\rho \, . \, D_{\mathrm{Nb}} = 11\cdot1$	$K_{D_{\mathrm{Nb}}} = 11\cdot2$
	$\rho \, . \, D_{\mathrm{Ta}} = 5\cdot0$	$K_{D_{\mathrm{Ta}}} = 5\cdot6$
éluant lent	$\rho \, . \, D_{\mathrm{Nb}} = 74\cdot1$	$K_{D_{\mathrm{Nb}}} = 74\cdot2$
	$\rho \, . \, D_{\mathrm{Ta}} = 179$	$K_{D_{\mathrm{Ta}}} = 181$

Les Fig. 3 et 4 montrent que pour les conditions expérimentales décrites ci-dessus la séparation niobium-tantale est quantitative.

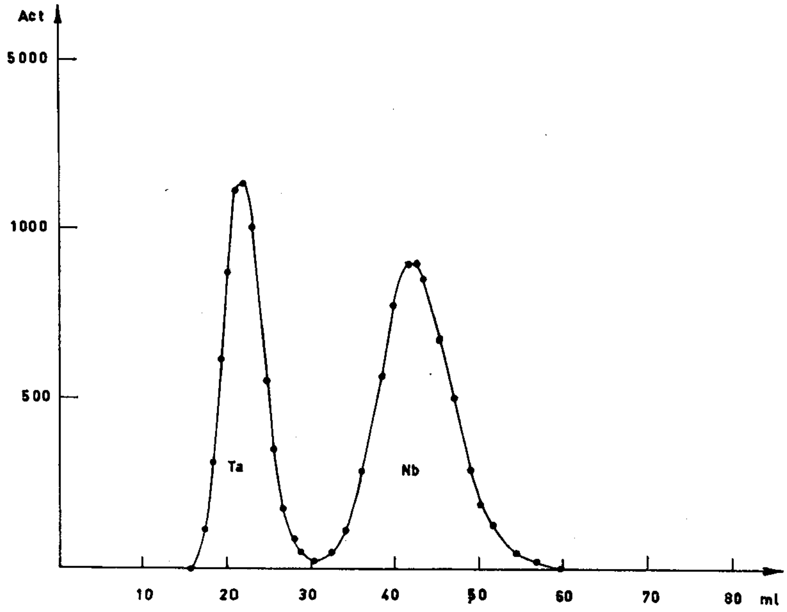
Act
5000
1000
500
Ta
Nb
10
20
30
40
50
60
70
80 ml

FIG. 3.

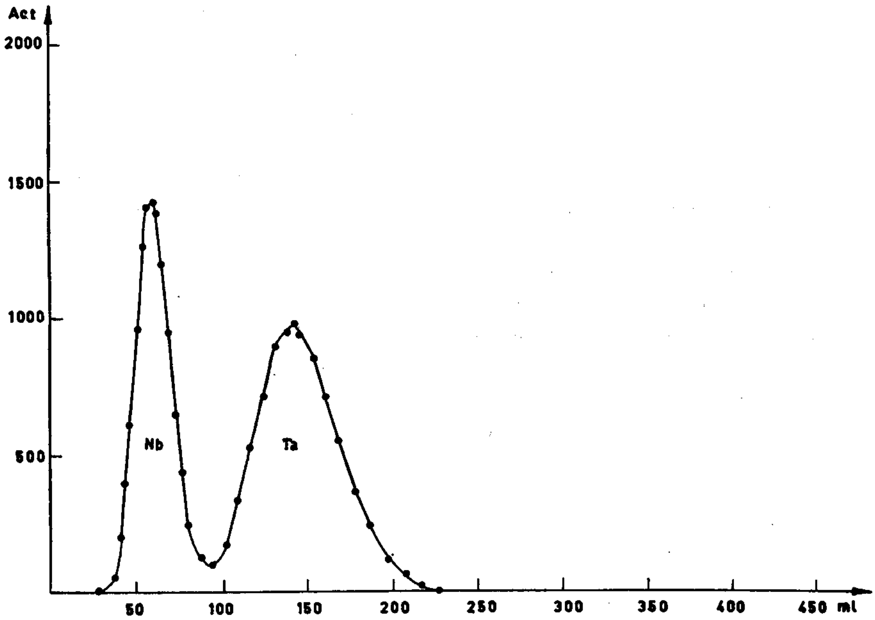
Act
2000
1500
1000
500
Nb
Ta
50
100
150
200
250
300
350
400
450 ml

FIG. 4.

RÉSULTATS ET DISCUSSION

Influence de la température

Pour les deux éluants mentionnés ci-dessus, la séparation niobium-tantale fut étudiée en fonction de la température, notamment de 15 à 45°. Les résultats sont résumés dans les Tableaux I et II.

TABLEAU I.—INFLUENCE DE LA TEMPÉRATURE (ÉLUANT RAPIDE).

$t°$	*d, cm*	*A*, cm^2	E_{Nb}	E_{Ta}	β	HEPT	
						Nb	Ta
15°	43·6	0·185	0·174	0·389	2·55	1·0	1·4
25°	43·6	0·185	0·204	0·402	1·97	0·59	0·69
35°	44·0	0·185	0·232	0·421	1·81	0·45	0·62
45°	44·6	0·185	0·257	0·457	1·78	0·41	0·58

TABLEAU II.—INFLUENCE DE LA TEMPÉRATURE (ÉLUANT LENT).

$t°$	*d, cm*	*A*, cm^2	$E_{Nb} \cdot 10^2$	$E_{Ta} \cdot 10^2$	β	HEPT	
						Nb	Ta
15°	7·75	0·255	3·04	1·18	2·58	0·31	0·30
25°	7·75	0·255	3·41	1·41	2·42	0·24	0·23
35°	7·75	0·255	3·60	1·56	2·31	0·18	0·16
45°	7·75	0·255	4·05	1·87	2·17	0·13	0·10

Il apparaît que pour les deux éluants le rapport β des constantes d'élution devient moins favorable à mesure que la température augmente. Les courbes d'élution montrent cependant que la séparation la plus favorable à l'aide de l'éluant rapide est obtenue à une température de 25°, tandis que la séparation la plus favorable à l'aide de l'éluant lent est obtenue à une température de 45°. Ceci est dû au fait que deux facteurs compétitifs déterminent la séparation, notamment le rapport β et la hauteur équivalente d'un plateau théorique (HEPT).

Ce dernier se laisse calculer approximativement d'après Verzele et Alderweireldt[17]

$$\text{HEPT (en cm)} = \frac{d\,B^2(K+1)}{18{\cdot}5} \tag{3}$$

où

$$B = \frac{V_{10}}{V_{\max}}$$

$$K = \frac{V_0}{V_{\max} - V_0} \cdot \frac{V_{\text{résine}}}{V_0}$$

V_{10} = volume total de toutes les fractions d'une bande éluée contenant plus de 10% de la concentration maximale.

$V_0 = d\,Ai$

Le rapport entre la constante de distribution K d'après Verzele et Alderweireldt et la constante d'élution d'après Kraus et Moore est par conséquent donné par (4):

$$K = \frac{E(1 - i)}{1 - Ei} \tag{4}$$

Comme l'ont démontré Verzele c.s.[18] le HEPT est fonction de la constante d'élution. Les valeurs HEPT calculées d'après les courbes d'élution du niobium et du tantale ne sont donc pas identiques, la différence étant surtout sensible pour l'éluant rapide.

Il apparait toutefois que les HEPT pour les deux élements se comportent de façon analogue. Dans le cas de l'éluant rapide le HEPT décroit d'environ 50% en passant de 15° à 25°, pour rester à peu près constant à partir de cette température. Il s'en suit que la meilleure séparation est obtenu à 25°. Pour l'éluant lent le HEPT décroit de manière continue de 15° à 45°, tandis que la diminution du rapport β est relativement faible. La meilleure séparation est par conséquent obtenue à une température de 45°.

Influence de la charge de la colonne

Afin d'étudier l'influence de la charge de la colonne, des quantités croissantes de niobium et de tantale furent introduite au sommet de la colonne (absorbés sur environ 50 mg de Dowex 2).

Les résultats sont résumés dans les Tableaux III et IV.

TABLEAU III.—INFLUENCE DE LA CHARGE (ÉLUANT LENT).

	Quantité introduite, *mg*	Quantité éluée, *mg*
Ta	9·8	9·4
	15·3	14·4
	28·5	27·8
Nb	14·7	13·9

TABLEAU IV.—INFLUENCE DE LA CHARGE (ÉLUANT RAPIDE).

	Quantité introduite, *mg*	Quantité éluée, *mg*
Nb	0·5	0·47
	3·0	2·84
	8·9	8·3
Ta	0·040	0·039
	0·22	0·073
	1·84	0·33
	18·1	1·63

Pour l'éluant lent l'élution du tantale et du niobium est donc pratiquement quantitative, même pour des charges relativement élevées.

Pour l'éluant rapide au contraire, l'élution du tantale n'est quantitative que pour une charge de tantale extrèmement faible, tandis que le comportement du niobium est normal. Cet éluant semble donc surtout indiqué pour séparer des traces de tantale du niobium.

Influence du pourcentage de copolymère

Plusieurs auteurs[19–21] ont démontré que le pourcentage de divinylbenzène (DVB) d'une résine du type Dowex 1 ou Dowex 2 influence fortement le pouvoir séparateur.

La résine Dowex 2 employée pour les recherches décrites ci-dessus était d'un type industriel dont le % en DVB n'était pas indiqué par le fabricant. D'après ses propriétés, il semble qu'il soit d'environ 8 %.

Il nous a semblé utile d'étudier le comportement des différents Dowex disponibles, notamment le Dowex 1–X2, –X4, –X8 et –X10 et le Dowex 2–X4, –X8 et –X10 (100–200 mesh).

Les résultats sont résumés dans le Tableau V et le Tableau VI.

TABLEAU V.—INFLUENCE DU % DVB (ÉLUANT RAPIDE).

Résine	ρ	E_{Nb}	E_{Ta}	β	HEPT		Δ (d = 40 cm)
					Nb	Ta	
Dowex 1X1	4·84	0·293	0·545	2·03	0·41	1·0	+2·8
X2	3·62	0·206	0·403	2·06	0·53	0·79	+4·5
X4	2·67	0·155	0·323	2·16	0·48	0·62	+8·6
X8	2·03	0·121	0·288	2·47	0·53	0·80	+14·0
X10	1·89	0·131	0·312	2·48	1·3	1·8	+2·4
Dowex 2X4	2·83	0·157	0·330	2·22	0·38	0·58	+9·6
X8	2·11	0·145	0·323	2·35	0·91	1·4	+4·2
X10	2·05	0·149	0·332	2·39	1·5	1·9	−2·1

TABLEAU VI.—INFLUENCE DU % DVB (ÉLUANT LENT).

Résine	ρ	E_{Nb}	E_{Ta}	β	HEPT		Δ (d = 10 cm)
					Nb	Ta	
Dowex 1X1	4·84	0·1011	0·0649	1·56	0·25	0·28	−9·5
X2	3·61	0·0687	0·0450	1·53	0·26	0·24	−11·3
X4	2·67	0·0375	0·0213	1·76	0·23	0·24	−8·1
X8	2·03	0·0167	0·0076	2·36	0·17	0·20	+56·6
X10	1·89	0·0163	0·00674	2·47	0·27	0·33	+18·2
Dowex 2X4	2·83	0·0300	0·0150	2·00	0·19	0·14	+17·4
X8	2·11	0·0199	0·0086	2·34	0·24	0·23	+27·9
X10	2·05	0·0170	0·0068	2·50	0·33	0·32	+20·5

Le Tableau V montre que, pour l'éluant rapide, un pourcentage croissant en DVB améliore le facteur de séparation β qui passe de 2·03 à 2·48 pour les Dowex 1 et de 2·22 à 2·39 pour les Dowex 2. Le HEPT par contre est du même ordre de grandeur pour le Dowex 1–X1, –X2, –X4 et –X8, notamment de 0,65 cm en moyenne, pour atteindre 1·55 cm pour le Dowex 1–X10. Pour le même éluant par contre, le HEPT des résines du type Dowex 2 croît de façon continue à mesure que le % de DVB augmente.

Le Tableau VI confirme un phénomène analogue pour l'éluant lent, puisque le facteur de séparation β passe de 1·56 à 2·47 pour les Dowex 1 et de 2·00 à 2·50 pour les Dowex 2. Le calcul des HEPT démontre cependant que pour les Dowex 1, le HEPT est minimum pour le Dowex 1–X8, tandis qu'il augmente de manière continue en fonction du % de DVB, dans le cas des Dowex 2.

Il s'en suit donc que la meilleure séparation sur colonne n'est pas nécessairement obtenue à l'aide de la résine donnant le rapport des constantes de distribution le plus favorable.

Pour comparer le pouvoir séparateur des différentes résines, il est évidemment nécessaire d'employer des colonnes de longueur identique, ce qui est difficile à réaliser en pratique. A partir des valeurs expérimentales $V_{\max}$ et V_{10}, nous avons calculé les valeurs de $V'_{\max}$ et V'_{10} correspondant respectivement à une longueur de colonne de 40 cm pour l'éluant rapide et de 10 cm pour l'éluant lent.

On démontre aisément que

$$V'_{\max} = V_{\max}\frac{d'}{d}$$

et que

$$V'_{10} = V_{10}\sqrt{\frac{d'}{d}}$$

L'équation (3) montre que la concentration du premier élément élué n'atteint plus que 10 % de la concentration maximale, aprés avoir passé un volume de $(V'_{\max_1} + \frac{1}{2}V'_{10_1})$ dans la colonne, ce qui correspond à une élution de 98·4 % du total introduit. Lorsque le volume élué atteint $(V'_{\max_2} - \frac{1}{2}V'_{10_2})$ la concentration du second élément aura atteint 10 % du maximum, correspondant à 1·6 % de la quantité totale introduite du second élément.

Il est évident que la valeur

$$\Delta = (V'_{\max_2} - \tfrac{1}{2}V'_{10_2}) - (V'_{\max_1} + \tfrac{1}{2}V'_{10_1})$$

est un critère pour l'efficience de la séparation. Pour $\Delta = 0$, nous savons en effet que de $(V'_{\max_1} + \frac{1}{2}V'_{10_1})$ ml à $(V'_{\max_2} - \frac{1}{2}V'_{10_2})$, l'éluant contiendra 1.6% du premier èlément, melange à une quantité égale du second élément. Le degré de contamination sera donc plus faible à mésure que la valeur de Δ augmente et vice versa.

Il apparait que parmi toutes les résines étudiées, la meilleure séparation est obtenu à l'aide du Dowex 1–X8, pour les deux éluants considérés.

Les auteurs remercient le Professeur Z. Eeckhaut pour de nombreux changes de vue fructueux.

Les recherches décrites ci-dessus furent subsidiées par l'Union Minière du Haut Katanga et par l'Institut Interuniversitaire des Sciences Nucléaires.

Summary—The systematic study of the distribution coefficients of niobium and tantalum have allowed the discovery of two eluents giving satisfactory separation, in a hydrochloric-oxalic medium, on a column of anion-exchange resin of the type Dowex 1 or Dowex 2. The first eluent, $0{\cdot}01M$ oxalic acid + $2M$ HCl, removes the tantalum, whilst with the second ($0{\cdot}5M$ oxalic acid + $1M$ HCl) the order of elution is reversed. This is especially important in the determination of traces of tantalum in niobium and vice versa.

The authors have studied in detail the influence of temperature, and of the charge and the degree of cross-linking in the exchange resin.

Experience has shown that the best separation is obtained at a temperature of 25° with rapid elution, or 45° with slow elution. Among all the resins studied, Dowex 1-X8 gave the most favourable separation with both eluents.

Zusammenfassung—Das systematische Studium der Verteilungskoeffizienten von Niob und Tantal im Salzsäure-Oxalsäure-Medium in Anionenaustauschern vom Typ Dowex I oder 2 führte zur Elutionsmitteln, die eine zufriedenstellende Trennung gestatten. Der erste Eluent, 0,01 m Oxalsäure + 2 m HCl entfernt das Tantal, während mit dem zweiten (0,5 m Oxalsäure + 1 m HCl) die Elutionsreihenfolge umgekehrt ist. Dies ist von besonderer Wichtigkeit bei der Bestimmung von Spuren Tantal in Niob und umgekehrt.

Die Autoren haben den Einfluss der Temperature und des Vernetzungsgrades der Ionenaustauscher studiert.

Die Versuche zeigten, dass die besten Trennergebnisse bei 25°C bei rascher Elution oder bei 45° bei langsamer Elution erzielt werden. Von allen Kunstharzen gab Dowex 1-X8 die besten Trennungen mit beiden Eluenten.

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SOLVENTS FOR ULTRAVIOLET SPECTROPHOTOMETRY

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Summary—Mathematical relations are presented showing the effect of light absorption by the solvent on the absorption measurements. A simple modification in the silica-gel adsorption method of purifying *iso*octane is described that greatly improves the transmittance in the 2000 Å region. A procedure of purifying dioxan is also included.

THE ultraviolet absorption of most materials is determined by measuring the absorption of the sample dissolved in a transparent solvent. The ideal solvent is perfectly transparent through the desired spectral region, non-toxic, not too volatile, chemically inert towards the samples being examined and available at an adequate purity and at a reasonable price. Since the solvent often affects the details of the spectrum it is desirable to use a pure compound rather than a mixture so that the solvent can be clearly specified and readily duplicated.

Securing a solvent that is completely transparent through the desired spectral region is often difficult to realize. Fortunately the transmittance can be considerably less than 100% for most applications. The effects of using a solvent that has some absorption are listed below together with expressions relating the percent transmittance, T, of the solvent (for the cell length used in the measurement) to some aspect of the measurement. In deriving these relations it is assumed that the absorption measurements are made in the usual manner by comparing the absorption of a solution of the sample in one cell against the absorption of the solvent in another cell.

1. The transmittance of the solvent affects the signal to noise ratio, (S/N) and/or the slit width, W, according to the following equation in which it is assumed that the noise is proportional to the square root of the signal:

$$\frac{1}{W}\left(\frac{S}{N}\right) = k_1\sqrt{T}$$

where k_1 is a proportionality constant.

2. If the stray radiation is not significantly absorbed by the solvent, then the transmittance of the solvent affects the percentage of stray radiation, s, as follows:

$$s = \frac{k_2}{T}$$

where k_2 is a proportionality constant.

3. If there is a difference between the thickness of the sample cell and the solvent cell, any absorption by the solvent will cause an error in the absorbance measurement

according to the following expression:

$$\Delta A = (b_1 - b_2) \log \frac{100}{T}$$

where ΔA = the error in the observed absorbance
b_1,b_2 = the length in cm of the sample and solvent cells, respectively.
T = percent transmittance of the solvent in a 1-cm cell.

4. A high concentration of the sample in the solution will cause an error in the observed absorbance in accordance with the following expression:

$$\Delta A = -\frac{1}{D} \log \frac{100}{T}$$

where ΔA = the error in the observed absorbance
D = the ratio of the volume of the solution to the volume of sample.

5. A high concentration of sample in a solvent with significant absorption will also cause an error in the observed absorbance if there is sufficient interaction between the sample and the solvent to cause a change in the solvent absorption.

6. Absorbing impurities present in the solvent may react with the sample or with reagents used in preparing the solution for the measurement. Although the latter effect can be minimized by treating the portion of the solvent used in the reference cell in exactly the same manner as the solution of the sample, slight variations in the procedure can be a source of error.

The effects listed under items 1–3 do not become significant unless the transmittance of the solvent is considerably less than 100%. The first two effects are probably the most common. The magnitude of these two effects is largely dependent on the quality of the instrument being used for the measurement. Since double monochromators generally have higher resolving power and lower stray radiation than single monochromators, such instruments can tolerate a less transparent solvent.

The effects listed under items 4 and 6 can cause a significant error even if the transmittance of the solvent is only slightly less than 100%. Fortunately these conditions are seldom encountered. The condition mentioned in item 5 is also very unusual.

The above considerations show that it is impossible to set any definite specification on the transmittance of the solvent since its effect is dependent on such factors as the sharpness of the absorption peak in relation to the resolving power of the spectrophotometer, the percentage of stray radiation, the actual absorbance of the sample, the relative length of the two cells, the dilution factor and other details of the particular application.

If absorption measurements are to be made on a wide variety of samples, several different kinds of solvents must be available. The solvents most commonly used in this laboratory for ultraviolet spectrophotometry include water, methanol, chloroform, dioxan and *iso*octane. A mixture of equal parts of dioxan and *iso*octane is used more than pure dioxan in order to reduce the consumption of the more expensive dioxan. In addition, this mixture is a better solvent for some materials than either solvent alone.

Fig. 1 shows absorption curves for all of these solvents, except water, of typical quality as used in these laboratories. The source of these solvents together with the details of any purification required is described in the following sections.

SOURCE AND PREPARATION OF SOLVENTS

Water

The transmittance of ordinary distilled water in a 1-cm cell should be very close to 100% through the spectral region from 4000 Å to 1900 Å. Water is commonly used as the standard of comparison for checking the transmittance of other solvents.

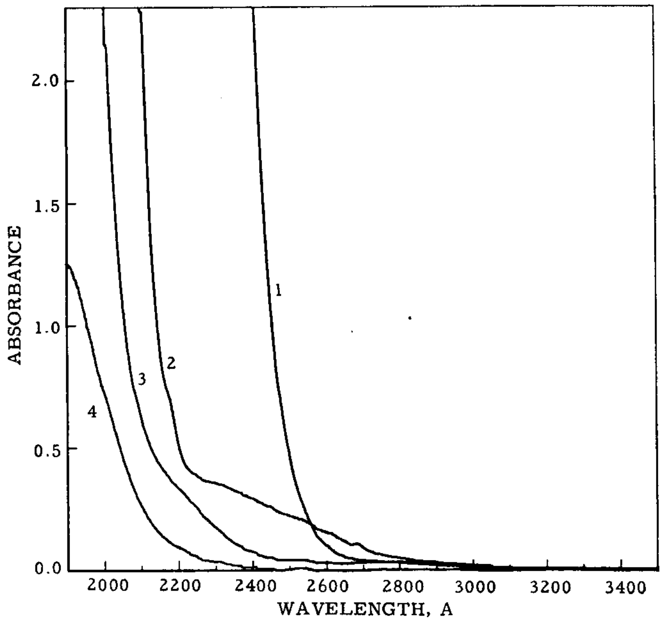

FIG. 1.—Absorption of solvents of typical quality in 1.00 cm cell.
1. Chloroform
2. Dioxan
3. Methanol
4. *iso*Octane

However, checking the transmittance of water, or of any other standard, presents a problem since this must be done on an absolute basis rather than by comparison with another material that is completely transparent. This can be accomplished by comparing the absorption spectrum of the solvent and cell to the absorption of the empty cell. If the solvent has no absorption the absorbance of the solvent and the cell should be a nearly constant amount less than the absorbance of the cell alone. Any increase in the relative absorbance of the filled cell above that observed in a region where the solvent is known to be transparent can be attributed to solvent absorption. Fig. 2 shows a check of this type on the absorption of distilled water and ordinary tap water. It will be noted that the distilled water shows no significant absorption above 2000 Å whereas the tap water shows slight absorption at 4000 Å which steadily increases at the shorter wave lengths.

Methanol

The U.S.P. grade of methanol is usually satisfactory for use in a 1-cm cell down to about 2100 Å. Although methanol is preferred because of its availability, some grades of ethanol may be satisfactory. Absolute ethanol prepared by removing the water in an azeotropic distillation with benzene is satisfactory if it does not contain too much benzene. The 3A grade of alcohol prepared by denaturing absolute ethanol with 5% of methanol may be satisfactory subject to the same limitations.

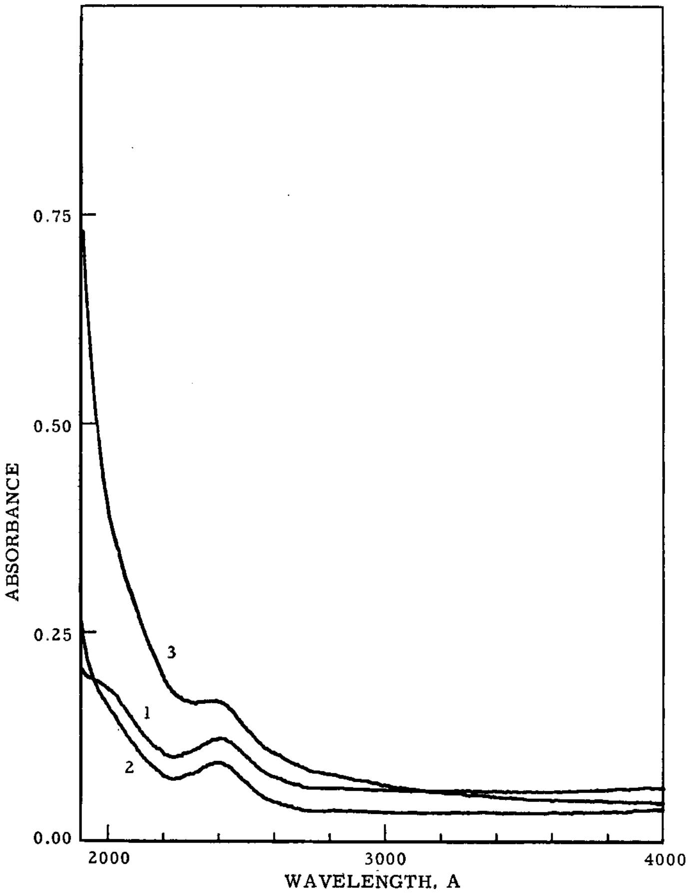

FIG. 2.—Test for a transparent solvent
1. Empty 1.00 cm cell
2. Cell filled with distilled water
3. Cell filled with tap water

Chloroform

The U.S.P. grade of chloroform is usually satisfactory down to 2500-2600 Å in a 1-cm cell without further purification.

Dioxan

Dioxan requires considerable purification before it is satisfactory for use as an ultraviolet solvent. The principal impurities affecting the ultraviolet transmittance of commercial grades are believed to be benzene, acetaldehyde, and unsaturated aldehydes. The unsaturated aldehydes are particularly objectionable since concentrations of a few parts per million considerably reduce the transmittance through a 1-cm cell. Although acetaldehyde does not have such strong absorption, it can condense and dehydrate yielding unsaturated aldehydes. The starting material for the purification described below has been a technical grade of dioxan obtained from Carbide and Carbon Company. The unsaturated impurities are removed by refluxing with aqueous alkaline permanganate. After the reaction is complete the water is salted out with sodium hydroxide and the dioxan distilled. A 20-plate distillation column has been found to be quite adequate for the distillation. This is operated at a 20 to 1 reflux ratio until the lower boiling impurities have been eliminated and then the reflux ratio reduced to 10 to 1 or 5 to 1 for the balance of the distillation.

Purification procedure

Place the dioxan in a distillation flask equipped with a reflux condenser and a means of regulating the addition of the alkaline permanganate. Heat the dioxan until refluxing commences and then start adding the permanganate reagent which contains 40 g of sodium hydroxide and 60 g of potassium permanganate per litre of water. Add the reagent fairly rapidly but not so fast that the mixture is cooled so much that the dioxan stops boiling (too low a temperature will permit the concentration of unreacted permanganate to build up and this will cause a very vigorous reaction if the temperature is increased). Add a volume of the alkaline permanganate equal to one-half of the volume of dioxan being treated. Reflux for 15 min after the addition of the last of the reagent and then cool to room temperature.

Decant the dioxan off from the bulk of the manganese dioxide (or filter) and then saturate with sodium hydroxide. Separate the dioxan layer and charge to the distillation column with a little solid sodium hydroxide and distil. The first cuts from the distillation will contain the benzene and the residual water in the form of a dioxan-water azeotrope boiling at 88°. Examine the ultraviolet absorption spectra of the cuts obtained on the dioxan flat and save all those which show a satisfactory transmittance. Most of the cuts obtained after elimination of the benzene should be suitable for use as an ultraviolet solvent. Store the purified dioxan under an inert atmosphere in order to reduce the rate of peroxide formation. A distillation from solid sodium hydroxide will clean up material that has deteriorated through air oxidation.

iso*Octane*

*iso*Octane is commercially available in a specially purified grade for use as an ultraviolet solvent. Since this grade is rather expensive, it is more economical to purify a cheaper grade whenever considerable solvent is required. The ASTM, Knock Test Reference Fuel *iso*octane sold by Phillips Petroleum Company is a satisfactory and relatively inexpensive starting material. A simple percolation through silica gel is satisfactory for use in a 1-cm cell down to about 2150 Å. However, residual traces (probably less than 0.1 %) of highly branched olefin cause considerable absorption at shorter wavelengths. These low concentrations of olefins are not readily removed by a simple treatment with silica gel. However a combination of a simple chemical treatment and a silica-gel percolation is quite effective. The chemical treatment is based on the reaction of nitrogen tetroxide with olefins[1] to form nitrosates which are adsorbed on silica gel. The excess nitrogen tetroxide is preferably removed by treatment with some alkaline reagent such as Ascarite prior to the silica gel treatment. The usual practice is to prepare two 1-gallon batches at

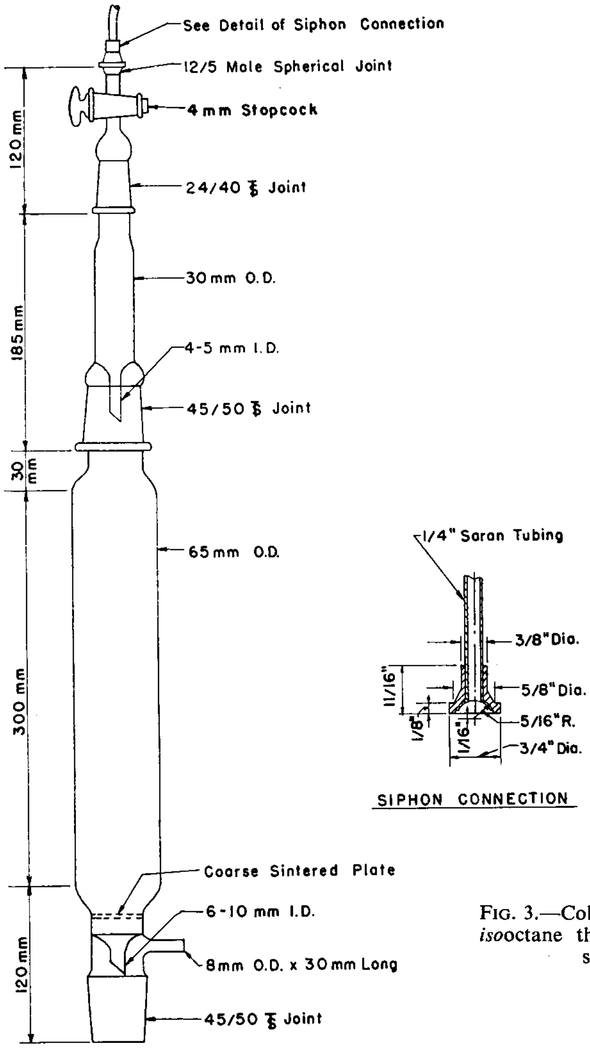

FIG. 3.—Column for percolating *iso*octane through ascarite and silica-gel.

the same time. The adsorption column used for the purification is shown in Fig. 3. It is identical to the column described previously[2] for treating *iso*octane except that a small tube for Ascarite has been added to the top.

Purification procedure

Prepare the nitrogen tetroxide required for the treatment ahead of time by sealing 2 g (1.4 ml) in each of a series of glass tubes. To accomplish this, first condense nitrogen tetroxide vapour from a cylinder in a cold trap immersed in ice water. (Tygon tubing can be used for connecting the cold trap to the cylinder). Then pour the desired quantity of liquid into 8-mm I.D. × 30-cm long glass tubes, also immersed in ice, and seal off the upper end. Store the sealed tubes in a cold chest at a temperature at which the nitrogen tetroxide solidifies in order to reduce danger of accidental loss when the tube is broken open. Pour the entire contents of one of the nitrogen tetroxide tubes into each gallon of the Phillips *iso*octane specified previously.

Charge the small upper tube of the silica-gel column with approximately 60 g of Ascarite and the lower tube with about 500 g of 28-200 mesh silica gel. (This charge is adequate to treat two gallons of *iso*octane.)

Allow the *iso*octane-nitrogen tetroxide mixture to stand for at least 30 minutes and then syphon the solution into the top of the column of Ascarite and silica gel.

The effluent from the column is ready for use. It should be satisfactory down to about 2100 Å in a 1-cm cell and to about 1900 Å in a 0.1-cm cell. The analytical method for determining olefins[1] upon which this procedure is based, recommends cooling the material in ice before adding the nitrogen tetroxide in order to avoid any danger of too vigorous a reaction. Although this precaution seems unnecessary in this instance where the olefin concentration is very low, this procedure should be applied with caution to the treatment of other materials that may be more reactive.

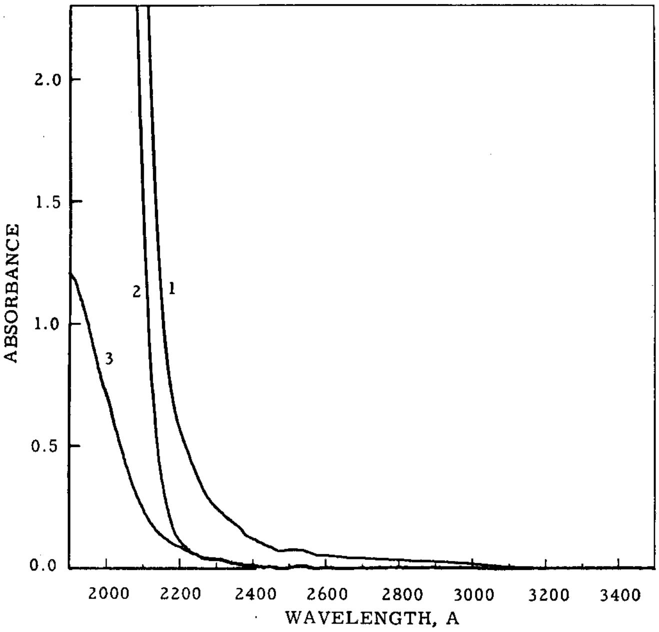

Fig. 4.—Purification of *iso*octane Absorption in 1.00 cm cell vs. distilled water

1. Original *iso*octane
2. Product from silica-gel treatment
3. Product from N_2O_4 plus silica-gel treatment

Fig. 4 shows the relative absorption of the original unpurified *iso*octane and the products obtained by silica gel treatment only and by treatment with nitrogen tetroxide, Ascarite and silica gel.

Zusammenfassung—Mathematische Berechnungen zeigen den Einfluss des Lösungsmittels auf die Lichtabsorption bei Absorptionsmessungen. Eine einfache Modifikation der Silikagelmethode zur Reinigung von Iso-Octan, welche eine Verbesserung der Durchlässigkeit bei 2000 Å zeigt, wird beschrieben, ebenso ein Verfahren zum Reinigen von Dioxan.

Résumé—L'auteur présente des relations mathématiques montrant l'effet de l'absorption de la lumière par le solvant sur les mesures d'absorption. Il décrit une modification simple de la méthode d'adsorption par le silica-gel pour la purifications de l'*iso*-octane, ce qui améliore beaucoup la transmission dans la région de 2000 Å. Le mémoire comprend aussi un procédé de purification du dioxane.

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THE FORMAL OXIDATION POTENTIALS OF SUBSTITUTED 1:10—PHENANTHROLINE FERROUS COMPLEXES OF LOW SOLUBILITY

THE PREPARATION AND REDOX POTENTIALS OF THE VANADATE-VANADYL SYSTEM OF POTENTIOPOISED SOLUTIONS

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Summary—The preparation of oxidation potentiopoised reference solutions is described. The oxidation potentials provided are stepwise in augmented values over the range 0.9 to 1.23 volt. The vanadate-vanadyl system is employed. The magnitude is dependent upon the increase in sulphuric acid formality over the range 0.1 to 6.0 formal. These solutions are of the potential buffered type. Their use in the determination of redox potential of a series of the ferrous complexes of a series of substituted 1:10-phenanthrolines is described. The accuracy attained is of the order 3% or less, compared to standard values following the potentiometric titration procedures. The determinations are outstanding in rapidity.

INTRODUCTION

MANY of the available and previously investigated ferrous complex anions formed by substituted 1:10-phenanthrolines are of low solubility in acid aqueous solvents. This fact does not inhibit their use as redox indicators. Solutions of 10^{-5} or less in indicator concentration are of sufficient colour intensity to serve. The usual potentiometric determination of their oxidation potential, even on a micro-analytical scale, is not without difficulty. Attaining of equilibrium potentials only at unreasonable time intervals at equivalence points is unavoidable. Their oxidation potentials are closely related to the pK_a of the nitrogens of their functional group. This is an added observation of theoretical interest to be substantiated. Other colligative property relationships as a function of the nature and position of substitution in the parent ligand are associated with the oxidation potential.

The application of the principle of the use of potentiopoised reference solutions for determination of redox potentials is thought to be new. It is rapid, adequately precise by comparison with the use of conventional methods of potentiometric evaluation, and economical in reagent consumption.

EXPERIMENTAL

Preparation of potentiopoised solutions and 1:10-*phenanthroline ferrous complexes*

The vanadate-vanadyl couple is pH dependent. The values range from 0.9 to 1.25 volts in 0.1 to 6.0 formal sulphuric acid. The increase in potential is linear between 0.5 to 6.0 formal acid concentration. Equi-molecular vanadate-vanadyl potentiopoised solutions were prepared as follows:

1. Eighteen grams of vanadyl chloride was dissolved in 360 ml of $0.5F$ sulphuric acid. 100 ml of this solution were transferred to a 250-ml volumetric flask. An equal portion was treated by addition of excess ammonium persulfate to oxidize V^{IV} to V^{V}. Excess oxidant was removed by boiling. The vanadate solution was then added to the vanadyl solution. The flask contents were then diluted to volume with $0.5F$ sulphuric acid. This solution was $0.14F$ in both V^{V} and V^{IV} and $0.5F$ in sulphuric acid. Five-ml portions of this solution were diluted with water and requisite sulphuric acid to make 500-ml volume. This solution was $0.1F$ in sulphuric acid and $0.0014F$ in vanadate and vanadyl ions.

A series of similarly prepared solutions of $0.10F$ to $6.00F$ in sulphuric acid, and $0.0014F$ in vanadate-vanadyl ions with gradual increase in acid formality in 25 steps were prepared. Such solutions bear but a faint tinge of colour. Equal concentration of the vanadium ions provided maximum potentiopoised capacity.

2. A weighed amount of Mohr's salt was dissolved in 0.0005F sulphuric acid to result in a 0.0023F ferrous ion concentration.

3. Solutions of complexing ligands (0.010F) in 95% ethanol were prepared.

4. The solutions 2 and 3 were mixed in equal 5-ml portions. The resulting ligand-ferrous complex solutions were 0.0012F and contained approximately 40% excess ligand.

TABLE I.—FORMAL POTENTIALS OF THE POTENTIOPOISED SOLUTIONS

H_2SO_4, F	E_0', *volts*	H_2SO_4, F	E_0', *volts*
0.10	0.910	3.0	1.103
0.30	0.934	3.3	1.110
0.40	0.940	3.5	1.120
0.50	0.975	3.8	1.132
0.75	0.993	4.0	1.143
1.0	1.008	4.3	1.160
1.3	1.018	4 5	1.182
1.5	1.030	4.8	1.189
1.8	1.047	5.0	1.193
2.0	1.056	5.3	1.206
2.3	1.072	5.5	1.211
2.5	1.089	6.0	1.226
2.8	1.095		

Determination of formal potentials of potentiopoised solutions

A. Leeds and Northrup student potentiometer and a platinum-saturated calomel electrode pair was employed. Approximately 40 ml of the potentiopoised solutions in 50-ml beakers served to determine their E.M F to the nearest millivolt Steady potentials were attained after 10 minutes. Duplicate values of the formal potentials (E_0') agreed in value within ±0.003 volt. The results are found in Table 1.

By graphical inspection, the values of Table I show a linear relationship between 0.5F and 6.0F sulphuric acid concentration, or an increase of 0.047 volt for each increase of one unit in formality.

Redox potential determination employing potentiopoised solutions

Ten-millilitre portions of the potentiopoised solutions were placed in 18- by 150-mm test tubes in the order of their increasing potential. Two drops of the 0.0012F ferrous complex to be tested were added to each of six consecutive solutions which were thoroughly mixed. One minute after the ferrous complex had been added, the colour remaining was recorded. The transition oxidation potential upon successive additions was observed. This was taken as the potential of the potentiopoised solution which effected a complete colour change of the complex. The value selected was established by interpolation between the solution in which the colour change was first complete and the next lower solution potential in which the colour of the reduced form of the complex was barely perceptible. A mid-point interpolation was made to establish E' values.

The point of visible colour change (red to very faint blue) corresponds to 90% oxidation. By using the expression $E_0' = E' - 0.6$ volt, the formal oxidation potential at a given sulphuric acid concentration was determined.

For the purpose of showing the adequacy of the procedure the method was applied to the ferrous complexes of 1:10-phenanthroline and its 5-nitro- and 5-methyl-substitution derivatives as well as to 2:2′-dipyridine. The formal oxidation potentials of the ferrous complexes of these four products have been previously determined by other procedures.[1] The results are given in Table II.

TABLE II.—A COMPARISON OF POTENTIOPOISED REFERENCE SOLUTION DETERMINATION OF REDOX POTENTIALS WITH PREVIOUS ACCEPTED VALUES

Iron^{II} complex of	Potentiopoised colorimetric		Literature reference values		Reference
	Acid formality, H_2SO_4	E_0' (volts)	Acid formality, H_2SO_4	E_0' (volts)	
1:10-Phenanthroline	2.2	1.00	2.0	1.03	(1)
	—	—	3.0	1.02	(1)
5-Methyl-derivative	1.6	0.98	1.0	1.02	(1)
	—	—	2.0	1.00	(1)
5-Nitro-derivative	5.4	1.15	4.0	1.12	(1)
	—	—	6.0	1.12	(1)
2:2′-Dipyridine	1.4	0.96	1.0	0.97	(1)
	—	—	4.0	0.92	(1)

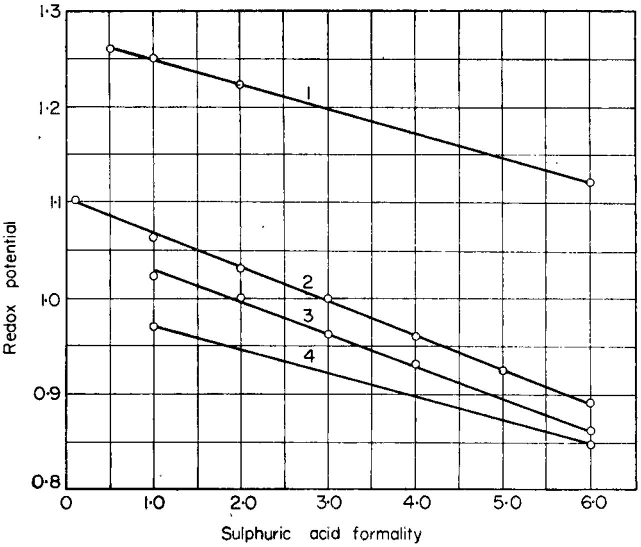

FIG. 1.—(1) 5-Nitro-1:10-phenanthroline-Fe^{II} ion.
(2) 1:10-Phenanthroline-Fe^{II} ion.
(3) 5-Methyl-1:10-phenanthroline-Fe^{II} ion.
(4) 2:2′-Dipyridyl-Fe^{II} ion.

The values of Table II show an agreement of from 0.00 volt to 0.03 volt between the exact values and those given graphically in Fig. 1. Such concordance is quite sufficient in utility for practical application. By reference to Fig. 1 the alteration in oxidation potential is seen to be linear with alteration in acid formality between 0.50 and 6.0. For the four reference standards the chief disadvantage of the procedure of the potentiopoised solution colorimetric estimation of redox potentials is its dependence upon the use of a particular acid formality. This limitation may be discounted provided the results given in Fig. 1 are assumed to be applicable in linearity over a wide range of acid formality as applied to other ferrous-1:10-phenanthrolines under consideration.

The concentration of the iron^{II} complexes in the potentiopoised solutions was approximately 10^{-5} formal. Even at this relatively low concentration a distinct colour (and hence colour change) was perceptible because of their large molecular extinction coefficients in absorption.

The formal oxidation potentials of 24 *substituted* 1:10-*Phenanthrolines*

The formal oxidation potentials of these phenanthrolines as their ferrous complexes were estimated using the above described procedure. The results are given in Table III. No difficulty was experienced in obtaining reproducible and duplicating results.

TABLE III.—COLORIMETRIC FORMAL OXIDATION POTENTIALS OF THE Fe^{II} COMPLEXES OF PREVIOUSLY UNDETERMINED 1:10-PHENANTHROLINES

1:10-Phenanthroline derivative	H_2SO_4 formality	E_0', volts	1:10-Phenanthroline derivative	H_2SO_4 formality	E_0', volts
5-fluoro-	3.2	1.05	3:7-dimethyl-	1.4	0.96
3-chloro-	4.4	1.11	3:8-dibromo-	5.4	1.21
3-phenyl-	2.4	1.02	4:7-dimethoxy-	0.1	0.85
3-ethyl-	2.1	1.00	4:7-diethyl-	0.9	0.94
4-bromo-	2.9	1.04	4:7-diphenoxy-	2.9	1.04
4-phenyl-	1.9	0.99	4:7-diphenyl-	4.6	1.13
4-ethyl-	1.4	0.96	4:6-diphenyl-	4.5	1.12
4-*n*-propyl-	1.4	0.96	5:6-*cyclo*hexeno-	1.4	0.96
3:4-*cyclo*penteno-	1.4	0.96	5:6-diethyl-	1.6	0.98
3:4-*cyclo*hexeno-	0.9	0.94	5:6-dimethoxy-	2.4	1.02
3:4-*cyclo*octeno-	1.0	0.95	5:6-dichloro-	4.4	1.11
(3:4)(7:8)-di*cyclo*-hexeno-	0.3	0.87	3:5:6-trimethyl-	1.0	0.95

GENERAL CONSIDERATIONS

The formal oxidation potentials of a large number of methyl substituted 1:10-phenanthrolines as their Fe^{II} complexes have been previously determined.[1] In all cases alterations in the determined values were additive and could be predicted with accuracy. A methyl substitution in the 4 or 7 position lowers the redox potential by a value 0.11 volt. The methyl group in the 3 or 8 position lowers the value 0.03 volt when compared with the unsubstituted ligand's Fe^{II} complex. A methyl group in the 5 or 6 position lowers the value by 0.04 volt.

These observations serve to validate some of the results of Table III. Thus it would be predicted that the Fe^{II} complex of the 3:5:6-trimethyl-1:10-phenanthroline would have the redox potential of 0.95 volt in formal sulphuric acid. By determination as above described the same value was found. For the 3:7-dimethyl complex the value found colorimetrically was 0.95 volt compared to 0.92 by calculation using the known value of the 1:10-phenanthroline ferrous complex as reference. The agreement to within a maximum deviation of 0.03 volt serves to define the limitations of the presently described procedure.

Relationship of redox potential of the ligand-Fe^{II} *complex to the* pK_a *value of the nitrogens of the ligand functional group*

If the stability constants of both the Fe^{II} and Fe^{III} complexes of a series of 1:10-phenanthrolines substituted in the same position are linearly dependent upon the basicity of the chelate ligand, then the formal oxidation potentials of the ferrous complexes should show linear relationship with the pK_a values of the ligands. This relationship has been demonstrated for the ferrous-phenanthroline complexes with nitro, methyl, bromo, or phenyl substitutents in the 5 position.

Using the known rate of diminution in the formal oxidation potential of the ferrous complex of 1:10-phenanthroline as a correction factor, the colorimetric formal oxidation potentials of the complexes in 1.0F sulphuric acid were estimated by applying the correction. These together with the pK_a value of the ligands are summarized in Table IV.

TABLE IV.—COLORIMETRIC FORMAL POTENTIALS RELATIVE TO LIGAND pK_a VALUES

Reference 4-number	1:10-Phenanthroline derivative	pK_a‡	Fe^{II} complex E_0' in 1.0F H_2SO_4
(9)	4:7-dimethoxy-	6.45	0.82
(6)	(3:4)(7:8)-di*cyclo*hexeno-	6.25	0.85
(6)	3:4-*cyclo*penteno-	5.78	0.97
(6)	3:4-*cyclo*octeno-	5.66	0.94
(7)	4:7-diethyl-	5.60	0.94
(1)	3:7-dimethyl-	5.57	0.97
(8)	4-*n*-propyl-	5.45	0.97
(7)	4-ethyl-	5.44	0.97
(9)	4:7-diphenoxy-	5.34	1.10
(1)	3:5:6-trimethyl-	5.34	0.95
(6)	5:6-*cyclo*hexeno-	5.30	0.97
—	5-methyl-	5.23†	0.99(1.02)*
(7)	3-ethyl-	4.98	1.03
(3)	4-phenyl-	4.90	1.02
—	1:10-phenanthroline	4.86	1.09(1.06)*
(3)	4:7-diphenyl-	4.84	1.24
(5)	3-phenyl-	4.82	1.06
(3)	4:6-diphenyl	4.69	1.23
(9)	5:6-dimethoxy-	4.42	1.06
(2)	4-bromo-	4.03	1.10
(4)	3-chloro-	3.99	1.21
(2)	3:8-dibromo-	3.90	1.28
—	5-nitro-	3.57†	1.28(1.25)*
(4)	5:6-dichloro-	3.47	1.21
(8)	5-fluoro-	—	1.12
(6)	3:4-*cyclo*octeno-	—	0.95
(7)	5:6-diethyl-	—	1.00

* Potentiometrically determined value. Ref. (1).
† Values of reference (2)
‡ Reference (3)

The results in Table IV indicate a direct relationship between ligand pK_a and the formal oxidation potential of its ferrous complex. Although the change is not linear the formal oxidation potentials of the complexes increase as the pK_a values decrease.

It is quite evident from the results in Table IV that the formal potentials for the complexes of 4:7-diphenoxy, 4:7-diphenyl and 4:6-diphenyl derivatives are not consistent with the potentials of the others in their pK_a value relationships. In all 3 cases the inconsistency amounts to approximately 0.15 volt.

It is probable that this apparent over-potential may be due to sluggishness in reaction kinetics for the oxidation of iron by the vanadium^{V} of the potentiopoised solutions. Since the dissociation of the Fe^{II} complexes and the rate of electron exchange with iron are very slight, the reaction mechanism probably involves electron transfer through the aromatic rings. Large substituent groups (phenyl and phenoxy) in the 4:6 and the 4:7 positions act as a shield in electron exchange when the complex is oxidized.

Proposed additional applications

The colorimetric potential determination should apply to such redox indicators as N-phenanthranilic acid, diphenylamine and its related derivatives. These redox indicators are not pH dependent.

For non-reversible dye indicators such as amaranth or others for use in iodate oxidations (improved to avoid the use of chloroform as extraction solvent for iodine or iodine monochloride) the method should serve for comparisons of indicator transition potentials.

All the 1:10-phenanthrolines, with but few exceptions, were synthesized in unequivocal processes by Professor Francis Case of Temple University in Philadelphia in co-operation with his associates.[4] Their syntheses have been described in current literature sources. This work on their analytical applications would otherwise not be possible.

Zusammenfassung—Die Bereitung "redox-beschwerter" Bezugslösungen wird beschrieben. Die Redoxpotentiale erstrecken sich stufenweise über einen Bereich von 0.9 bis 1.23 V. Das System Vanadate-Vanadyl wird verwendet. Das Potential hängt im Bereiche 0.1– 6.0 formal vom Anstieg der Schwefelsäurekonzentration ab. Diese Lösungen sind vom Typ Potentialpuffer. Ihr Gebrauch bei der Bestimmung von Redoxpotentialen einer Reihe von Ferrokomplexen substituierter 1,10-phenanthroline wird beschrieben. Die Genauigkeit ist etwa 3 Prozent (oder sogar weniger) geringer im Vergleich mit der auf potentiometrischer Titration basierenden Standardmethode. Die Bestimmung der Potentiale benötigt aussergewöhnlich kurze Zeit.

Résumé—Les auteurs décrivent la préparation de solutions de référence tamponnées en potentiel. Les valeurs des potentiels d'oxydation fournis augmentent graduellement dans le domaine de 0,9 à 1,23 volt. On emploie le système vanadate-vanadyl. La valeur du potentiel augmente avec la concentration de l'acide sulfurique dans le domaine 0,1 à 6 N. Ces solutions sont du type tamponnées en potentiel. On décrit leur utilisation dans la détermination des potentiels d'oxydo-réduction d'une série de complexes ferreux avec les 1-1 ortho-phenanthrolines substituées. La précision obtenue est de l'ordre de 3% au moins comparée aux valeurs standard obtenues à partir des procédés de titrage potentiométriques.

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THE SEPARATION AND DETERMINATION OF NICKEL, CHROMIUM, COBALT, IRON, TITANIUM, TUNGSTEN, MOLYBDENUM, NIOBIUM AND TANTALUM IN A HIGH TEMPERATURE ALLOY BY ANION-EXCHANGE

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Summary—An anion-exchange method of separating the constituents in high temperature alloys has been devised. Nine elements including titanium, tungsten, molybdenum, niobium and tantalum are determined in an alloy on a single sample weight. Any combination of the elements mentioned above may be determined in steels and high temperature alloys with a simple ion-exchange scheme suitable for routine analysis.

THE separation of mixtures of titanium, tungsten, molybdenum, niobium and tantalum by classical methods is one of the most difficult problems in metallurgical analysis. It is not unusual to have these elements as alloying constituents in high temperature alloys. In addition, high temperature alloys usually contain cobalt, nickel, chromium and iron in varying proportions. The classical methods for the separation of titanium, tungsten, molybdenum, niobium and tantalum consist of numerous precipitations which are strongly influenced by the presence or absence of the other elements. Some of the precipitations must be repeated several times in order to obtain satisfactory results. Attempts to analyze these alloys by instrumental means have not been particularly successful. As a result the chemical analysis of the alloying constituents of these materials requires time-consuming work by an experienced analyst.

After a few rather frustrating experiences with alloys of this type, it became apparent that a simplified procedure was desirable in which the presence or absence of a particular element would not alter the procedure appreciably.

Since the author had already made successful applications of ion-exchange resins to other problems in metallurgical analysis,[2,4] a similar approach was selected for the analysis of high temperature alloys. It has already been demonstrated that the separation of some of the refractory elements is possible in mixed HCl–HF medium on strongly basic anion-exchange resins.[1]

Preliminary experiments were based on the precipitation of the refractory metal oxides as a group followed by the ion-exchange separation of the individual elements. This approach was not particularly successful. The difficulty in the method appeared to be in the incomplete precipitation of the oxides. In addition the dissolution of the oxides by a pyrosulphate fusion introduced an amount of salts which caused difficulty in the ion-exchange separations. In view of these difficulties it became apparent that the ideal solution to the problem would be to introduce the entire sample into the ion-exchange column. Several mixtures of HCl–HF were used with some success. However, the most successful medium was found to be a dilute HF solution. If the dilute HF solution of the sample is passed through an anion-exchange resin and eluted with 2.5% HF, the sample constituents are divided into two distinct groups and may be treated separately. The column retains titanium, tungsten, molybdenum, niobium and tantalum and the eluate contains nickel, manganese, aluminium, chromium, cobalt and iron. Subsequent experiments were based on this preliminary separation of the sample into two groups. The refractory elements were separated by successive elutions with various acid solutions and the elements in the 2.5% HF eluate were subjected to a second column separation after evaporation to dryness with hydrochloric acid.

EXPERIMENTAL

Column preparation

The ion-exchange column consisted of 16-inch lengths of one-inch ID polystyrene tubing with a one-quarter inch wall. The lower end of the column was closed off with a section of Lucite rod with three-sixteenths inch hole drilled through its axis. A section one inch long on the end of the Lucite rod is machined down to a three-eighths inch diameter so as to permit the connection of a short length of polyethylene tubing to the column. The other end of the Lucite rod, which is glued to the bottom of the column, is machined so as to have a 45° taper from the one-inch ID of the column to the three-sixteenths inch diameter hole through the rod. This taper eliminates the hold up of the eluted species in the "corner" at the bottom of the column. A short length of quarter inch polystyrene tubing is inserted into the wall of the column about two inches from the top. This piece of tubing allows the connection of the column to an overhead gravity feed by means of polyethylene tubing. The top of the column is sealed with a rubber stopper when the overhead gravity feed is in use. The top of the column should also be threaded and capped with a threaded Lucite cap. This prevents the inadvertent removal of the rubber stopper during the elution. The resin bed is supported by means of a layer of Teflon shavings.

The column is filled with 80 grams of a strongly basic anion-exchange resin, 200–400 mesh, chloride form, after the fine particles are removed from the resin by means of several decantations with water. This quantity of resin will give a column bed 8 in. long which is adequate for the separations in the procedure given below. A $\frac{7}{8}$ in. polyethylene sphere inserted in the column serves to maintain a level surface in the resin bed. Without the sphere the introduction of the sample solution and the eluents to the column disturbs the surface of the resin in such a manner as to cause the sample constituents to be eluted in diagonal instead of horizontal bands. The polyethylene sphere breaks the fall of the solutions sufficiently so as to keep the surface level and give horizontal bands during the elution. Polyethylene is an ideal material for this purpose since it rests on the resin bed when the column is empty, serves as a shield when the solutions are being added to the column, and floats to the surface during the elution so as to give the eluents free access to the entire cross section of the column. In addition polyethylene is not wet by the solution and as a result the last quantities of the sample solution are easily rinsed on to the resin bed. The freshly prepared ion-exchange column should be washed several times alternately with 50-ml portions of 9*M* HCl and 0.5*M* HCl followed by 100 ml of 2.5% HF. A column which has been in use previously may be prepared for separations merely by washing with 50 ml of 2.5% HF.

Procedure

Column separations. Dissolve a 1-gram sample in an appropriate mixture of hydrofluoric, hydrochloric and nitric acids and evaporate to dryness on the steam bath. Take up the sample residue in 5 ml of concentrated HF plus 25 ml of water. Warm on the steam bath for about 10 min. and then add an additional 75 ml of water. Transfer the sample solution to the anion-exchange column with 2.5% HF and after the sample solution is rinsed on to the resin bed, elute with 250 ml of 2.5% HF. This eluate will contain elements such as iron, cobalt, nickel, chromium, manganese, aluminium and copper. Further treatment of this eluate will be discussed below.

The column retains elements such as titanium, tungsten, molybdenum, niobium and tantalum. Elute the titanium with 250 ml of 8*M* HCl. Elute the tungsten with 300 ml of a solution which is 10% HF–60% HCl. Elute the molydbenum with 300 ml of a solution which is 20% HF–25% HCl. Elute the niobium with 300 ml of a solution which is 14% NH_4Cl–4% HF. Elute the tantalum with 300 ml of a solution which is 14% NH_4Cl–4% NH_4F.

The material which was used for this particular project contained nickel, chromium, cobalt and iron in the 2.5% HF eluate. Add ten ml of conc. HCl to this fraction and evaporate to dryness on the steam bath. Take up the residue with 9*M* HCl and transfer the solution to a strongly basic anion-exchange column with 9*M* HCl. Elute the nickel and chromium together with 9*M* HCl. Elute the cobalt with 4*M* HCl and finally elute the iron with 0.5*M* HCl.

Treatment of the eluates

Titanium. Add 6 ml of 1 : 1 sulphuric acid to the titanium fraction and evaporate to fumes of sulphuric acid. Cool to room temperature, add several grams of ice from distilled water and 0.5 ml of 30 vol. per cent hydrogen peroxide and dilute to 100 ml in the volumetric flask. Transfer an appropriate aliquot to a 250-ml beaker, add 150 ml of water and a measured excess of EDTA. Add 10 ml of a sodium acetate-acetic acid buffer and if necessary adjust the pH to approximately 4.8 with a concentrated sodium hydroxide solution. Add two to three drops of a metalfluorechromic indicator and back-titrate the excess of EDTA with a standard copper solution using ultraviolet light as the sole source of illumination.

Tungsten. To the tungsten fraction add 6 ml of 1 : 1 sulphuric acid and evaporate the solution to fumes of sulphuric in order to remove the fluoride. Cool to room temperature and add several grams of ice followed by 25 ml of water, and 1 : 1 ammonium hydroxide until the tungstic acid precipitate just redissolves. Add 20 ml of the sodium acetate–acetic acid buffer and if necessary adjust the pH to approximately 4.8 with dilute acid. Add a small excess of 8-hydroxyquinoline in dilute acetic acid. Bring the solution to the boil on the hot plate and then digest for about 5 minutes at about 80° to 90°. Cool the solution to room temperature and filter the tungsten 8-hydroxyquinolate on a weighed Gooch crucible. Wash the precipitate several times with water, dry at 110° for 1 hour and weigh the crucible plus precipitate. The factor for tungsten is 0.365.

Molybdenum. Treat the fraction containing the molybdenum in an identical manner as that described above for tungsten. The factor for molybdenum is 0.2305.

Niobium. Add 9 g of boric acid to the niobium fraction. After the boric acid is dissolved, transfer the solution to a glass beaker, add 60 ml of 1 : 1 sulphuric acid and cool to 10° in ice. Add a slight excess of cupferron and filter the niobium cupferrate. Wash the precipitate thoroughly with a 5% sulphuric acid solution which is saturated with cupferron in order to remove the ammonium salts from the precipitate. Cautiously ignite the niobium cupferrate to the oxide and weigh as Nb_2O_5.

Tantalum. Treat the tantalum fraction in the same manner as is described above for niobium.

Nickel and chromium. Evaporate the nickel and chromium fraction to dryness to remove the excess of hydrochloric acid. Dissolve the residue with water plus a small amount of dilute HCl and tranfser to a 100-ml volumetric flask. Transfer an appropriate aliquot to a 250-ml beaker. Add 150 ml of water, 10 ml of sodium acetate-acetic acid buffer and a measured excess of EDTA over that which would be necessary for the nickel which is present in the sample. Add 2 to 3 drops of a metalfluorechromic indicator and back-titrate the excess of EDTA with a standard copper solution. This titration should be carried out at room temperature in order to avoid interference from the chromium present in this aliquot. Calculate the per cent nickel in the sample from the excess of EDTA and the copper used in the back-titration. To the solution in which the nickel was just determined add a measured excess of EDTA over that which would be required for the chromium present in the solution. Place the beaker on a hot plate and boil the solution for 15 minutes in order to form the chromium-EDTA complex. Back-titrate the excess of EDTA with the standard copper solution using ultraviolet light. Calculate the per cent chromium from the amount of EDTA added and the copper used in the back-titration.

Cobalt fraction. Transfer the cobalt fraction to a 100-ml volumetric flask and take an appropriate aliquot in a 250-ml beaker. Add 150 ml of water, a measured excess of EDTA, and 10 ml of ammonium chloride ammonium hydroxide buffer (pH approximately 9.5). If necessary adjust the pH to approximately 9.5 with ammonium hydroxide, add 2 to 3 drops of a metalfluorechromic indicator, and back-titrate the excess of EDTA with a standard copper solution. Calculate the per cent cobalt from the amount of EDTA added and the volume of standard copper solution used for the back-titration.

Iron fraction. Transfer a suitable aliquot of the iron fraction to a 250-ml beaker. Add a measured excess of EDTA, dilute to approximately 150 ml, and adjust the pH to approximately 4.8. Add 2 to

3 drops of a metalfluorechromic indicator and back-titrate the excess of EDTA with a standard copper solution to the quenching of the fluorescence of the free indicator.

DISCUSSION

The volumes of eluents used during the elutions from the polystyrene column are suitable for the column dimensions and the resin particle size given under *Column Preparation.* If a smaller amount of eluent is used there is a possibility of obtaining incomplete separations of the refractory metals. The use of larger volumes of eluent does not alter subsequent separations. The elution scheme shown in Fig. 1 is quite versatile and may be used for many combinations of refractory elements. In the event that some of the elements are absent in a sample one merely skips the elution step for those elements and proceeds with the elution of the next element on the flow sheet. If one or more elements are missing the volumes of eluents for the elements present are unchanged. In addition any eluent on the flow sheet will elute (in 300 ml) all the elements that precede the eluent on the flow sheet. For example, the 20% HF–25% HCl eluent elutes titanium and tungsten as well as molybdenum. This is advantageous on occasions where one desires to determine one or two of the elements at the end of the flow sheet and does not need to conduct all the elutions preceding it. The procedure may be applied to the determination of one or all of the above mentioned elements in stainless steels as well as in high temperature alloys.

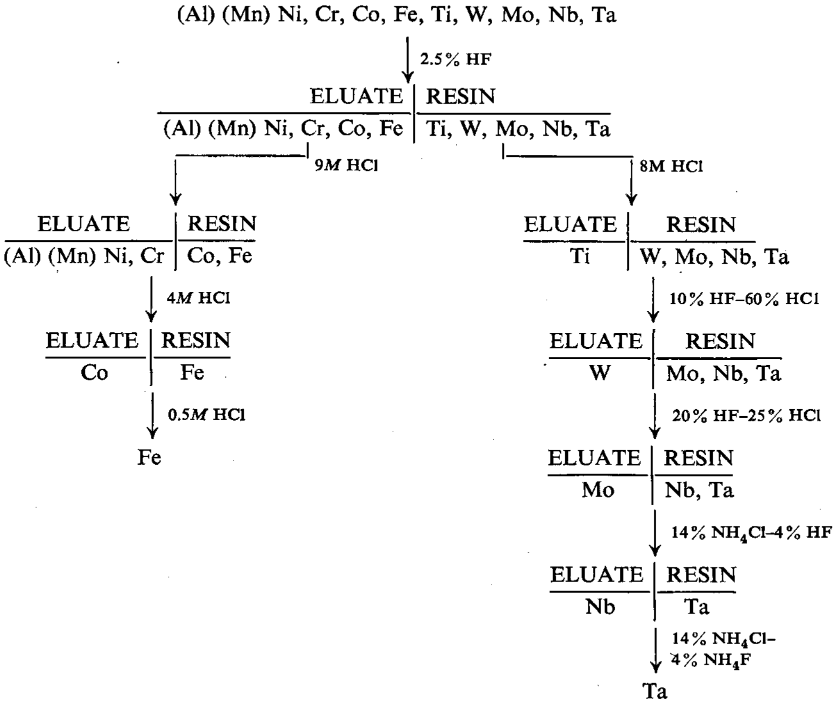

FIG. 1.—Flow sheet for the analysis of a high temperature alloy

The 2.5% HF fraction which is first converted to a chloride solution is usually separated in small glass columns. For example with the alloy shown in Table I the glass columns contained 10 gms of Dowex 1 × 8, 200–400 mesh, chloride form, in a resin bed 1 cm ID × 12 cm long. The use of a smaller column permits more rapid separations with smaller volumes of eluents.

Additional elements may be accommodated in this portion of the procedure. For example aluminium and manganese will be found in the 9*M* HCl eluent along with nickel and chromium. With all four elements the most suitable procedure is to take an aliquot for an aluminium, manganese and nickel determination and remove the chromium by volatilization of chromyl chloride from a perchloric acid solution. The diluted solution is then passed through a cation-exchange resin. Aluminium may then be eluted with a dilute HF solution and then nickel and manganese with 4*M* HCl. Chromium is determined in a separate aliquot.

TABLE I.—COMPOSITE SAMPLE TO SIMULATE A HIGH TEMPERATURE ALLOY

Ni found, *mg*	Cr found, *mg*	Co found, *mg*	Fe found, *mg*	Ti found, *mg*	W found, *mg*	Mo found, *mg*	Nb found, *mg*	Ta found, *mg*
19.2	17.6	43.0	22.0	70.6	45.9	38.5		
19.2	17.6	43.0	22.0	70.6	45.9	38.5	31.6	22.3
19.2	17.6	43.0	22.0	70.1	46.1	39.1	31.5	22.3
19.3	17.6	43.0	22.1	70.7	46.6	39.4	32.6	22.6
19.1	17.7	43.0	22.0	69.7	46.3	39.6	32.8	22.4
19.2	17.7	43.0	21.9	69.4	46.4	39.4	33.4	22.7

Nominal values—Ni, 19.2 mg; Cr, 17.5 mg; Co, 42.9; Fe, 22.0 mg; Ti, 70.5 mg; W, 46.2 mg; Mo, 39.8 mg; Nb, 32.1 mg; Ta, 22.0 mg.

If copper is present in the original sample it will be found in the 2.5% HF eluate. In this case the separation of the elements in the 2.5% eluate must be done on a larger column in order to separate copper from cobalt.[2]

Calcein W (0.1% in water) was used as a metalfluorechromic indicator for all the chelometric titrations in order to avoid any interference in the detection of the end-point by highly coloured EDTA complexes.[5,6] An apparatus for these titrations has been previously described.[3]

Zusammenfassung—Eine Anionenaustauscher-Methode zur Trennung der Bestandteile in Hochtemperaturlegierungen wird beschrieben. Neun Elemente, darunter Titan, Wolfram, Molybdän, Niob und Tantal werden in einer Einwaage bestimmt. Jede beliebige Kombination der oben erwähnten Elemente in Stählen und Hochtemperaturlegierungen kann mittels der einfachen Methode rutinemässig bestimmt werden.

Résumé—L'auteur a imaginé une méthode par échange anionique pour séparer les constituants des alliages réfractaires. On a dosé neuf éléments, dont le titane, le tungstène, le molybdène, le niobium et le tantale, dans un alliage sur une seule prise d'essai.

On peut doser, dans des aciers et des alliages réfractaires toute combinaison des éléments mentionnés ci-dessus par un procédé simple d'échange d'ions adapté à l'analyse de routine.

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THE REDOX PROPERTIES OF SOME ALKOXYL-SUBSTITUTED BENZIDINES

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Summary—An account is given of the redox properties of 3-methoxy-, 3-ethoxy-, 3:3′-dimethoxy- and 3:3′-diethoxybenzidine. These compounds are oxidised to cherry-red or orange-red colours. Their sensitivities towards oxidants and their transitional potentials have been determined and their behaviour as indicators in redox titrations has been examined.

INTRODUCTION

WEEKS[1] first proposed *o*-dianisidine (3:3′-dimethoxybenzidine) as a redox indicator in dichromate titrations, but it has not come into general use for this purpose. Although it has been extensively used as an indicator in the titration of zinc with ferrocyanide,[2,3] a new range of naphthidine indicators proposed by Belcher, Nutten and Stephen[4–6] have end-point colour changes considerably better than those of *o*-dianisidine. Better end-points have also been obtained when 3-methyl- and 3:3′-diethylbenzidine are used as indicators in the microdetermination of gold with quinol[7] in place of *o*-dianisidine which was normally used for this determination.[8,9] Although these new indicators have tended to replace *o*-dianisidine in most titrations, the redox properties of the latter have even recently been applied in analytical chemistry; the determination of chromate,[10] ferricyanide,[11] and blood and urine glucose[12] are examples. In addition, like other benzidine compounds, it has the property of forming complexes and salts with metals and acids respectively and it has been recommended as a reagent for copper and thiocyanate,[13] and for molybdenum,[14] tungsten[15] and vanadate.[16]

In view of the considerable interest in *o*-dianisidine as an analytical reagent an investigation of other benzidine derivatives containing alkoxyl groups has been made. 3-Methoxy-, 3-ethoxy- and 3:3′-diethoxybenzidine have been prepared and their redox properties examined spectrophotometrically and potentiometrically (together with *o*-dianisidine) in order to assess their applicability as analytical reagents.

EXPERIMENTAL

Indicator solutions: 0·5% in glacial acetic acid.

Sensitivity determinations

(*i*) *Neutral solution:* 2 ml of the neutral test solution and 1 drop of the indicator solution were added to a micro-test tube. The contents of the tube were shaken and the colour formed was viewed against a white background. The procedure was repeated with more dilute solutions of the oxidising ions until a yellow or light brown colour was just detectable after 2 minutes of mixing.

(*ii*) *Acid solution:* The above procedure was repeated but with 1 ml of the test solution, 1 ml of 0·2*N* hydrochloric acid and 1 drop of the indicator solution.

When ferricyanide was used as the neutral ion test solution, 1 drop of 0·01*M* zinc sulphate solution was added before adding the indicator solution.

The results obtained for benzidine and the four alkoxyl derivatives are given in Table I.

TABLE I.—SENSITIVITIES TOWARDS OXIDANTS

Identification limit (μg) in 2 ml of solution

Reagent	Oxidant										
	$Cr_2O_7^{2-}$	VO_3^-	IO_4^-	MnO_4^-	Fe^{3+}	$S_2O_8^{2-}$	IO_3^-	BrO_3^-	Ce^{4+}	OCl^-	$Fe(CN)_6^{3-}$
(i) Neutral solution											
Benzidine	100	40	80	0·2	16	4	>2000	>2000	1	0·6	1·0
3-MeO-benzidine	10	20	20	0·4	11	6	2000	>2000	1	0·7	0·6
3-EtO-benzidine	10	30	40	0·4	16	3	>2000	>2000	3	1·9	0·6
3:3′-diMeO-benzidine	4	13	10	0·2	10	2	400	>2000	1	0·6	0·4
3:3′-diEtO-benzidine	4	10	10	0·3	11	3	1000	>2000	1	0·6	0·6
(ii) Acid solution											
Benzidine	5	50	200	0·2	25	20	20	250	1·0	0·7	13
3-MeO-benzidine	2	20	40	0·2	13	50	10	500	1·3	0·7	10
3-EtO-benzidine	2	20	100	0·3	20	33	8	500	1·3	0·7	5
3:3′-diMeO-benzidine	1	13	40	0·2	10	20	7	200	1·0	0·4	4
3:3′-diEtO-benzidine	1	20	40	0·2	20	33	7	250	1·3	0·4	2

Spectrophotometric studies

Five drops of the indicator solution were mixed with 100 ml of 0·5*M*–5*M* sulphuric acid, followed by 1 drop of 0·1*N* ceric sulphate solution. The colours formed were too unstable for the absorption spectra of the red oxidation products to be plotted and only λ_{max} values could be recorded. A Unicam S.P. 600 spectrophotometer was used.

TABLE II.—TRANSITION POTENTIALS AT 18°–20°, REFERRED TO THE STANDARD HYDROGEN ELECTRODE

Indicator	Acid concentration, M H_2SO_4				
	0·1	0·5	1·0	2·0	4·0
3-MeO-benzidine	0·79	0·83 (0·81)	0·82 (0·80)	0·83 (0·83)	0·84 (0·85)
3-EtO-benzidine	0·78	0·82 (0·80)	0·80 (0·80)	0·82 (0·81)	0·83 (0·85)
3:3′-diMeO-benzidine	0·75	0·79 (0·77)	0·78 (0·76)	0·80 (0·79)	0·81 (0·82)
3:3′-diEtO-benzidine	0·76	0·79 (0·78)	0·79 (0·75)	0·81 (0·80)	0·81 (0·83)
Diphenylamine-sulphonic acid	0·81	0·82 (0·81)	0·83 (0·85)	0·80 (0·82)	0·75 (0·76)
Ferroïn		(1·08)	(1·10)	(1·07)	(1·00)

Values not in parentheses are those for the Fe^{2+}–Fe^{3+} and the $Cr_2O_7^{2-}$–Cr^{3+} systems, whilst those in parentheses are for the Fe^{2+}–Fe^{3+} and the Ce^{4+}–Ce^{3+} systems.

Transition potentials

The apparatus, reagents and procedure are described by Belcher, Nutten and Stephen.[17] A 0·1*N* solution of ferrous ammonium sulphate of known acid content was titrated potentiometrically against a 0·01*N* solution of the oxidant of the same acid content, in the presence of 5 drops of the indicator solution. Just before the theoretical end-point, the 0·1*N* solution of the oxidant was replaced by a 0·01*N* solution which was added dropwise. The transition potential was obtained when the first trace of a red coloration appeared. The results obtained when using dichromate and cerium^{IV} as oxidants are given in Table II.

Application as redox indicators

The solutions and titration procedures have been described previously.[6] Ten drops of the indicator solutions were required for the titrations of dichromate and cerium^{IV} with iron^{II} solution.

Preparation of amines

The preparations of 3-methoxy-,[18] 3-ethoxy-[19] and 3:3′-diethoxybenzidine[20] are described in the literature. *o*-Dianisidine is available commercially.

RESULTS AND DISCUSSION

Colour reactions and sensitivity tests

The two disubstituted derivatives give a bright cherry-red colour on being oxidised in acid solutions whereas the monosubstituted derivatives give a more orange coloured oxidation product. This visual observation is confirmed by the λ_{max} values, those of the oxidised monosubstituted derivatives being 435 mμ to 440 mμ in 0·5*M* to 4*M* sulphuric acid solutions and those of the oxidised disubstituted derivatives being 450 mμ except in the case of 3:3′-diethoxybenzidine in 4*M* sulphuric acid solution, where the value is 455 mμ.

The stability of the colours increase with increasing acidity, but even in 4*M* sulphuric acid solution the colours are too unstable for an accurate plot of the absorption spectra to be made. The colours formed at these high acidities are less intense, however, than those formed at lower acidities. The disubstituted derivatives oxidise to more stable colours than the monosubstituted derivatives.

The reduction of the red colours back to the colourless free amines is very sluggish. This is the reason for the appearance of a red coloration before the true end-point has been reached and is the chief cause for the replacement of *o*-dianisidine with more reversible redox indicators in most titrations.

In the sensitivity tests it is interesting to note that only in the case of ferricyanide ion in acid solution is 3:3′-diethoxybenzidine much more sensitive than the other three compounds. The sensitivities of the amines to $Cr_2O_7^{2-}$, IO_3^- and BrO_3^- is greater in acid solution than in neutral solution, whilst it is the reverse in the case of IO_4^-, $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$, and approximately of the same order in the case of VO_3^-, MnO_4^- and Ce^{IV}. In general, the order of the sensitivities in both acid and neutral solutions is 3:3′-dimethoxy- = 3:3′-diethoxy- > 3-methoxy- > 3-ethoxybenzidine > benzidine.

Transition potentials

Although Crawford and Bishop[3] determined the oxidation potential of *o*-dianisidine by direct titration with ceric sulphate, it has been pointed out[17] that this value is of little practical importance. The potentials recorded in Table II are the potentials at which the amines, used as indicators, first show a change of colour in actual redox titrations. In most cases the transition potentials found when using cerium^{IV} as oxidant are slightly less than those found when using dichromate. This observation which is probably associated with the so-called inductive effect of iron^{II} in the dichromate-chromous system has also been made in the naphthidine series.[21] At all the acid concentrations examined, the two monosubstituted derivatives have higher transition potentials than the disubstituted derivatives with 3-methoxy- and 3:3′-dimethoxybenzidine having the highest and lowest values respectively.

Application as redox indicators

As a result of the appearance of a slight red coloration before the end-point and the slow development of the bright cherry-red colour from an initially orange colour, none of the alkoxybenzidines is wholly satisfactory as a redox indicator. The former disadvantage is overcome to some extent if the indicator is added just before the end-point. Under these conditions the indicator blank is equivalent to 0·04 ml of

$0{\cdot}1N$ oxidant. In the titration of iron^{II} with dichromate, the presence of phosphoric acid, which is necessary when using diphenylaminesulphonic acid, causes over-titration and a retardation of the development of the full red colours. In general, the monosubstituted derivatives give better end-points in the various concentrations of sulphuric acid solutions. These indicators are more suitable than diphenylaminesulphonic acid at higher acidities ($4M$ sulphuric acid), as the marked drop in the transition potential of the latter indicator gives rise to undertitrations. In fact the transition potentials of the alkoxybenzidines increase to values greater than those of diphenylaminesulphonic acid at these high acid concentrations.

Much better end-points are obtained in the titration of iron^{II} with ceric sulphate, especially with 3:3′-diethoxybenzidine. Stoicheiometric results are obtained in $0{\cdot}5$–$4{\cdot}0M$ solutions of sulphuric acid. None of the indicators can be recommended in place of ferroïn, although it should be noted that this latter indicator does not give a satisfactory colour change at concentrations above $4M$ with respect to sulphuric acid; the alkoxybenzidines behave normally under these conditions.

o-Dianisidine has been extensively used in the titration of zinc with ferrocyanide, but the present comparison shows that, whereas the two monosubstituted derivatives give only slightly inferior end-points to that of *o*-dianisidine, 3:3′-diethoxybenzidine gives a much sharper end-point. In the titration of cadmium with ferrocyanide, all four alkoxybenzidines give end-points which are difficult to detect. This observation has already been made in the case of *o*-dianisidine.[22]

CONCLUSION

Although the four alkoxybenzidines studied cannot be recommended for most titrations where there are already suitable redox indicators available, they may be of some importance (especially 3:3′-diethoxybenzidine which gives sharper end-points) in titrations of dichromate and cerium^{IV} with iron^{II} at higher acidities ($>4M$ sulphuric acid) where the redox indicators normally used do not function satisfactorily.

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Zusammenfassung—Das Redox-Verhalten folgender Substanzen wird studiert: 3-Methoxy-, 3-Äthoxy-, 3,3′-Dimethoxy- und 3,3′-Diäthoxybenzidin. Die Substanzen werden leicht zu kirschroten oder orangeroten Verbindungen oxydiert. Die Empfindlichkeit gegenüber oxydierenden Substanzen und das Oxydationspotential wurde bestimmt. Über die Anwendung der Verbindungen als Redox-indicatoren wird berichtet.

Résumé—Les auteurs donnent une interprétation des propriétés oxydoréductrices de dérivés de la benzidine (méthoxy-3, ethoxy-3, dimethoxy-3.3′ et diethoxy-3.3′ benzidine). Ces composés sont oxydés en substances rouge cerise ou rouge orangé. Leur sensibilité à l'égard des oxydants et leur potentiel de transformation ont été déterminés et leur comportement comme indicateur dans les titrages d'oxydo-réduction a été étudié.

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AN EDTA-POLAROGRAPHIC METHOD FOR THE DETERMINATION OF TELLURIUM IN LEAD ALLOYS*

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Summary—A procedure is described for the polarographic determination of tellurium in lead alloys, without resorting to prior separative techniques. Interference by Cu, Cd, Tl, As, and Sb is discussed.

EXISTING polarographic,[1] spectrophotometric,[2–5] and other,[6–7] procedures for the determination of tellurium have not proved wholly satisfactory in the presence of large amounts of lead, as, for example, in alloys with this element. Here prior separative procedures involving precipitation[1,2,15] or extraction[16] have proved difficult, if not impossible,[17] in conjunction with polarography. The half wave potentials of Te^{IV} and Pb^{II} are almost identical and a survey of the literature reveals that no polarographic technique applicable to this determination has been developed.

However, it is known,[12,13] that in the presence of EDTA the half wave potential of the lead ion is shifted with increase in pH of the solution towards more negative values. Lead occurs usually as a complex cation and tellurium as the tellurite anion. In Group VIa of the Periodic Classification, metallic character, as well as tendency towards formation of complex ions, increases with increasing atomic number. Tellurium, however, differs considerably from such a metallic element as lead in its behaviour towards EDTA, being complexed more strongly than selenium, although much less strongly than polonium. On the basis of these facts, this paper describes a procedure for the polarographic determination of tellurium in the presence of lead.

EXPERIMENTAL

A standard aqueous solution of tellurium was prepared from TeO_2, or alternatively by dissolving metallic tellurium in nitric acid. Polarographs LP55 (Czechoslovakia) and PO3 (Radiometer, Copenhagen) were employed, deaeration of solutions being accomplished with propane gas.[11]

PRELIMINARY INVESTIGATIONS

The polarographic characteristics of tellurium may be recommended for analytical purposes. In the most common state, +4, a well defined wave is obtained in NH_3—NH_4Cl solution,[8,9] at −0·7 V (S.C.E.), involving reduction to metallic Te(O). Within limits, wave height is here linearly proportional to concentration. At −1·1 V further reduction to the −2 state takes place, an exceptionally high maximum being observed, and reaction between Te (+4) and Te(−2) occurring in the vicinity of the mercury drop.[9,10] This potential should be avoided in analytical work, owing to the large amount of free tellurium formed, with the consequent possibility of damage to the capillary orifice. Even at the lower potential free tellurium is liberated, but its adherence to the mercury drop protects the capillary tip from such damage. The observed disturbances in the solution at −1·1 V (appearance of Te suspension during maximum) were recorded cinematographically; further observations and conclusions concerning the lowering of current after the maximum will be published later.

In the presence of EDTA, in solution of pH 10, the lead half-wave potential is shifted to −1·1 V.

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Under these conditions, however, the tellurium wave at −0·7 V cannot be utilised for measuremen since the high instrumental sensitivity necessary for the determination of tellurium in small amoun reveals the beginning of an increase in current at −0·6 V, due to the high concentration of lea present. Furthermore, the definition of the tellurium wave is seriously affected in solutions of hig pH, although the influence of EDTA is negligible.

A satisfactory compromise with these conflicting pH requirements was found in EDTA—NH_4Cl- NH_4NO_3 solution, adjusted using ammonium hydroxide to pH 8–9. The concentrations of the reagents are not critical, but best results were obtained using the following procedure.

Detailed procedure

1. Dissolve 0·5 g of Pb/Te alloy in 6 ml of nitric acid (1 : 1), add 10 ml of 10% EDTA solutio and adjust to approximately pH 7 using ammonium hydroxide. Add 0·5 g of ammonium chlorid followed by 1 ml of 15% ammonia solution, and make up to 25 ml.
2. Remove oxygen from solution by means of a stream of propane, nitrogen or argon gas.
3. The half-wave potential of the Te^{IV}–Te^0 wave is −0·45 V with respect to internal mercury poo Record the polarogram from −0·2 V onwards, increasing the voltage very gradually (100 mV/cm
4. Calculate the amount of tellurium present from the prepared calibration curve.

RESULTS

Fig. 1 shows a typical polarogram obtained by this procedure. The minimum amount of telluriu which can be determined is 0·01% of the lead concentration, the calibration graph being strictly line in the range 0·01–0·20%. The precision of the determination was investigated statistically,[14] th value of 2·4% error being obtained for samples containing 0·1% tellurium.

Interferences of some cations were investigated. Both the copper and cadmium waves are shifte to more negative potentials in the presence of EDTA, sufficiently far from that of tellurium to preclud their interference. Arsenic, antimony and thallium interfere when present in concentration greater tha 0·01%, but in the case of the last-named the tellurium wave height may be corrected for the amou of thallium present.

The results are very satisfactory and the method appears superior to existing gravimetric an colorimetric procedures. The time required is relatively short and no special technique is demande of the operator.

Acknowledgement—Sincere thanks are expressed to Dr. J. H. W. Forsythe for assistance in th preparation of this paper.

Zusammenfassung—Eine Methode zur polarographischen Bestimmung von Tellur in Bleilegierunge ohne vorhergehende Trennungen wurde entwickelt. Störungen durch Cu, Cd, Tl, As und Sb sin besprochen.

Résumé—Les auteurs décrivent une méthode de dosage polarographique du tellure dans des alliage de plomb, sans recourir à des techniques de séparation préalables. On discute l'interférence d Cu, Cd, Tl, As et Sb.

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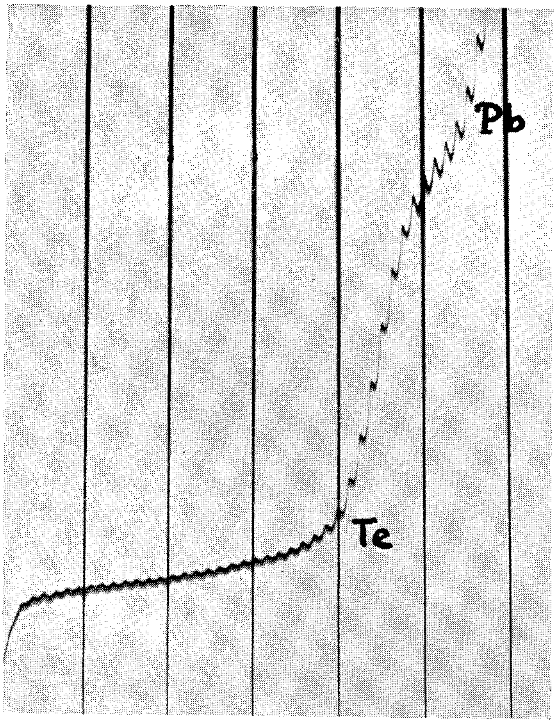

FIG. 1.—Polarogram of tellurium in the presence of lead, using the procedure described. 0·1 % Te alloy. Polarograph LP55, simple vessel with mercury pool anode, 100 mV per abscissa, sensitivity 1/10.

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TITRATION OF OXALIC ACID WITH CERIUM^{IV} SULPHATE AT ROOM TEMPERATURE USING FERROÏN AS INTERNAL INDICATOR

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Summary—Evidence is presented to show that, contrary to the statements of earlier workers, the reaction between ceric sulphate and oxalic acid is quite rapid in hydrochloric acid medium specially in the presence of iodine monochloride as catalyst. We have now found that the need for a temperature of 50° in the cerimetric titration of oxalic acid using ferroïn as indicator is not due to the sluggishness of the reaction between oxalic acid and Ce^{IV} (as believed by Willard and Young) but because of the slow reaction between oxidised ferroïn and oxalic acid in the presence of sulphate ion derived from ceric sulphate. Conditions have now been developed for the titration of oxalic acid with ceric sulphate at room temperature in $1N$ hydrochloric acid medium using ferroïn as indicator, and barium ion as scavenger for sulphate ion, which latter markedly retards the reaction between oxalic acid and oxidised ferroïn, as well as that between oxalic acid and Ce^{IV}. The method now developed has several advantages over that prescribed by Willard and Young because it avoids the high temperature of 50°, where the ferroïn indicator is found to undergo some dissociation. It also avoids the use of the iodine monochloride catalyst.

BENRATH and Ruland[1] studied the kinetics of the reaction between cerium^{IV} sulphate and oxalic acid and showed that at room temperature the reaction is very slow in dilute solutions, especially towards the completion of the reaction. Furman[2] appears to be the first to make a study of this reaction for the purpose of titrimetric analysis. He obtained satisfactory results when the titration of ceric sulphate with an oxalate was carried out in sulphuric acid medium at 50°–60°, the end-point being detected electrometrically. Using the disappearance of the yellow colour of the ceric ion as end-point with decinormal solutions gave a value 0·03 ml earlier than the potentiometric end-point. Furman stated that the reverse titration, namely, the titration of oxalate with ceric sulphate is not practicable in sulphuric acid medium because of the slow rate of reaction. Willard and Young[3] investigated in detail the titration of oxalate with ceric sulphate over a wide range of concentration and temperature. They observed that below 70° the potential equilibrium at the end-point was attained too slowly. The equilibrium was established rapidly if the titration was carried out "near boiling point" in hydrochloric acid solution. The titration could be carried out in the presence of as much as 60 ml of 73% perchloric acid or 50 ml of glacial acetic acid per 200 ml of solution instead of sulphuric or hydrochloric acid and the end-point equilibrium was rapid. The presence of even 5 ml of conc. nitric acid in this same volume, however, gave too high a value for the ceric sulphate, showing that this acid had a slight effect on the oxalate. Phosphoric and hydrofluoric acids must be absent, even if considerable hydrochloric acid was present, as they caused the formation of insoluble cerium salts. They further observed that the electrometric titration of oxalic acid could be satisfactorily carried out at room temperature in a hydrochloric acid medium if iodine chloride was present as a catalyst. Iodide and iodate were also found to act as catalysts but not as effectively as iodine chloride. Willard and Young also stated that the titration of oxalate could be satisfactorily carried out at room temperature in the presence of iodine monochloride, using methylene blue as internal indicator in hydrochloric acid medium. It was recommended that the indicator should be added towards the close of the titration, as it tended to be destroyed if present from the start.

In a subsequent communication, Willard and Young[4] examined the use of ferroïn as internal indicator in the titration of oxalate with ceric sulphate. They stated that the reaction of sodium oxalate with ceric sulphate at room temperature in a hydrochloric acid solution containing iodine chloride as catalyst was not rapid enough for the use of *o*-phenanthroline ferrous complex as indicator; and that "a temperature of 50° seemed most satisfactory, for at higher temperatures, too much of the indicator was destroyed, *while at much lower temperatures this reaction was not sufficiently rapid*". It was possible to titrate rapidly to within five or six drops of the end-point. The solution was then reheated to 50° and the titration completed. The Willard and Young procedure does not yield satisfactory results in the hands of all workers. Vogel[5] has stated that "he could not obtain satisfactory results by the use of the iodine monochloride as catalyst and ferroïn as indicator". He has recommended running the ceric sulphate solution into a hot solution of oxalic acid solution until the solution acquires a permanent faint yellow colour, and applying a blank correction; or alternatively adding an excess of ceric sulphate solution to the oxalic solution warming the mixture to 50° for five minutes, and, after cooling, titrating the excess of ceric sulphate with a standard ferrous ammonium sulphate solution, using N-phenylanthranilic acid or ferroïn as indicator as recommended earlier by Hammet, Walden and Edmonds,[6] Lindner and Kirk[7] and others. Rappaport[8] determined the excess ceric sulphate iodimetrically. Szebellédy and Tanay[9] investigated the use of manganous salts as catalysts. For the microtitration of oxalate in N sulphuric acid at 50° with $0{\cdot}01N$ ceric sulphate using ferroïn as indicator, they employed 2% of manganous sulphate or chloride. Wheatley[10] stated that the titration can be performed in the cold if the manganous salt concentration is increased to 5 per cent. Watson[11] prefers to employ a temperature of 40°–50° in the same titration.

In our opinion, the explanation offered by Willard and Young for the need of a temperature of 50° for the titration of oxalate with ceric sulphate using ferroïn as indicator is not quite satisfactory. If the reaction between ceric sulphate and oxalate is slow (as believed by Willard and Young) at room temperature in hydrochloric acid medium, even in the presence of iodine monochloride as catalyst, one fails to understand how the titration is possible at room temperature with an electrometric end-point or with methylene blue as internal indicator. In this connection, it is pertinent to note that in the electrometric titration Willard and Young observed that the equilibrium potentials were attained rapidly after the addition of each drop of ceric sulphate. The retardation of the reaction by sulphuric acid introduced through the ceric sulphate must be applicable equally to the titrations with the electrometric and colorimetric end-points. We believe that the explanation for the need of a temperature of 50° must be sought in quarters other than the slowness of the reaction between ceric sulphate and oxalic acid.

The present investigation has been undertaken with the purpose of clarifying the position.

EXPERIMENTS AND OBSERVATIONS

We have observed that the reaction between cerium^{IV} sulphate and oxalic acid is rapid at low concentrations of reactants and at all concentrations of hydrochloric acid between 0·2*N* and 6·0*N*. This can be seen by the fact that the yellow colour of ceric ion is rapidly discharged when one drop of 0·05*N* cerium^{IV} sulphate is mixed with one drop of 0·1*N* oxalic acid in a total volume of 5 ml of hydrochloric acid (0·2*N* to 6·0*N*). The reaction is very fast even in the absence of a catalyst like iodine monochloride. If the cerium^{IV} sulphate and oxalic acid are taken at high concentrations (0·05*N*), the reaction, although quite rapid in the early stages, becomes rather slow towards the end. We have also observed that the reaction is strongly retarded by the sulphate ion. The inhibition can be observed even at 0·5*N* sulphate ion concentration. The retardation of the cerium^{IV} oxalate reaction by the sulphate ion is counteracted by iodine monochloride. In view of this, the titration of oxalic acid with cerium^{IV} sulphate is possible in hydrochloric acid medium at room temperature, when iodine monochloride is used as a catalyst as already observed by Willard and Young in their electrometric titrations.

For the above titration to be carried out using redox indicators, one has to take into account not merely the speed (1) of the reaction between oxalic acid and ceric sulphate but also of the reactions between (2) the indicator and ceric sulphate and (3) oxidised indicator and oxalate. Reaction (3) has not been apparently taken into account by Willard and Young in their study of this titration with ferroïn as indicator. It is well known that the reaction between ferroïn and cerium^{IV} sulphate is quite fast in either sulphuric or hydrochloric acid medium. In order to ascertain the nature of the reaction between oxidised ferroïn (ferriïn) and oxalic acid, we have now carried out experiments of which the results are summarised in Table I.

From these results it may be concluded (1) that the reduction of oxidised ferroïn by oxalic acid is very rapid in 0·2*N* to 0·5*N* hydrochloric acid. But it is retarded as the acid concentration is increased. (2) Sulphate ion retards the reaction very markedly even in 0·2*N* hydrochloric acid. (3) From Experiments IIIa and IVa, although the reduction of ferriïn is very slow in 1*N* and 2*N* hydrochloric acid, the addition of a trace of cerium^{IV} produces the red colour due to ferroïn. Thus it is evident that the slow reaction between ferriïn and oxalic acid is induced by the rapid reaction between cerium^{IV} and oxalic acid. (4) This induction does not occur in 3*N* hydrochloric acid as evidenced by Experiment Va. (5) The induction noted in Experiments IIIa and IVa does not occur in the presence of sulphate ion as can be seen from Experiments IIIc and IVc. (6) The slow reaction between ferriïn and oxalic acid in 1*N* to 2*N* hydrochloric acid is markedly catalysed by iodine monochloride at the room temperature. But this catalysis is not much in evidence in the presence of sulphate ion (*Vide* Experiments IIIe and IVe). (7) The catalysis by iodine monochloride becomes prominent only at 50° in the presence of sulphate ion. From Experiment IIIf, it is evident that a bright red colour results from the reduction of ferriïn by oxalic acid in 30 seconds in 1*N* hydrochloric acid; if the acid concentration is 2*N*, the bright red colour appears in 45 secs (Experiment IVf). If the hydrochloric acid concentration is 3*N*, the reduction of ferriïn takes 60 secs as evidenced by Experiment Vf.

Now, from Experiments IIIf, IVf and Vf, it becomes clear that the reduction of ferriïn by oxalic acid is so greatly retarded by sulphate ion that it can only take place with noticeable speed provided (1) the temperature is 50° and (2) iodine monochloride is present as a catalyst. Even under these conditions, the speed is not fast enough with the result that one has to wait for 30 secs, 45 secs, or 60 secs, according as the hydrochloric acid medium used is, 1*N*, 2*N* or 3*N*. Our experiments also indicate that titration of oxalic acid with cerium^{IV} sulphate should be more satisfactory in 1*N* than in 2*N* or 3*N* hydrochloric acid, which is actually the case. Also the need for a higher temperature and the iodine monochloride catalyst arise more from the retarding effect of the sulphate ion on the reaction between the oxidised ferroïn and oxalic acid, rather than because of any other system involved in the titration. Sulphate ion does not retard the oxidation of ferroïn by ceric sulphate.

From the foregoing, we may also conclude that if the sulphate ion is removed from the system, the titration of oxalic acid with ceric sulphate should be possible even at room temperature using ferroïn as indicator and without the use of the iodine monochloride catalyst. The validity of this conclusion has been tested by titrations of oxalic acid with ceric sulphate, adding sufficient barium chloride to remove the sulphate ion from the system as insoluble barium sulphate as the titration proceeds. In consequence, the following procedure is recommended.

Table I.—25 ml of hydrochloric acid + 1 drop of oxidised ferroïn (0·01M) + 1 drop of 0·05N oxalic acid. The time required for the appearance of the red colour due to the formation of ferroïn from the time of the addition of oxalic acid is noted.

Experiment No.	Concentration of hydrochloric acid, N	Other solutions added	Observation
I a	0·2	Nil	Intense red colour immediately.
b	0·2	1 ml Na_2SO_4 10%	Faint red colour immediately; does not intensify even after 10 minutes.
c	0·2	2 ml Na_2SO_4 10%	Very faint red colour immediately; does not intensify even after 10 minutes.
d	0·2	5 ml Na_2SO_4 10%	No red colour within 5 minutes.
II a	0·5	Nil	Intense red colour immediately.
b	0·5	1 ml Na_2SO_4 10%	Very faint red colour almost immediately; does not intensify even after 10 minutes.
IIIa	1·0	Nil	Very faint red colour immediately; does not intensify with time; but addition of a trace of Ce^{IV} produces an intense red colour immediately.
b	1·0	5 ml ICl 0·005M	Red colour immediately.
c	1·0	5 ml Na_2SO_4 10%	Very faint red colour after one minute; no intensification of the colour with time; not intensified by a trace of Ce^{IV}.
d	1·0	5 ml Na_2SO_4 10%	Faint red colour in one minute; does not intensify with time.
e	1·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005M	Perceptible red colour in 30 secs; does not intensify with time.
f	1·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005M at 50°	Perceptible red colour in 15 secs; intensifies in 30 secs.
IVa	2·0	Nil	No red colour even after 5 minutes; addition of a trace of Ce^{IV} produces an intense red colour immediately.
b	2·0	5 ml ICl 0·005M	Red colour immediately.
c	2·0	5 ml Na_2SO_4 10%	No red colour even on addition of a trace of Ce^{IV}.
d	2·0	5 ml Na_2SO_4 10% at 50°	Faint red colour in two minutes; does not intensify with time.
e	2·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005M	Very faint red colour in 30 secs; does not intensify with time.
f	2·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005M at 50°	Perceptible red colour in 30 secs; intensifies in 45 secs.
V a	3·0	Nil	No red colour even after 5 minutes; addition of a trace of Ce^{IV} does not produce any red colour.
b	3·0	5 ml ICl 0·005M	Red colour in one minute.
c	3·0	Nil at 50°	No red colour; addition of ICl produces red colour immediately.
d	3·0	5 ml Na_2SO_4 10%	No red colour.
e	3·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005M	Perceptible red colour in 30 secs; does not intensify with time.
f	3·0	5 ml Na_2SO_4 10% +5 ml ICl 0·005M at 50°	Perceptible red colour in 30 secs; intensifies in 60 secs.

Procedure

Place 5–10 ml of the oxalic acid solution (about 0·05*N*) in a conical flask, treat with 15 to 20 ml of concentrated hydrochloric acid and 20 ml of 0·5 molar barium chloride and dilute to 150–200 ml. Add 3–4 drops of 0·01*M* ferroïn, and titrate the mixture in the cold with 0·05*N* ceric sulphate solution. Titration can be carried out rapidly till about 99% of the oxalic acid is oxidised. At this stage add the oxidant dropwise and stir the solution for about 30 seconds. The disappearance of the red colour is noticed sharply enough, without any masking by the precipitated barium sulphate, if the total volume of the titration mixture is about 150–200 ml. The method has been found to work very satisfactorily even in the titration of 0·01*N* oxalic acid solutions.

Some typical results obtained in the determination of oxalic acid by the procedure now described are given in Table II.

In the titration of decinormal solutions of oxalic acid; it is desirable to dilute the reaction mixture to 300 ml to avoid masking of the red colour of ferroïn by the precipitated barium sulphate.

TABLE II.

Oxalic acid taken, *millimoles*	Oxalic acid found, *millimoles*
0·0250	0·0250
0·0500	0·0500
0·0800	0·0795
0·1000	0·0995
0·1500	0·1500
0·2000	0·1995
0·2500	0·2495

Acknowledgement—One of us (Dr. V. Panduranga Rao) desires to thank the Ministry of Education, Government of India, for the award of the National Research Fellowship.

Zusammenfassung—Der Beweis wurde, erbracht, dass, im Gegensatz zu der Auffassung früherer Autoren, die Reaktion zwischen Cerisulfat und Oxalsäure in salzsaurem Medium schnell verläuft, besonders, wenn Jodmonochlorid als Katalysator anwesend ist. Die Notwendigkeit, während der cerimetrischen Titration von oxalsäure die Temperatur der Lösung auf 50°C zu halten, ist nicht durch die langsame Reaktion zwishcen oxalsäure und Ce^{+4} bedingt, sondern vielmehr auf die langsame Reaktion zwischen Oxalsäure und oxydiertem Ferroin in Gegenwart von Sulfation (vom Cerisulfat stammend) zurückzufähren. Es wurden die Bedingungen gefunden um Oxalsäure mit Cerisulfat in 1 n Salzsäure bei Zimmertemperatur zu titrieren; Bariumionen werden zugesetzt um die Sulfationen abzufangen, die sowohl die Reaktion zwischen Oxalsäure und Ce^{+4} als auch die zwischen Oxalsäure und oxydiertem Ferroin stark verlangsamen. Die neue Methode hat mehrer Vorteile gegenüber der von Willard und Young beschriebenen. Die Temperaturerhöhung auf 50°C ist nicht nötig, was wichtig ist, da bei höherer Temperatur Ferroin ziemlich dissoziiert; ferner erübrigt sich Zugabe von Jodmonochlorid als Katalysator.

Résumé—Les auteurs montrent qu'il est évident que, contrairement aux conclusions des premiers chercheurs, la réaction entre le sulfate cérique et l'acide oxalique est très rapide en milieu acide chlorhydrique, spécialement en présence de monochlorure d'iode comme catalyseur. La nécessité d'une température de 50° dans le titrage cérimétrique de l'acide oxalique utilisant l'*o*-phénanthroline ferreuse comme indicateur n'est pas due à la lenteur de la réaction entre l'acide oxalique et le cérium (IV), mais à celle de la réaction entre l'*o*-phénanthroline ferreuse oxydée et l'acide oxalique en présence d'ion sulfate provenant du sulfate cérique. On a élaboré les conditions du titrage de l'acide oxalique par le sulphate cérique à la température ambiante en milieu acide chlorhydrique *N*, en utilisant l'*o*-phénanthroline ferreuse comme indicateur et l'ion baryum pour la précipitation de l'ion

sulfate, qui retarde notablement les deux réactions suivantes: acide oxalique -*o*.phénanthroline ferreuse et acide oxalique-Ce (IV). La méthode que les auteurs viennent de développer présente différents avantages sur celle prescrite par Willard et Young, puis-qu'elle évite la haute température de 50°, à laquelle on trouve que l'indicateur *o*-phénanthroline ferreuse subit une faible dissociation. Elle évite aussi l'utilisation de monochlorure d'iode comme catalyseur.

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PRELIMINARY COMMUNICATION

Some aspects of the polarographic behaviour of technetium and rhenium*

(*Received* 30 *May* 1959)

TECHNETIUM, element No. 43, was first obtained in 1937, by Perrier and Segré, by neutron-bombardment of a molybdenum target.[1] This is the method by which the main supply of the element available today has been obtained, but attempts have also been made[2] to extract workable amounts of technetium from the fission products of ^{235}U. Large quantities, however, are still not freely available for a complete investigation of its chemistry. Gerlit,[3] in a recent report on some chemical properties of the element, states that the chemical, and especially the analytical properties are comparatively little known.

A survey[4] of methods for the determination of technetium shows that the number of published methods is very small. Meggers[5] has suggested spectral lines suitable for the spectrographic determination of the element, and recently a colorimetric method based on thiocyanate has been reported.[6] Rulfs and Meinke[7] have determined the ultra-violet absorption spectrum.

In this laboratory, the amount of technetium available for study was originally about 30 micrograms, and later approximately 1 milligram. To carry out investigations on the analytical and general chemical behaviour of the element it was necessary to employ techniques requiring only very small amounts of the element. By means of ultramicro methods reagents for the detection[8] of Tc and for its separation from a number of associated elements and determination[9] have been developed. It was decided to investigate the oxidation-reduction behaviour of the element polarographically; and at the same time to examine rhenium as a control and a guide, since, as might be expected, work carried out in this laboratory on the separation of Tc from other elements indicated that its behaviour was much more similar to that of rhenium than to that of manganese. Other workers have drawn similar conclusions about its oxidation-reduction behaviour.[10]

A number of polarographic studies on rhenium have been reported.[11] As far as can be ascertained from the literature, no information on the polarographic behaviour of technetium has been published.† The results of the polarographic investigations are reported in this paper.

EXPERIMENTAL

Apparatus and solutions

Polarograms were determined using the conventional-type Tinsley Pen-Recording Polarograph. In some cases checks have been carried out using the Rapid-Sweep K1000 Southern Instruments Polarograph, but these results are not reported in the present paper.

To accommodate the small volume of solution, micro-cells with external calomel and silver electrodes were employed. De-aeration was carried out with argon. The dropping mercury electrode was calibrated and all measurements were made at 25° unless otherwise stated. All the values given for $E_{1/2}$ are with reference to the Standard Calomel Electrode. Technetium was present as pertechnetate, the solutions being $10^{-5}M$ in TcO_4^-.

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* This paper has been presented at a Joint Meeting of the Polarographic Society and the Scottish Section of the Society for Analytical Chemistry held in the Department of Chemistry, The Queen's University, Belfast on Friday 26 June 1959. Part of the material had previously been presented in preliminary form at a Joint Czech-Hungarian Polarographic Symposium held in Prague, Czechoslovakia in July 1958.

† After the announcement of the Meeting at which this paper was presented, the authors were kindly supplied by Dr. P. F. Thomason of the Oak Ridge National Laboratory with a copy of a paper dealing with work of a similar nature, to be presented by Dr. M. T. Kelley of that Laboratory at the 2nd International Congress of Polarography in Cambridge in August 1959.

The supporting electrolytes were as follows:

(*a*) $12N\ H_2SO_4$.
(*b*) $2N$ KCl.
(*c*) $2N$ NaOH.
(*d*) $4N$ HCl.
(*e*) $2N$ KOH buffered with sodium potassium tartrate.

RESULTS

(*a*) *In 12N H_2SO_4*

In the polarogram for pertechnetate there appeared to be a wave in the range from −0·3 volt to −0·8 volt, but this was not well formed. This is quite surprising, since in the reduction of perrhenate ion under the same conditions three well-defined waves were found. If the acid strength in the perrhenate solution was less than 8*N*, two waves only appeared.

The oxidation states to which the rhenium waves refer were observed visually by microscopic examination of the region in the vicinity of the mercury cathode, and yellow-orange and black products were found to form. On the basis of this examination it is suggested that the mechanism of reduction of perrhenate in sulphuric acid solution is as follows:

$$Re^{+7} + 3e^- \rightarrow Re^{+4}$$
$$Re^{+4} + 4e^- \rightarrow Re^0$$

In $8N\ H_2SO_4$ the wave obtained at $E_{1/2} = -0{\cdot}8$ volt was found to be ideal for the determination of rhenium occurring as perrhenate, and details will be published elsewhere.[12]

(*b*) *In 2N KCl*

The polarogram showed two waves. The first has a value $E_{1/2} = -0{\cdot}65$ volt and the second $E_{1/2} = -1{\cdot}30$ volt. Under the same conditions of reduction perrhenate showed waves at $E_{1/2} = -1{\cdot}1$ volt and $E_{1/2} = -1{\cdot}7$ volt.

To decide the oxidation states to which Tc^{VII} and Re^{VII} were reduced use was made of the Ilkovic equation. This may be written in the form

$$\frac{i_d}{c} = 607nD^{1/2}m^{2/3}t^{1/6}$$

where

i_d = diffusion current,
c = concentration
n = number of electrons transferred,
D = diffusion coefficient in cm^2/sec,
m = weight of mercury in mg/sec,
t = drop time in sec.

For the pertechnetate wave at $E_{1/2} = -0{\cdot}65$ volt, with the following values: $i_d = 0{\cdot}2\ \mu A$; $c = 10^{-2}\ mM$; $m^{2/3}t^{1/6} = 2{\cdot}40$; the value for n was found to be $\simeq 3$. This would indicate the reduction

$$Tc^{+7} + 3e^- \rightarrow Tc^{+4} \qquad (E_{1/2} = -0{\cdot}65 \text{ volt})$$

The second wave, occurring at $E_{1/2} = -1{\cdot}30$ volt rises to a maximum and then falls rapidly. Because of the nature of the wave it was not possible to apply calculations, but it is suggested that it might represent initial reduction to Tc^- followed by a reaction at the mercury surface. For the perrhenate reduction at $E_{1/2} = -1{\cdot}1$ volt calculations gave n = 8 indicating the reaction

$$Re^{+7} + 8e^- \rightarrow Re^-$$

i.e. the formation of rhenide as found by Lingane.[13]

(*c*) *2N NaOH*

In the pertechnetate solution a clearly defined step occurs at $E_{1/2} = -0{\cdot}85$ volt with the indication of a second step at $E_{1/2} = -1{\cdot}0$ volt. Under similar conditions per-rhenate shows a wave at $E_{1/2} = -1{\cdot}1$ volt.

Calculations from the Ilkovic equation indicate the transfer of 3 electrons for pertechnetate at $E_{1/2} = -0{\cdot}85$ volt:

$$Tc^{+7} + 3e^- \rightarrow Tc^{+4}.$$

The second wave again (as in the case of the 2*N* KCl solution) rises to a maximum and then falls off rapidly.

For rhenium the wave at $E_{1/2} = -1{\cdot}1$ volt also indicates a three-electron transfer:

$$Re^{+7} + 3e^- \rightarrow Re^{+4}.$$

(*d*) *In 4N HCl*

For pertechnetate two waves are obtained at $E_{1/2} = -0{\cdot}15$ volt and $E_{1/2} = -0{\cdot}35$ volt. There is also an indication of a third wave starting at $-0{\cdot}7$ volt. Under the same conditions per-rhenate shows waves at $E_{1/2} = -0{\cdot}1$ volt and $E_{1/2} = -0{\cdot}8$ volt.

(*e*) *In buffered 2N KOH*

The pertechnetate solution shows a well-defined wave at $E_{1/2} = -0{\cdot}65$ volt, and there is an indication of a second wave at $E_{1/2} = -1{\cdot}2$ volt. This solution was investigated in order to provide a comparison with manganese, where three waves are obtained[14] at $E_{1/2} = -1{\cdot}1$ volt, $E_{1/2} = -1{\cdot}3$ volt and $E_{1/2} = -1{\cdot}7$ volt.

The technetium wave at $-0{\cdot}65$ volt is well-defined, and promises to be suitable for the determination of technetium down to low concentration. This aspect is at present being studied.

A complete examination of all the reductions described here is being carried out with the rapid-sweep polarograph, and will be reported in due course.

Acknowledgement—We are indebted to the United Kingdom Atomic Energy Authority for facilities for separating small amounts of technetium from fission-product waste, and to U.K.A.E.A. and Professor R. S. Nyholm, University College, London for their loan of 1 milligram of technetium which was of great value in permitting confirmation of the preliminary results obtained on ultramicro quantities.

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DISCUSSION

MR. TYRRELL: Is it the intention to use the K1000 Polarograph to detect unstable intermediate valency states of technetium?

DR. MAGEE: Yes. Some investigations have been carried out, but these are not yet complete enough to give a full picture of the reductions.

Mr. TYRRELL: Is any work on rhenium and manganese reported in which the K1000 Polarograph has been used?

Dr. MAGEE: No investigations on rhenium or manganese using this instrument appear to have been reported in the literature. As a guide to the behaviour of technetium we, however, have carried out investigations, particularly on rhenium.

Mr. TYRRELL: You say that in 2*N* KOH manganese goes from the VII state to the II state. Are there intermediate states?

Dr. MAGEE: Yes. Three waves occur which indicate the following reduction steps: VII → IV: IV → III: III → II. Similar results have been reported in the literature by other workers.

Mr. FAIRCLOTH: Why do you use the Ilkovic equation to calculate n, and therefore assume a value for the diffusion coefficient?

Dr. MAGEE: The Ilkovic equation was used because, for rhenium, D_{ReO_4} had been determined. Until the exact value for D_{TcO_4} was determined, however, an approximate value based on that for rhenium indicated the order of n. I do agree, however, that from the shape of the plot E vs. $\log \frac{i_d - i}{i_d}$, n could also have been obtained.

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SHORT COMMUNICATIONS

The determination of tellurium in the presence of antimony in alloy amounts, using EDTA

(*Received* 6 *April* 1959)

An existing turbidimetric method,[1] modified as follows, has been extended to the determination of tellurium in alloys containing antimony.

Procedure

To 1 g of Te-Sb-Pb alloy add 50 ml of concentrated hydrochloric acid containing bromine, and leave until dissolved. Expel bromine by boiling, and make up to 100 ml with hydrochloric acid (2 : 1). Take a 25-ml aliquot of this solution, evaporate to 2-3 ml, and add 5 ml of 10% EDTA solution, 6 ml of 4% gum arabic solution and 40 ml of water. Dissolve any precipitate by heating, and add 5 ml of a solution of 32 g of sodium hypophosphite in 100 ml of 1 : 1 hydrochloric acid. Heat for 15 min, cool, and adjust to pH 1–2 with 0·88 ammonia solution. Make up to 100 ml and measure the optical density at 435 mμ. The error is 4–5%.

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Der Einfluss von Phosphorsäure auf die Uranbestimmung mit Ammoniumthiocyanat

(*Received* 12 *June* 1959)

Currah und Beamish[1] und vor kurzem Javanović und Zucker,[2] haben den Einfluß von Salz-, Salpeter- und Schwefelsäure auf die Farbbildung des Urans nach der Thiocyanatmethode wie sie von Nelson und Hume[3] beschrieben wurde, studiert. Sie fanden daß die Säuremenge genau bekannt sein muß, um die Resultate reproduzieren zu können. Der Einfluß der Phosphorsäure war nur bis 20 mg/ml untersucht worden, eine Konzentration bei der noch kein Einfluß bemerkt werden konnte. Da beabsichtigt war, in eigener Arbeit die Urankonzentration bei höherer Phosphorsäurekonzentration zu messen, wurde der Einfluß von Phosphorsäure auf die Farbbildung untersucht.

Es wurde gefunden, daß die Farbeintensität mit zunehmende Säurekonzentration abnimmt, wie in Tabelle I und Fig. 1 gezeigt ist.

Daneben zeigt es sich noch, daß die Farbe bei den höheren Phosphorsäurekonzentration sehr unbeständig ist und schon nach kurzer Zeit einen rötlichen Ton annimmt. Blanklösungen die kein Uran enthalten, zeigen ebenfalls einen rötlichen Ton bei höheren Phosphorsäurekonzentrationen wenn sie gegen dest. Wasser gemessen werden, wie in Tabelle II und Fig. 2 gezeigt ist.

TABELLE I.—Der Einfluß von Phosphorsäure auf die kolorimetrische Bestimmung des Urans mit Ammoniumthiocyanat.

H_3PO_4 *M*	Optische Absorption*		
	0,1 *mg U/ml*	0,2 *mg U/ml*	0,4 *mg U/ml*
1	10,0	19,0	29,0
2	7,5	13,5	21,5
4	5,0	12,5	19,5
8	6,0	10,5	18,0

* Farbe gemessen gegen Blanklösung

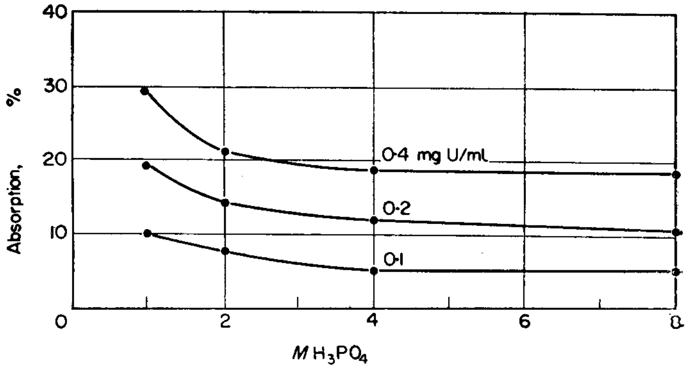

FIG. 1.—Der Einfluß von H_3PO_4 auf die kolorimetrische Bestimmung des Urans mit Ammoniumthiocyanat.

TABELLE II.

H_3PO_4 *M*	Optische Absorption* der Blanklösungen
1	5,0
2	5,5
4	6,0
6	6,5
8	11,0

* Farbe gemessen gegen dest. Wasser

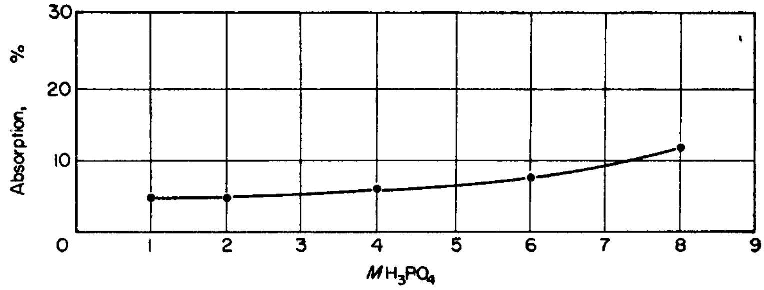

FIG. 2.—Optische Absorption der Blanklösungen.

Gemessen wurde in Lange-Kolorimeter mit Blaufilter sofort nach Zusatz der Reagenzien. Für die Uranbestimmung bei diesen Phosphorsäurekonzentrationen, muß die Phosphorsäure vor der kolorimetrischen Bestimmung abgetrennt werden.

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The improved preparation of sulphatoceric acid for preparation of standard titrimetric solutions

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PROBABLY the most frequent difficulty met with in popularizing the use of sulphatoceric acid as a standard oxidant involves the preparation of the solution of Ce^{IV} in sulphuric acid without the troublesome appearance upon standing of an insoluble residual cerium compound.

Ceric hydroxide, $Ce(OH)_4$, when properly prepared eliminated this difficulty entirely.

PREPARATION OF CERIC HYDROXIDE

Add a saturated solution of ammonium nitratocerate, $(NH_4)_2Ce(NO_3)_6$, in water to an excess of reagent ammonia, sp.gr. 0.90, diluted with an equal volume of water, and stir vigorously. Ceric hydroxide, $Ce(OH)_4$, is quantitatively precipitated in readily filterable form. Filter precipitate, and wash it free of ammonia and ammonium nitrate. Air dry this precipitate, requiring two to three weeks. Do not carry the dehydration lower than that which corresponds to the formula $Ce(OH)_4$ preferably leaving 2 to 3% unremoved moisture. Grind the horny product thus obtained to pass a 100-mesh sieve.

PREPARATION OF SULPHATOCERIC ACID IN SULPHURIC ACID

Place 10.4 g of $Ce(OH)_4$ in a dry 800-ml beaker. Add 50 ml of reagent sulphuric acid. Stir well, best with a magnetic stirring rotor. Now add slowly 150 ml of water. In 30 to 60 seconds the solution will be clear and reddish-orange in colour. If a minute insoluble portion remains, added heat with stirring is required. Dilute to 650–750 ml with water, transfer to a 1000-ml graduated flask and dilute to the mark. An approximately 0.05 normal solution of Ce^{IV} which is 0.75 formal in sulphuric acid is obtained (actual standard factor 0.0485 normal). The solutions thus obtained do not form any insoluble product upon long continued storage and their standard factor does not change.

This quality of $Ce(OH)_4$ is available commercially and one pound will prepare more than 40 litres of approximately 0.05 normal solution at a cost of less than 20 cents (1s 6d) per litre.

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Metal complexes of N:N:N′:N′ tetrakis-(2-hydroxypropyl)-ethylenediamine

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THE structural similarity of N:N:N′:N′-tetrakis-(2-hydroxypropyl)-ethylenediamine,* THPED (Figure 1), to ethylenediaminetetraacetic acid, EDTA, suggests that THPED may form complexes of analytical interest similar to those formed by EDTA.

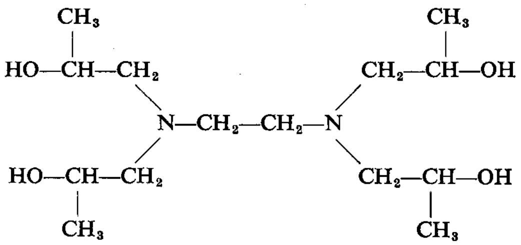

Fig. 1. N:N:N′:N′-Tetrakis-(2-hydroxypropyl)-ethylenediamine

TABLE I.—N:N:N′:N′-TETRAKIS-(2-HYDROXYPROPYL)-ETHYLENEDIAMINE METAL ION COMPLEXES

Cation	Complex	K_f	D_1	D_2	Colour
Cu^{++}	$Cu(THPED)^{++}$	$2{\cdot}6 \times 10^{9}$	$8{\cdot}8 \times 10^{-7}$	$6{\cdot}3 \times 10^{-10}$	blue
Ni^{++}	$Ni(THPED)^{++}$	$7{\cdot}1 \times 10^{6}$	$3{\cdot}2 \times 10^{-10}$	—	blue
Zn^{++}	$Zn(THPED)^{++}$	$2{\cdot}2 \times 10^{5}$	$5{\cdot}0 \times 10^{-8}$	$1{\cdot}0 \times 10^{-9}$	colourless
Cd^{++}	$Cd(THPED)^{++}$	$4{\cdot}2 \times 10^{7}$	$3{\cdot}2 \times 10^{-11}$	—	colourless
Pb^{++}	$Pb(THPED)^{++}$	$3{\cdot}1 \times 10^{7}$	$5{\cdot}0 \times 10^{-7}$	$8{\cdot}0 \times 10^{-11}$	colourless
Co^{++}	$Co(THPED)^{++}$	$5{\cdot}0 \times 10^{5}$	$4{\cdot}5 \times 10^{-8}$	$1{\cdot}3 \times 10^{-10}$	purple
Hg^{++}	$Hg(THPED)^{++}$	$1{\cdot}2 \times 10^{8}$	$1{\cdot}0 \times 10^{-7}$	$4{\cdot}0 \times 10^{-11}$	colourless
Ag^{+}	$Ag(THPED)^{+}$	$2{\cdot}4 \times 10^{4}$	—	—	colourless

Constants were determined at 27°, ionic strength $\mu = 0{\cdot}05$. THPED complexes of Ni^{+2} and Cu^{+2} have been previously reported by Hall *et al.*[1]

A survey of common metal cations (Fe^{+3}, Fe^{+2}, Cr^{+3}, Hg^{+2}, Cd^{+2}, Al^{+3}, Bi^{+3}, Pb^{+2}, Zn^{+2}, UO_2^{+2}, Sn^{+2}, Mg^{+2}, ZrO^{+2}, Ba^{+2}, Ca^{+2}, Sr^{+2}, Co^{+2}, Ag^{+}, Cu^{+2}, Ni^{+2}, Pt^{+4}, Ce^{+4}, Ce^{+3} and Th^{+4}) showed that Ag^{+}, Pb^{+2}, Hg^{+2}, Cu^{+2}, Cd^{+2}, Co^{+2}, Ni^{+2} and Zn^{+2} were sequestered by THPED. The formation constants, K_f, were estimated by potentiometric titrations. The complexes showed acidic properties; and where the acidity was titratable in aqueous solutions with $0{\cdot}1N$ NaOH potentiometrically, first (D_1) and second (D_2) acid dissociation constants were estimated (Table I).

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* N:N:N′:N′-tetrakis-(2-hydroxypropyl)-ethylenediamine is commercially available from Wyandotte Chemicals Corporation, Wyandotte, Michigan, under the registered trademark "QUADROL."

THPED is a colourless liquid amine, miscible with water in all proportions. It is commercially available at low cost. THPED solutions are readily standardized acidimetrically. THPED shows more selectivity than EDTA in formation of metal complexes. These chemical and physical properties of THPED suggest possible uses in compleximetry, as masking agent or a titrant, and as a colorimetric analytical reagent.

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Notes on the reduction of nitrates

(*Revised communication received* 16 *May* 1959)

THERE are many papers dealing with the reduction of nitrates,[1] but very few which consider the mechanism of the reduction. In connection with our new nitrate determination described elsewhere[2] we have examined this problem.

EXPERIMENTAL

(a) First an attempt was made to measure the effectiveness of the reduction with various metals. To a known amount of sodium nitrate (1 millimole) was added an equivalent amount of the well-powdered metal, the same sulphuric acid concentration and temperature being used in all cases. Using metals with a range of standard potentials (Ni, Cd, Fe, Zn, Al, Ti) iron was found to be the most effective reducing agent although its standard potential lies in the middle of the series. It was shown also that using a stoichiometric amount of the metal, reduction is not complete even in the case of iron ("*ferrum reductum*); this reduced nitrate ions to ammonia to an extent of 87%.

(b) The lowest limit of the amount of iron which produces complete reduction of 1 millimole of nitrate was investigated; 1·5 g of iron is sufficient for this purpose. Other metals must be added in much greater amounts for complete reduction.

(c) Finally an attempt was made to reduce the amount of iron needed for complete reduction. Some catalysts are very effective and in the presence of these the amount of iron can be reduced substantially. Results of these experiments are shown in Table I. In the presence of 0·3 g of cupric copper, nickel or cobaltic salt, 0·5 g metallic iron is sufficient for quantitative reduction of 1 millimole of nitrate ion. It is quite obvious that metals are deposited from the solution on the surface of iron and the effectiveness of this mixed catalyst is much greater than that of iron. To use Co or Ni salts is convenient from other aspects too; metallic Co or Ni, which is formed, was dissolved in the sulphuric acid present and so the determination could be carried out in homogenous medium.

DISCUSSION

According to these results complete reduction of nitrate to ammonia can be carried out only when iron is present. Using other metals a negative error occurs in all cases due to losses (some intermediate products, such as nitrogen dioxide, nitrous acid, nitric oxide or nitrogen are volatile). Moderate amounts of iron prevent the formation of volatile products, although the reduction takes place in several steps, as it was shown by Acworth and Armstrong.[3] Complete reduction of nitrate ions needs 8 electrons:

$$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O$$

but one atom of metallic iron produces only 2 electrons:

$$Fe = Fe^{2+} + 2e^-$$

TABLE I.—REDUCTION OF NITRATE WITH METALLIC IRON IN THE PRESENCE OF VARIOUS METAL SALT CATALYSTS

NaNO$_3$ taken, *mg*	Catalyst, *g*	0·1*N* HCl consumed by the ammonia, *ml*	Average consumption, *ml*	NaNO$_3$ found, *mg*	Difference	
					mg	%
85·51		8·60 8·77 8·94	8·77	74·54	−0·97	−13·0
	0·50CuSO$_4$·5H$_2$O	10·05 10·06 10·04	10·05	85·42	−0·09	−0·1
	0·50NiSO$_4$·7H$_2$O	10·05 10·06 10·05	10·05	85·42	−0·09	−0·1
	0·50CoSO$_4$·7H$_2$O	10·03 10·09 10·04	10·04	85·34	−0·17	−0·2
	0·50Cr$_2$(SO$_4$)$_3$·18H$_2$O	9·39 8·28 8·84	8·83	75·05	−10·46	−12·3
	0·50Na$_2$MoO$_4$·2H$_2$O	5·59 5·84 6·05	5·82	49·47	−36·04	−42·4

The oxidation number of nitrogen alters in stages so that N^{+5}, N^{+3}, N^{+1}, N^{-1}, N^{-3} are formed. Corresponding ions to these oxidation states are shown in Fig. 1. It may be seen from this scheme that the oxidation states N^{+4}, N^{+2} and N^{0}, corresponding to the volatile products NO$_2$, NO and N$_2$ respectively, are missing. Thus volatile nitrogen compounds can be formed only by secondary reactions.[4] Among these the following reactions can occur:

$$3HNO_2 = HNO_3 + 2NO + H_2O \tag{1}$$

$$2HNO_2 = N_2O_3 + H_2O \tag{2}$$

$$H_2N_2O_2 = N_2O + H_2O \tag{3}$$

$$HNO_2 + NH_3 = N_2 + 2H_2O \tag{4}$$

$$HNO_2 + H_2NOH = N_2O + 2H_2O \tag{5}$$

$$HNO_2 + HNO_3 = 2NO_2 + H_2O \tag{6}$$

$$HNO_3 + NH_3 = N_2O + 2H_2O \tag{7}$$

The rate of reaction (3), which is the decomposition of hyponitrous acid, is very small in strongly acidic dilute solution[5] and therefore it is impossible to show the presence of nitrous oxide in the gases after reduction by metals. Reaction (7) takes place only in non-aqueous media when temperature is raised above 150°C. The remaining possibilities (1, 2, 4–6) are concerned with the decomposition of free nitrous acid. It was possible to detect nitrous acid by the Griess–Ilosvay reagent in all the reductions[6,7] except those carried out with metallic iron. An attempt to detect nitrite ions in the presence of iron^{II} ions with the Griess–Ilosvay reagent was unsuccessful. It was possible to establish that on adding a dilute nitrous acid to an iron^{II} sulphate solution the pH of the solution increases somewhat. Nitrous acid may therefore form a stable complex with iron$^{\text{II}}$ ions, probably according to equation (8)

$$[Fe(H_2O)_6]^{2+} + HNO_2 = [Fe(H_2O)_5NO]^{3+} + OH^- + H_2O \tag{8}$$

It is possible that nitroprusside complex is formed from hexacyanoferrate$^{\text{II}}$ ions and nitrous acid by reaction (9) as follows:

$$[Fe(CN)_6]^{4-} + HNO_2 \rightleftarrows [Fe(CN)_5NO]^{2-} + OH^- + CN^- \tag{9}$$

This reaction is analogous to the reaction (8), the only difference being that in the latter NO^+ ions displace cyanide ions instead of water molecules from the inner sphere of the complex. Displacement of cyanide ions is accompanied by less decrease of free energy than the decomposition of the aqueous complex since the stability constant of the former is much greater than that of the latter. Thus, the exceptional function of iron during the reduction of nitrate ions can be explained by the fact that the nitrous acid which is primarily formed reacts with iron$^{\text{II}}$ ions (which are also products of the reaction) giving a stable complex in an acidic solution. There is therefore no possibility of decomposing the nitrous acid or of reaction between the latter and other products of the reduction forming nitrogen or nitrogen oxides.

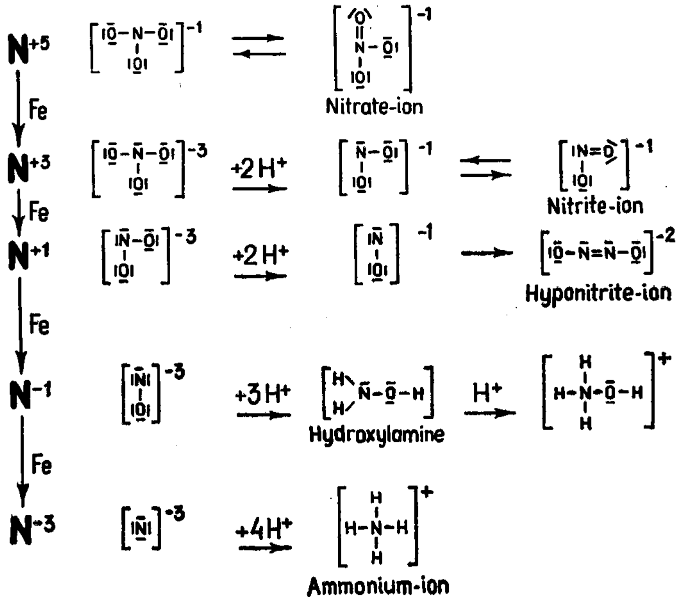

FIG. 1.

When, however, some traces of nitrogen oxides are formed during the reaction, they react with iron$^{\text{II}}$ sulphate (which is present in the solution owing to the reduction) forming nitroso-iron$^{\text{II}}$ sulphate. The latter reacts, as Tribalat suggested,[3] with nitrous acid instantaneously. We are of the opinion that the product of this reaction is also $[Fe(H_2O)_6NO]^{3+}$, and so the presence of iron$^{\text{II}}$ sulphate assures that all nitrogen formed having oxidation number +2 or +4 is transformed into a complex containing nitrogen with oxidation number +3. When nitrous acid is bound to a complex, the reaction goes readily without side reactions through N^{+1} and N^{-1} to ammonia.

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Komplexometrische Bestimmung von Bor neben Barium

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BEI der Wärmebehandlung von Werkzeugen aus Werkzeug-oder Schnellstahl werden vielfach Salzbäder verwendet, die neben viel Bariumchlorid einen geringen Anteil an Borax oder Borverbindungen enthalten.

Nach Angaben von Gautier und Pignard[2] ist es möglich, die Borsäure als Bariumborotartrat $Ba_5B_2C_{12}H_8O_{24}H_2O$ zu fällen. Das Bariumborotartrat ist sehr schwer löslich und eignet sich sowohl zu einer gravimetrischen quantitativen Halbmikrobestimmung der Borsäure, als auch zum qualitativen mikrochemischen Nachweis. Der qualitative Nachweis ist bis zu einer Grenzkonzentration von $1 \cdot 10^{-5}$ möglich, wobei 5 mg Bor erkennbar sind.

Gautier und Pignard bestimmen den Borgehalt bei ihren Analysen nach diesem Verfahren entweder durch Auswägen des bei 110° getrockneten Niederschlages oder durch jodometrische Titration des Bariums des Barium-borotartrates nach vorheriger Umsetzung mit Kaliumbichromat. Die mitgeteilten Beleganalysen für Mengen von 0,03–1 mg Bor zeigen Abweichungen von $\pm 3\%$.

Das Grundprinzip der neuen Methode beruht darauf, dass mit einer bekannten Bariummenge das Bor gefällt wird und im Filtrat der Überschuss an Barium mit Komplexon III bestimmt wird. Bei der direkten Titration des Bariums kann Phthaleinpurpur als Indikator verwendet werden. Es ist aber auch möglich, die Bariumbestimmung nach der Methode von Ballczo und Doppler[1] unter Verwendung eines Mischindikators auszuführen. Hierbei wird das gesamte Barium erst an Komplexon III gebunden und der Überschuss an ÄDTA mit genau eingestellter Magnesiumsalzlösung zurücktitriert.

Die Rücktitration der überschüssigen ÄDTA in Gegenwart von Bariumkomplexonat mit einer genau eingestellten Magnesiumchloridlösungberuht auf der Tatsache der sehr kleinen Komplexbildungskonstante des Bariums gegenüber Eriochromschwarz T und der äusserst starken Komplexbildung des Magnesiums mit diesem Farbstoff. Es ist daher unmöglich, das Barium aus seinem Komplexonkomplex durch Magnesiumionen bei Gegenwart von Eriochromschwarz T zu verdrängen, trotzdem der Magnesiumkomplexonatkomplex praktisch eine Zehnerpotenz stärker ist als der entsprechende Bariumkomplexonatkomplex.

$$\begin{array}{lccccc} & \text{Mg Erio} & + \ \text{BaH}_2\text{Y} & \rightleftharpoons & \text{MgH}_2\text{Y} & + \ \text{BaErio} \\ \log K & 7{,}0 & 7{,}76 & & 8{,}69 & 2 \end{array}$$

Aus dieser Gleichung ist zu ersehen, dass die Reaktion von links nach rechts nicht ablaufen kann, da das Produkt der Komplexbildungskonstante auf der linken Seite um einige Zehnerpotenzen grösser ist als auf der rechten Seite. Ein weiterer Vorteil bei der Rücktitration ist darin noch zu sehen, dass keine Komplexumbildung erfolgen muss und der erste Überschuss an Magnesiumionen sofort den festen Eriochromschwarz T-Komplex bildet und der bekannte Farbumschlag erfolgt. Nach Ballczo und Doppler wurde diese Methode noch insofern verbessert, dass sie an Stelle von Eriochromschwarz

TABELLE I.—ABSCHLIESSEND SOLLEN NOCH EINIGE VERSUCHSERGEBNISSE MITGETEILT WERDEN

Nr.	Borax		Bor		Verbr. ml 0,01 m ÄDTA		% Fehler
	gegeb. *mg*	gef. *mg*	err. *mg*	gef. *mg*	gef.	err.	
1	16	16,020	1,8155	1,818	2,100	2,097	+0,12
2	11	10,910	1,2480	1,238	1,430	1,420	−0,91
3	8	8,010	0,9078	0,9089	1,050	1,049	+0,12
4	5,6	5,569	0,6354	0,6319	0,730	0,734	−0,55
5	2,8	2,746	0,3177	0,3116	0,360	0,367	−1,93
6	1,6	1,602	0,1816	0,1818	0,210	0,2097	+0,12
7	0,8	0,788	0,0908	0,0892	0,103	0,1049	−1,50

T folgenden Mischindikator verwenden: 1 g Tropäolin OO, 2 g Eriochromschwarz T und 500 g NaCl.

Auf Grund der von mir durchgeführten Versuche haben sich folgende Arbeitsvorschriften zur Bestimmung von Borsäure in bariumhaltigen und bariumfreien Salzen und Lösungen am besten bewährt:

Verwendete Lösungen und Reagenzien

1. Fällungsreagenz für bariumfreie Salze:

13 g Bariumchlorid, krist.
14 g Weinsäure
240 g Ammoniumchlorid
} in 1 Liter dest. Wasser lösen

2. Fällungsreagenz für bariumhaltige Salze:

14 g Weinsäure
240 g Ammoniumchlorid
} in 1 Liter dest. Wasser lösen

Vor der Fällung wird dem verwendeten Fällungsreagenz 1/10 seines Volumens konz. Ammoniak (D. 0,910) zugesetzt.

3. 0,01–0,1 m Komplexon-III-Lösung (Dinatriumsalz der Äthylendiamintetraessigsäure).
4. 0,01–0,1 m Magnesiumchloridlösung.
5. Phthaleinpurpur 0,1 %ige alkoholische Lösung.
6. Mischindikator: 1 g Tropäolin OO
   2 g Eriochromschwarz T
   500 g Natriumchlorid p.a.
   werden fein verrieben.
7. Bariumchlorid p.a.
8. Borax und Borsäure p.a.
9. Puffer pH 10: 54 g NH$_4$Cl, 350 ml NH$_3$ (D. 0,910) auf 1 l. Wasser.

Arbeitsvorschrift für bariumfreie Salze

0,1 g bis 1 g Substanz werden in 100 ml destilliertem Wasser gelöst. 10 ml dieser Lösung sollen 0,1–3 mg Bor enthalten und werden mit dem mit Ammoniak versetzten Fällungsreagenz bis zur 100 ml Marke aufgefüllt. Nach 2 Std. wird durch ein trockenes Filter filtriert. 10 ml des Filtrates pipettiert man in einen 100 ml Messkolben, füllt mit dest. Wasser bis zur Marke auf und pipettiert 25 ml ab.

(a) Bei der direkten Titration und Verwendung von Phthaleinpurpur als Indikator werden die 25 ml mit 10 ml conc. Ammoniak, 15 ml dest. Wasser und 50 ml Alkohol verdünnt, einige Tropfen der alkoholischen Indikatorlösung zugegeben und sofort mit Komplexon III-Lösung titriert.

(b) Bei der indirekten Titration unter Verwendung des oben beschriebenen Mischindikators werden

15 ml 0,01 m Komplexonlösung, 20 ml Pufferlösung und ca. 30 mg des Mischindikators zugegeben und mit 0,01 m Magnesiumchloridlösung von blaugrün über grau auf rot titriert.

Bei dem Blindversuch werden 10 ml dest. Wasser mit dem Fällungsreagenz bis zur 100 ml Marke aufgefüllt und dann weiter wie oben beschrieben verfahren.

Da zur Ausfällung von 2 Mol. Borsäure 5 Mol. Bariumchlorid und zur Umsetzung von 1 Mol. Borax sogar 10 Mol. Bariumchlorid benötigt werden, entspricht

1 ml 0,01 m Komplexonlösung = 0,04328 mg Bor
1 ml 0,01 m Komplexonlösung = 0,38143 mg Borax ($Na_2B_4O_7$) 10 HO_2

Arbeitsvorschrift für bariumhaltige Salze

10 g Salz genau abgewogen werden in dest. Wasser gelöst und die Lösung bis zur 100 ml Marke aufgefüllt. Lösung 1: 10 ml dieser Lösung werden in einen Messkolben pipettiert und mit dem Fällungsreagenz 2 bis zur Marke aufgefüllt. Nach 2 Std. wird dann wie oben beschrieben weiter verfahren.

Der Blindversuch wird folgendermassen durchgeführt: 10 ml der Lösung 1 werden in einem 100 ml Messkolben mit destilliertem Wasser bis zur Marke aufgefüllt und dann, wie bereits beschrieben, weiter verfahren. Der Verbrauch an Komplexon III kann hierbei gleich auf $BaCl_2$ umgerechnet werden. Es ist also möglich, in einer Einwaage neben dem Borax-Gehalt auch gleich ben Bariumchloridgehalt zu bestimmen.

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LITERATUR

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Semi-micro determination of silicon and phosphorus in organic compounds

(*Received* 30 *May* 1959)

No method applicable when both silicon and phosphorus were present in a compound has been mentioned in recent reviews of methods for the determination of silicon[1,2] and phosphorus[3,4] in organic compounds. In the analysis of silicon in rocks, Brabson *et al.*[5] precipitated phosphorus with the silicon and corrected for the phosphorus content; and Wilson[6] prevented co-precipitation of silicate with phosphate without separation when analysing fertilisers.

It is, perhaps, relevant to note here that, during some preliminary experiments, it was found that silicon could not be determined in the presence of phosphorus-containing materials by simple wet oxidation of the organic material in a platinum crucible followed by weighing the silica produced. Very high results were obtained.

In order to permit analysis of some high-boiling liquids containing silicon and phosphorus, two semi-micro methods used in our laboratory for the determination of phosphorus have been modified to allow the determination of phosphorus and silicon on one individual sample.

Acid digestion method

The method of Belcher and Godbert[7]—digestion with nitric and sulphuric acids followed by gravimetric determination of phosphate after precipitation with Jörgensen's reagent—although shown not to be universally applicable,[8] had given satisfactory results for the determination of phosphorus in a variety of organic compounds. It was established that, after acid digestion of compounds containing silicon and phosphorus, the phosphate-containing acid liquid could be quantitatively separated from the silica precipitated in the glass boiling tube by use of an elongated glass filter stick (porosity 4). However, it was found impossible to dry the residue of silica in the glass tube so as to give consistent weights (*in situ*) for the determination of silicon.

In order to overcome this difficulty, a reasonably non-hygroscopic form of silica was prepared by removing the digestion liquid and then washing the residue with nitric acid (1 + 1) followed by alcohol. The residue was then dried at 100° under reduced pressure, cooled in a desiccator and weighed. The majority of this silica was then tipped into a platinum crucible, weighed, ignited to bright red heat and weighed again. The correction factor (weight after ignitition/weight of silica ignited) was applied to the original total weight of silica in the boiling tube and the silicon content calculated from this corrected figure.

TABLE I

Compound	% Si calculated	% Si found	% P calculated	% P found
$C_{22}H_{32}N_2O_3Si_2$	13·09	13·22		
		13·18		
		13·14		
		12·94		
$C_{26}H_{60}O_9P_2Si_2$	8·84	8·50	9·75	9·75
		8·52		9·76
$C_{38}H_{52}O_9P_2Si_2$	7·28	7·17	8·04	7·80
		7·49		7·80
		7·53		7·78
		7·59		

The results obtained for the analysis of three research compounds (one not containing phosphorus) by this method are shown in Table I.

Peroxide bomb method

The second, and more universally successful, method[8] used in our laboratory for phosphorus determination involves decomposition of the organic material (in a micro bomb) with sodium peroxide followed by precipitation of phosphate in the acidified bomb leachings as quinoline phosphomolybdate. Co-precipitation of silicomolybdate could be avoided by complexing with citric acid[6] or by removal of the silicon[8] by volatilisation as tetrafluoride or precipitation as silica. The latter procedure was found to provide a means for the determination of silicon.

The normal procedure for the determination of phosphorus[8] was followed except that the acidified bomb leachings were evaporated to dryness and baked at 110°. After cooling, the crystals were moistened with concentrated hydrochloric acid, dried and baked again. The soluble salts were dissolved in hot water and filtered through a paper-pulp pad, the filtrate and washings being collected in a conical flask for precipitation of phosphate in the usual way. All the insoluble residue was collected on the paper pad during the filtration and the whole was quantitatively transferred into a platinum crucible. The paper was ashed and the residue was weighed, treated with hydrofluoric acid and reweighed. From the loss in weight, the silicon content of the organic material was calculated.

Results obtained for the analysis of three organic compounds are shown in Table II. A gravimetric finish[9] for the determination of phosphorus was used.

Discussion

From the limited number of samples available, both methods have produced results which are within the normally accepted limits (±0·3 %) for organic analysis but it is considered that the procedure following peroxide bomb fusion is superior, being manipulatively simpler, more precise and, probably, more universally applicable.

TABLE II

Compound	% Si calculated	% Si found	% P calculated	% P found
$C_{14}H_{36}O_9P_2Si_2$	12·03	11·81	13·28	13·16
		11·91		13·18
$C_{26}H_{60}O_9P_2Si_2$	8·84	8·68	9·75	9·72
		8·74		9·75
$C_{38}H_{52}O_9P_2Si_2$	7·28	7·15	8·04	8·00
		7·15		7·99

Both methods suffer from the disadvantage that the conversion factor for silicon (Si/SiO_2 = 0·4672) is poor, requiring a sample containing at least 2·5 mg of silicon to provide a reasonable weight of silica for determination. Precipitation as the silicomolybdate of an organic base[10-12] might provide a better means for determining silicon after separation from phosphate.

Interference in the determination of silicon by fluoride, after mineralisation in the peroxide bomb, can be overcome by the addition of boric acid to the bomb leachings before acidification.

Acknowledgements—We are indebted to Mr. E. J. P. Fear and Dr. I. M. White for the provision of samples, and to Mrs. M. W. Roberts for experimental work on the acid digestion procedure.

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Talanta, 1959, Vol. 2, pp. 392 to 393. Pergamon Press Ltd. Printed in Northern Ireland

LETTERS TO THE EDITOR

Ion-exchange separation from alcoholic medium

SIR:

The great value of analytical separation of metals in solution by anion-exchange from hydrochloric acid solution is now firmly established. Kraus and Moore have studied the distribution coefficients of most metals as a function of aqueous hydrochloric acid concentration. Working at General Electric Research Laboratory and at Iowa State, we have discovered independently that anion-exchange separations in the system hydrochloric acid–water–alcohol offer great versatility. One group (G.E.) used ethyl alcohol, and the other (Iowa State) uses *iso*propyl alcohol.

The distribution coefficients for most metals are significantly higher in systems containing an appreciable quantity of alcohol. This makes a partly nonaqueous medium especially valuable for retention of metals, such as copper^{II} and manganese^{II}, which have low distribution coefficients in aqueous hydrochloric acid solution. Also, most metals are strongly taken up by anion-exchange resins at a much lower hydrochloric acid concentration in alcohol–water than in water alone. The altered exchange behaviour of metals in partly alcoholic medium permits some separations which are not possible in aqueous hydrochloric acid. Detailed papers concerning analytical aspects of ion-exchange separations from alcoholic medium will be forthcoming.

Schenectady, New York, U.S.A.
DONALD H. WILKINS
GEORGE E. SMITH

Ames, Iowa, U.S.A.
JAMES S. FRITZ
DONALD J. PIETRZYK

17 *July* 1959

Precipitation of nickel dimethylglyoximate from homogeneous solution by direct synthesis of the organic reagent

SIR:

Although metal chelates, *e.g.* nickel dimethylglyoximate and aluminium 8-hydroxyquinolinate can be precipitated from homogeneous solution by raising the pH through the hydrolysis of urea,[1,2] there have been but few and only recently reported methods involving the synthesis *in situ* of the organic chelate reagent. For example, Tarasevich[3] has precipitated copper and silver with 1H-benzotriazole synthesized by reacting nitrous acid and *o*-phenylene-diamine, and Heyn and Brauner-have precipitated cobalt with 1-nitroso-2-naphthol synthesized by reacting nitrous acid and 2-naphthol.

We have been able to precipitate nickel^{II} from homogeneous solution with dimethylglyoxime generated by reacting biacetyl with hydroxylamine in aqueous solution under controlled conditions; the chelate is precipitated in the form of red needles. The results of this investigation, which includes the synthesis of other oximes, will subsequently be reported in *Talanta.* (**Note**: At the time this note was written, Ramette[5] reported to us that he has precipitated nickel dimethylglyoximate as long red needles of the order of 2 mm in length by the replacement method.[6] Ramette uses a slight excess of EDTA to complex nickel^{II} in the presence of dimethylglyoxime and then adds zinc ions which slowly replace the nickel ions, thus effecting precipitation of nickel dimethylglyoximate.)

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29 *July* 1959

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Talanta, 1959, Vol. 2, p. 394. Pergamon Press Ltd. Printed in Northern Ireland

TALANTA MEDAL

The Publishers of TALANTA, Pergamon Press Limited, have generously offered to provide the funds for the institution and award, from time to time, of a TALANTA Medal. This Medal will be awarded for outstanding contributions to analytical chemistry, and will have a value of 100 guineas.

CONDITIONS OF AWARD

1. The TALANTA Medal will be awarded for really outstanding contributions to analytical chemistry made by scientists in any area of research endeavour.

2. Any outstanding paper or papers contributed to TALANTA will automatically be considered for the Medal. Other work may be proposed by any member of the Advisory Board of TALANTA to the Editors for consideration. The award will not be confined to current work, but may be made for work already completed which has since been recognised as outstanding.

3. The Medal will only be awarded on the unanimous recommendation of a committee composed of the Editor-in-Chief, the Regional Editors, and the Chairman of the Advisory Board. In addition, the recommendation must be supported by at least two-thirds of the members of the Advisory Board. Although normally the TALANTA Medal will not be awarded more frequently than once in each year, no attempt will be made to award it at fixed intervals.

Talanta, 1959, Vol. 2, pp. 395 to 399. Pergamon Press Ltd. Printed in Northern Ireland

BOOK REVIEWS

Precipitation from Homogeneous Solution. LOUIS GORDON, MURRELL L. SALUTSKY and HOBART H. WILLARD. John Wiley and Sons, Inc., New York: Chapman and Hall, Limited, London, 1959. pp. viii + 187. 60s. $7.50.

FOR a number of years the reviewer has used the field of precipitation from homogeneous solution as a very effective example to show that vital developments in "classical" analysis are still possible. It is therefore to him a particular pleasure to welcome this account of the subject by authors whose names are so closely associated with the field and who have done so much to develop it.

After a brief introductory chapter, the book goes on to deal with the main categories of compound which can be precipitated from homogeneous solution—hydroxides and basic salts, phosphates, oxalates, sulphates, sulphides and miscellaneous compounds. In all of these chapters the general principles are discussed, and then detailed procedures for the analytical applications of the technique are given. These chapters therefore give an excellent account, compact but comprehensive, of the use of the technique in analytical chemistry.

If the book stopped at this point it would be a useful contribution to the practice of analytical chemistry, but would fail to bring out some of the most important implications of the technique. However, the next two chapters, dealing with co-precipitation and fractional precipitation, are a welcome contribution to the theory of precipitation, and at the same time an admirable account of the way in which this new technique has contributed (and is capable of further contribution) to our knowledge of that complex phenomenon, precipitation, about which, after effectively centuries of use, so much still is not understood. These two chapters, and in particular the former, should stimulate a considerable amount of thought about an everyday procedure which is too often taken for granted.

A final chapter discusses the application of the principles of precipitation from homogeneous solution to several regions of chemical technology—separation processes, the production of reproducible carriers for radioactive products, and other materials not otherwise readily manufactured. This emphasises the fact that a field which is often thought of as purely analytical has much wider applications.

The book, as would be expected by anyone who knows the authors and their contributions to analytical chemistry, is pleasantly written, concise, and easy to read. It is a valuable survey of this field at a time when the literature is becoming sufficiently extensive to require it, and it will be found indispensable to all analytical chemists dealing (and which of them does not?) with precipitation processes. As would be expected from the publishers' imprint, the production is above criticism.

If the reviewer may, in the end, be permitted to utter one very gentle reproach, it is that the authors have succumbed to the all too prevalent practice of using "data" when they mean "results".

CECIL L. WILSON

EDTA Titrations. An Introduction to the Theory and Practice. H. FLASCHKA. Pergamon Press, London, 1959. Pp. 138. 42s.

EDTA is now established as an analytical reagent, not merely for water hardness determination by the Schwarzenbach procedure, but as one of the most widely-used and versatile of organic compounds in the whole field of analytical chemistry. A glance through an index of the 1500 or so papers which have now appeared on this single topic shows that, with the possible exception of a rare metal or two, no single metallic element has altogether escaped the attentions of EDTA in the course of its determination, detection or separation.

If it is not a very long-felt want (for the major development of the subject has been within the past five years) the need of a teaching manual on the analytical uses of EDTA has certainly become keenly-felt. This lacuna Professor Flaschka, whose wide teaching and research experience render him particularly well fitted for the task, has now most ably filled. As its title implies, his book has, probably wisely, been restricted in scope to titrimetric methods, and does not refer to the use of EDTA as a masking agent in gravimetric analysis and so forth. The brief theoretical treatment with which it opens is of exceptional clarity and there is included a discussion of the more important metallochromic indicators and of potentiometric and photometric methods of end-point determination. Full instructions, with the more important references to the literature, are given for the determination of most of the common metals and of a few representative mixtures of cations, and in the course of these the various ways in which EDTA can be used as a titrant are well exemplified. The use of masking agents and of indirect methods such as those for determining phosphate and halogens are also described. Above all, this is a *practical* book, the short chapter dealing with the possible reasons for the failure of a method in practice being of particular value. The reviewer's only important criticism is, in fact, purely one of economics: the price of 42s. is surely far too high for so comparatively small and specialised a book which is, moreover, primarily intended for students.

J. K. AIKEN

Trace Analysis. JOHN H. YOE and HENRY J. KOCH, JR. John Wiley and Sons, Inc. New York, Pp. xiii + 672. $12.00.

HIDING under the simple title of *Trace Analysis* this book may, at first meeting, convey the idea that it is a textbook of qualitative methods for the detection of small amounts of metals, or just another book on spot tests. A study of the contents, or even a quick glance at the "Foreword" will, however, soon dispel this idea and reveal that it has a *raison d'être* and is something new in the field of trace constituents. It is a report of papers presented at a Symposium on Trace Analysis held at the New York Academy of Medicine in November 1955. The Symposium itself was the outcome of a general feeling that, despite the importance of trace elements in chemistry, medicine, biology, industry, etc., the subject had not received the co-operative effort it deserved as a unified field of science.

In soil chemistry, as catalytic agents in chemical processes, and in alloy steels, to mention only a few examples, trace elements have important effects on the qualities and behaviour of the whole material. Although the discovery of the function of the trace element is in the hands of the soil chemist, the enzyme chemist or the metallurgist, it is the analytical chemist whose job it is to demonstrate the presence and quantity of the element.

The number of ways in which the above objectives can be achieved may amaze some and surprise many for, in this book there are 24 contributions by authors, many of whom are internationally well-known, on topics which cover the whole field of analytical chemistry and part of what is sometimes regarded as the realm of physical chemistry.

After a brief introduction by one of the editors, the book is divided into three parts. Part I comprises 20 chapters under the general heading of "Methodology". The first chapter by H. H. Strain deals with the use of Chromatography and Electrochromatography in trace analysis. This is followed by chapters on Ion Exchange (K. A. Kraus); Extraction (L. C. Craig); Chemical Microscopy (W. C. McCrone); Spot Tests (F. Feigl and P. W. West); Colorimetry (M. G. Mellon); Fluorometry (C. E. White); Flame Spectrometry (B. L. Vallee); Potentiometry (N. H. Furman); Coulometry (L. B. Rogers); Polarography and Voltammetry (P. Delahay); Amperometry (C. N. Reilley); Emission Spectrochemical Analysis: Basic Principles and Applications (L. W. Strock); Emission Spectrochemical Analysis: Determination of Trace Elements in Plants and other Biological Material (R. L. Mitchell); γ-Ray Spectroscopy (H. W. Koch); Mass Spectroscopy (M. G. Inghram); X-ray Spectroscopy (T. Hall); X-ray Micrography (A. Engstrom); Neutron-Activation Analysis (A. A. Smales); Microbiological Techniques: Inorganic Ions (E. E. Snell).

In Part II, which is given the general heading of instrumentation, two chapters are supplied by R. H. Muller entitled "Instrumentation," and "The Interaction of β-particles with Matter."

Part III has the general title of "Sensitivity, Separation, Concentration and Contamination." This contains two chapters. The first is Trace-Element Sensitivity: Comparison of Activation Analysis with other Methods (W. W. Meinke) and the second, Separation, Concentration and Contamination (R. E. Theers).

Each chapter is followed by a discussion, prepared by a discussion leader and, in the references, which refer to original papers where details of theory, procedures, apparatus and applications may be found, selected references to books on specific subjects are also given. An abstract is given at the beginning of each chapter.

Since the book is merely a report of each paper read at the Symposium, little criticism can be made of the choice of subjects by the authors. A case, however, might be made against the arrangement. At present each chapter stands independently without link to the authors. It would have made easier reading, particularly for non-analysts, if the authors had, for example, started with "Spot Tests" and provided a short link between this and other chapters, thus showing the development of trace analysis. Further, the chapter "Interaction of β-particles with Matter" is included under instrumentation, although it appears to have little to do with instrumentation.

Despite these minor criticisms, this is a really valuable book and, in its 672 pages, must offer something for those who are interested in the various techniques which can be applied to the various fields of trace element detection and determination. It has placed trace analysis on a level which before has been denied to it. It must, therefore, be welcomed.

R. J. MAGEE

Actas do XV Congresso Internacional de Química Pura e Aplicada, 1956, Volume I. Secretario-Geral do XV Congresso, Instituto Superior Téchnico, Lisboa, Portugal. 1957. pp. 1028. Escudos 320$00 (for 3 volumes).

THIS massive volume, which suffers from being paper-bound, is only the first of three presenting the papers given at the XVth International Congress of Pure and Applied Chemistry (Analytical Chemistry) held in Lisbon in September 1956. This volume contains the Addresses to the Congress, the principal Lectures, and the papers contained in Section I (Microchemical Methods) and Section 3 (Electrical Methods). Papers belonging to Section 2 (Biological Methods), being very few in number, will be included in Section IX (General).

It is stated that the other two volumes will be ready early in 1959. It is regrettable that there has been such a long delay in the publication of these proceedings, but no doubt the fact that all now are, or are about to be, available, will be welcomed. A number of the papers are presented in abstract form only, and presumably have been published elsewhere in full.

The printers and proof-readers, as might be expected in a multilingual volume, have found some difficulty, and the English at least reads a trifle peculiarly at times, though it is usually comprehensible. The running heads have not always been happily chosen.

Summaries to the papers are sometimes missing, sometimes given in a single language at the beginning or at the end of the paper, and sometimes given in several languages. This volume is undoubtedly a problem for abstractors. The lack of an index, also, makes it very difficult to use, but the latter may perhaps be supplied in a subsequent volume.

Tables of Constants and Numerical Data. Pergamon Press Limited, London, New York, Paris. **Volume 8: Selected Constants: Oxidation-Reduction Potentials.** G. CHARLOT. 1958. pp. vi + 41. 30s. **Volume 9: Selected Constants: Optical Rotatory Power, II: Triterpenes.** J.-P. MATHIEU and G. OURISSON. 1958. pp. 302, £7. **Volume 10: Selected Constants: Optical Rotatory Power, III: Amino-acids.** J.-P. MATHIEU, P. DESNUELE and J. ROCHE. 1959. pp. 61. 40s.

THESE valuable additions to chemical reference literature are produced under the aegis of the International Union of Pure and Applied Chemistry, and with the full co-operation of commissions and members of that body.

The complete work is, of course, quite outside the reach of the private individual, but no scientific library which aims to be well equipped can afford to be without them. In addition, individual volumes may well be expected to have such constant use as to make them a desired possession for the individual analytical chemist or at least for the analytical laboratory, so that they may be more readily available for frequent consultation. Optical rotatory power has, perhaps, a limited application, but the number of fields of modern chemistry which can make use of the most reliable and up-to-date information on oxidation-reduction potentials is nowadays legion.

The volumes are attractively and very sturdily bound, and should stand up well to the excessive amount of handling to which they may expect to be subjected. Some comment is perhaps called for about the lack of uniformity in the presentation of the title on the cover: in one of the present volumes this in English, in another in French, and in the third is given in both languages.

Annotated Bibliography of α-Benzildioxime. CHARLES V. BANKS, MICHAEL J. MAXIMOVICH, NELSON J. FOWLKES and PETER A. BEAK. United States Atomic Energy Commission, Research and Development Report ISC 1038. 1958. pp. 60, $1.75.

THIS booklet contains 150 references, covering the period from 1883 to 1956, dealing with α-benzildioxime, together with summaries of the contents of each reference. It is not restricted to the analytical uses of the material, but covers all aspects of its chemistry and application.

It is available from the Office of Technical Services, U.S. Department of Commerce, Washington, 25, D.C., U.S.A.

Source Material for Radiochemistry. Sub-Committee on Radiochemistry, Committee on Nuclear Science. Publication No. 654, National Academy of Sciences, National Research Council, U.S.A. 1959, pp. 23.

THIS booklet contains some 60 references, with brief abstracts, to papers dealing with radiochemical topics or topics which may have some bearing on radiochemical problems. Many of these references are to documents, and the availability of each item is listed. Material up to early 1959 is included.

The booklet is available free of charge from the Division of Physical Sciences, National Research Council, National Academy of Sciences, 2101 Constitution Avenue, Washington, 25, D.C., U.S.A.

Zincon: Organic Chemical Reagents, Monograph No. 37. EILEEN A. JOHNSON and W. JABLONSKI. Hopkin and Williams, Ltd., 1959. pp. 6.

THIS little booklet deals with the detection and absorptiometric determination of zinc and mercury by zincon (2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene), and with the use of the reagent as an indicator in the complexometric determination of zinc. Detailed procedures are described, interferences are fully dealt with, and a bibliography of 14 references is supplied.

It may be obtained from Messrs. Hopkin and Williams Limited, Chadwell Heath, Essex, England.

The following publications have been received:

Oak Ridge National Laboratory, Analytical Chemistry Division, Annual Progress Report for period ending December 31, 1958; 3 March 1959, M. T. KELLEY and C. D. SUSANO, ORNL-2662, TID-4500 (14th Ed.) Pp. xiii + 100. $2.50.

Neutron Activation Analysis Methods for the Group VIII Elements. C. E. MILLER. ORNL-2715, 21 May 1959. Pp. viii + 108. $2.50.

Analysis of Uranium Solutions using Anion Exchange in Nitrate Media. O. A. VITA, C. F. TRIVISONNO and C. W. PHIPPS. A.E.C. Research and Development Report GAT-283, April 28 1959. Pp. 14. $0.50.

Ion Exchange-Spectrographic Determination of Arsenic and Phosphorus in River Water. R. KO. A.E.C. Research and Development Report HW-59008, 21 January 1959. Pp. 14. $0.50.

Precipitation of Manganese Dioxide. J. T. GRACE, H. E. HENRY and D. KARRAKER. A.E.C. Research and Development Report DP-346, December 1958. Pp. 10. $0.50.

Internal Standard Method of General Spectrographic Analysis. F. M. SMITH. A.E.C. Research and Development Report HW-59864, 9 April 1959. Pp. 16. $0.50.

These are all available from Office of Technical Service, Department of Commerce, Washington, 25, D.C., U.S.A.

Talanta, 1959, Vol. 2, pp. 400 to 401. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

The following meetings have been arranged:

Friday 25 *September* 1959: **Society for Analytical Chemistry,** North of England and Scottish Sections: *Water: Determination and Examination. Determination of Water:* Dr. J. H. THOMPSON, *Water Analysis as a Guide to Potability:* Mr. J. G. SHERRATT. *Determination of Radioactive Contaminants in Water:* Mr. G. E. EDEN. Central Hotel, Victoria Viaduct, Carlisle, England. 7.15 p.m.

Monday–Wednesday 26–28 *October* 1959. **Seventh Detroit Anachem Conference.** Memorial Conference Center, Wayne State University, Detroit, Michigan, U.S.A.

Enquiry regarding registration may be made from Mr. J. W. COMPTON, Research Department, Wyandotte Chemicals Corporation, Wyandotte, Mich., U.S.A.

On the Tuesday afternoon will be held the Anachem Award Session in honour of G. FREDERICK SMITH, Emeritus Professor, University of Illinois. At the Conference Dinner JOHN C. BAILAR, Jr., President of the American Chemical Society will be guest speaker.

Wednesday–Friday 4–6 *November* 1959: Analytical Groups of the New York and North Jersey Sections of the **American Chemical Society,** New York, Delaware Valley, New England and Baltimore–Washington Sections of the **Society for Applied Spectroscopy, Metropolitan Microchemical Society:** Eastern Analytical Symposium and Instrument Exhibit. Hotel New Yorker, New York City.

The meeting will consist of a series of 3-hour symposia of invited papers of extended length by experts in a number of fields of interest to analysts. The emphasis will be on recent developments in these specialities. Features of the meeting will include the Annual Medal Award of the Society for Applied Spectroscopy and the banquet address by Dr. W. F. MEGGERS of the National Bureau of Standards.

For further information about the meeting contact PAUL LUBLIN, Publicity Chairman, Sylvania Research Laboratories, Bayside, New York, U.S.A.

Monday 29 *February–Friday* 4 *March* 1960: Analytical Chemistry Group, Pittsburgh Section, **American Chemical Society** and **Spectroscopy Society of Pittsburgh:** Eleventh Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. Penn-Sheraton Hotel, Pittsburgh, Penna., U.S.A.

This will include symposia on Statistical Control of Laboratory Operations, Gas Chromatography Nuclear Magnetic Resonance, Molecular Fluorescence Spectroscopy, Application of Infra-red Spectroscopy to Trace Analysis, Applied Nucleonics, and X-Ray Fluorescence Spectroscopy. In addition, papers are invited in all fields of analytical chemistry and spectroscopy.

Authors planning to submit papers should note that the last date for receipt of abstracts is 15 October 1959.

Information regarding papers may be obtained from Mr. JAMES E. PATERSON, Program Chairman, The Pittsburgh Conference, Jones and Laughlin Steel Corporation, Graham Research Laboratory, Pittsburgh, 30, Penna., U.S.A.

Wednesday–Friday 8–10 *June* 1960: **Society for Analytical Chemistry** and **the Gas Chromatography Discussion Group,** under the auspices of the **Hydrocarbon Research Group of the Institute of Petroleum:** Third Symposium on *Gas Chromatography.* The Assembly Rooms, Edinburgh, Scotland.

The papers presented will be in a similar form to those presented at the 2nd Symposium on Gas Chromatography held in Amsterdam and will be classified under three headings:— 1. Theory: 2. Apparatus and Techniques: 3. Applications.

Those papers concerning the application of the technique must have some novel feature to warrant their inclusion in the programme. Authors who wish to submit papers must forward an abstract (250 words) to the Secretary by 31st October, 1959. Abstracts received after this date cannot be considered for inclusion.

Papers to be read will be chosen by an editorial committee and the authors will be informed before 14th November, 1959.

Those wishing to attend the Symposium should apply to the Secretary for registration forms which will be sent as soon as they are available. The fee for the Symposium and receptions will be about £4. *Secretary:* Mr. L. BREALEY, Boots Pure Drug Co. Ltd., Standards Department, Station Street, Nottingham, England.

The *B.S.I. News* announces, among others, the following revised British Standard:

B.S. 1016: *Methods for the analysis and testing of coal and coke,* Part 7: 1959: *Ultimate analysis of coke.* This deals with the determination of carbon, hydrogen, nitrogen and total sulphur in coke. (Price 7s. 6d.) Part 11: 1959: *Forms of sulphur in coal.* This deals with the determination of sulphate, pyritic and organic sulphur in coal. (Price 4s. 6d.)

Amendment slips have been issued for the following Standards: PD 3315: Amendment No. 1 to B.S. 1428, Part D1: 1952: *Burettes with pressure-filling device and automatic zero.*

PD 3334: Amendment No. 3 to B.S. 846: 1952: *Burettes and bulb burettes.*

PD 3385: Amendment No. 1 to B.S. 1428 Part 1: 1953: *Combustion boats, sheaths and contact stars for microchemical analysis.* This amendment includes an alteration to the title, which will now read *Combustion boats and sheath for microchemical analysis.*

B.S.I. Publications may be obtained from the B.S.I. Sales Branch, 2, Park Street, London, W.1., England.

EDITORIAL NOTE

Two further issues of TALANTA will be published before the end of this year in order to complete the six issues due for 1959.

At a recent editorial meeting the problems raised by the increasing number of papers of high quality submitted to the Journal were discussed. Up to the moment, in spite of printing difficulties, an average publication rate close to our aim of 3–4 months for long communications and 30–60 days for preliminary communications and letters to the Editor has been maintained. It was decided, however, that if an increased period between acceptance and publication was not to be imposed upon contributors, it would be necessary to go over to monthly publication. Therefore, as from 1st January 1960, TALANTA will be published monthly.

In spite of the greater number of pages thereby involved, subscription rates **per annum** to **private subscribers** will remain the same (5 guineas or $15.00).

The subscription rate **per volume** to **libraries and institutions** will remain the same (£6 or $17.00). Since the new production schedule will be at the rate of 3 volumes per year, the charge will therefore be £18 or $51.00 **per annum.**

Talanta, 1959, Vol. 2, p. 402. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

The Formal Oxidation Potentials of Substituted 1:10-Phenanthroline Ferrous Complexes of Low Solubility. The Preparation and Redox Potentials of the Vanadate-Vanadyl System of Potentiopoised Solutions. G. FREDERICK SMITH and WM. M. BANICK, JR. (27 *May* 1959).

A Gamma Absorptiometer for Laboratory Analysis of the Heavy Metals. W. L. MADDOX and M. T. KELLEY. (28 *May* 1959).

A Critical Study of the Precipitation of Ammonium Phospho-12-molybdate. PETER CANNON. (2 *June* 1959).

Der Einflus von Phosphorsäure auf die Uranbestimmung mit Ammoniumthiocyanat. FATHI HABASHI. (12 *June* 1959).

Über das Verhalten von isolierten Einschlüssen auf Eisenwerkstoff bei hohen Temperaturen. HANNS MALISSA. (15 *June* 1959).

Metal Complexes of N:N:N′:N′-Tetrakis-(2-hydroxypropyl)-ethylenediamine. D. A. KEYWORTH. (16 *June* 1959).

The Improved Preparation of Sulphatoceric Acid for Preparation of Standard Titrimetric Solutions. HARVEY DIEHL and G. FREDERICK SMITH. (18 *June* 1959).

Quantitative Spectrochemical Analysis of Minor Elements in Silicates with Double Internal Standards. HIROSHI HAMAGUCHI, ROKURO KURODA and RYOKICHI NEGISHI. (8 *July* 1959).

The Application of the Cathode Ray Polarograph to the Analysis of Explosives, II. The Determination of Mercury Fulminate. J. HETMAN. (9 *July* 1959).

Analytical Applications of Xylenol Orange, IV. A Spectrophotometric Study of the Ferric Xylenol Orange Complex. K. L. CHENG. (14 *July* 1959).

Nucleation and Precipitation of Silver Chloride from Homogeneous Solution. DAVID H. KLEIN, LOUIS GORDON and THOMAS H. WALNUT. (17 *July* 1959).

The Precipitation Nucleus of Silver Chloride. DAVID H. KLEIN, LOUIS GORDON and THOMAS H. WALNUT. (17 *July* 1959).

Dosage Colorimétrique du Soufre en Faibles Teneurs dans les Aciers, les Fers et Cobalts Purs. P. TYOU and L. HUMBLET. (20 *July* 1959).

Organic Analysis, XX. Microestimation of Blood Sugar with 5-Hydroxy-1-tetralone. TSUTOMU MOMOSE and YOSUKE OHOKURA. (21 *July* 1959).

A Comparison of the Alkali Methoxides in the High-Frequency Titration of Acids in Dimethylformamide. S. F. TING, W. S. JEFFERY and E. L. GROVE. (22 *July* 1959).

Titration of Metal Oxinates with Potassium Methoxide. ELIZABETH E. UNDERWOOD and A. L. UNDERWOOD. (20 *July* 1959).

Tesla-luminescence Spectra, I. The Spectra of Some Inorganic Gases. T. GIVEN, R. J. MAGEE and C. L. WILSON. (28 *July* 1959).

Talanta, 1959, Vol. 2, p. 403. Pergamon Press Ltd. Printed in Northern Ireland

BOOKS RECEIVED

Source Material for Radiochemistry. Subcommittee on Radiochemistry, Committee on Nuclear Science. Publication No. 654, National Academy of Sciences, Washington, D.C., March 1959. pp. 23.

Monographien aus dem Gebiete der qualitativen Mikroanalyse, Edited by A. A. BENEDETTI-PICHLER: **Volume I. Anorganische Qualitative Mikroanalyse.** H. MALISSA and A. A. BENEDETTI-PICHLER. Springer-Verlag, Wien, 1958. pp. vii + 333. £4 3s 6d: $11.65: DM 49—.

Zincon: Organic Chemical Reagents, Monograph No. 37. EILEEN A. JOHNSON and W. JABLONSKI. Hopkin and Williams, Ltd., Chadwell Heath, Essex, England, 1959. pp. 6.

Comprehensive Analytical Chemistry, Volume I A. Classical Analysis. Edited by CECIL L. WILSON and DAVID W. WILSON. Elsevier Publishing Company, Amsterdam: D. Van Nostrand Co., London and New York, 1959. pp. xix + 577. 105s.

Ionenaustauscher, Band I: Grundlagen. F. HELFFERICH. Verlag Chemie, Weinheim, 1959. DM 48—. pp. viii + 520.

Progress in Nuclear Energy, Series IX. Analytical Chemistry, Volume I. Edited by M. T. KELLEY. Pergamon Press Limited, London, Paris and New York, 1959. pp. 372. £5 5s.

Advances in Inorganic and Nuclear Chemistry, Volume I. Edited by H. J. EMELEUS and A. G. SHARPE. Academic Press Inc., New York. 1959. pp. xi + 449. $12.00

Fluorocarbons. M. RUDNER. Rheinhold Publishing Corporation, New York. Chapman and Hall, London, 1958. pp. x + 238. 46s.

Fundamentals of High Polymers. O. BATTISTA. Rheinhold Publishing Corporation, New York. Chapman and Hall, London, 1958. pp. vii + 140. 44s.

Electrophoresis: Theory, Methods and Applications. Edited by M. BIER. Academic Press, Inc., New York, 1959. pp. xx + 563. $15.00

Analytical Chemistry in Nuclear Technology: Specific Applications of Diverse Methods of Chemical Analysis. Second Gatlinburg Conference. U.S. Atomic Energy Commission, Technical Information Service. April 1959. Pp. vii + 298. $3.00.

Analytical Chemistry in Nuclear Technology: Instrumentation, Remote Control Techniques and Nucleonics. Second Gatlinburg Conference. U.S. Atomic Energy Commission, Technical Information Service. April, 1959. Pp. vi + 236. $2.50.

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced. Where possible, research papers should follow the pattern: *Introduction*, *Discussion*, *Conclusion*, *Experimental* (or such of these headings as apply).

3. Summaries will not be required for short or preliminary communications. For other contributions the essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

4. Illustrations should be separated from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The following standard symbols should be used on line drawings, since they are easily available to the printers:

△ △ ⊡ □ ● ○ ◬ ⊙ ⦶ ⊖ ⏀ ⊗

5. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, e.g., standard deviation. The same information should not be reproduced in both tables and figures.

6. References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired should be given in a list at the end of the paper in the following form:

[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds.* Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

7. Except in the case of preliminary communications, proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, when the amount of alteration makes it advisable.

8. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units.

AUGUST 1959 VOLUME 2 NUMBER 4

CONTENTS

Preliminary Communication:

Short Communications:

Letters to the Editor:

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