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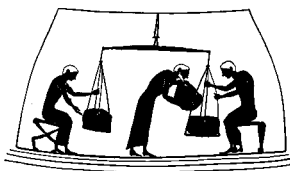
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THIOUREA COMPLEXES OF SOME NOBLE METALS

A POLAROGRAPHIC DETERMINATION OF RHODIUM

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(Received 21 January 1960)

Summary—Rhodium^{III}, stabilised by heating in thiourea solution, gives a polarographic irreversible wave, suitable for its determination. The influence of supporting electrolyte, rhodium and thiourea concentrations, as well as of pH and gelatin are fully investigated. Platinum interferes, iridium does not, and palladium can be determined at the same time as rhodium. Evidence is given for the presence of a bi-coordinated platinum complex, and mono- and tetra-coordinated palladium complexes.

SOME thiourea complexes with platinum metals have already been investigated in the solid state; but the ionic species existing in solution are very poorly defined. Thiourea appears to be a suitable colorimetric reagent for osmium and ruthenium;¹ however, where other metals of the family are concerned, a survey of the literature shows that only one investigation has been carried out in respect of the colorimetric determination of palladium;² the yellow colour of the thiourea-palladium complex was first noted by Yoe and Overholser³.

In the course of an extensive investigation carried out in this Institute^{4,5,6} on the chemistry of noble metals, a well-defined polarographic wave, previously quite unknown, was observed in thiourea solutions of rhodium. The behaviour of this element, together with metals of the same group, was therefore investigated thoroughly. Rhodium was investigated primarily for analytical purposes, as polarographic determinations of this element are seldom found in the literature.^{7,8,9,10}

EXPERIMENTAL

A Leybold polarograph and a Beckman DU spectrophotometer were used. A forward-and-backward recording of current-potential curves was carried out, and the mean value taken, in order to minimise the hysteresis effect. The temperature was held at 25° and the reference electrode was a saturated calomel electrode; purified nitrogen was used for deoxygenation; the capillary characteristics were: $m^{2/3}t^{1/6} = 2.125$.

Standard solutions: Na₃RhCl₆, $2.5 \cdot 10^{-2}M$; PdCl₂, $5 \cdot 10^{-2}M$, HCl, 0.1M; H₂PtCl₆, $5 \cdot 10^{-2}M$; K₂PtCl₄, $5 \cdot 10^{-2}M$; IrCl₄, $1 \cdot 10^{-2}M$, HCl, $2 \cdot 10^{-2}M$. Suitable volumes of these solutions were mixed with the determined amount of thiourea and supporting electrolyte and were held on a boiling water-bath for at least 10 min. Such heating is necessary in order to stabilise rhodium complexes, whereas reaction takes place at room temperature where platinum, iridium and palladium are concerned.

RESULTS

Rhodium solutions, after heating with an excess amount of thiourea, show a yellow-brown colour. Polarographic examination gives a well-shaped step at about -0.4 volt v. S.C.E. The characteristics of the wave are affected by several factors and extensive investigation was necessary in order to establish the best conditions for analytical determination.

Influence of the supporting electrolyte: When sulphates or nitrates are present, the waves are ill-developed and half-wave potentials cannot be measured, though the limiting current may still be well enough defined. On the other hand, reliable and reproducible results are obtained when potassium chloride is used, although its concentration is not without effect on the rhodium wave; in fact, the higher the chloride concentration, the more is the wave shifted to negative potentials, this variation being accompanied by a decrease of the diffusion current. Such phenomena are strictly correlated with variation of ionic strength, and therefore a fixed KCl concentration, such as 0.5M, must be used.

TABLE I. HALF-WAVE POTENTIALS OF $5 \cdot 10^{-4}M$ Rh IN 0.5M KCl AT SEVERAL CONCENTRATIONS OF THIOUREA (neutral solutions, without gelatin)

Thiourea, moles/litre	$E_{\frac{1}{2}}$, V(vs S.C.E., 25°)
0.01	-0.27
0.02	-0.28
0.04	-0.291
0.06	-0.306
0.08	-0.319
0.1	-0.330
0.2	-0.372
0.3	-0.398
0.4	-0.415
0.5	-0.430
0.6	-0.441

pH: Reproducibility is secured in neutral or slightly acidic medium. At a pH higher than 7 a turbid solution is obtained; at a pH lower than 2, the H^+ wave is shifted to more positive potentials by the electrodeposition of rhodium, and therefore the limiting current is stable only over a very small range, after which discharge of H^+ occurs.

Maximum suppression: Sometimes a maximum is present; occasionally, however, a surface-active substance such as gelatin, in concentration not less than 0.002%, may be used. When such a maximum suppressor is used, the half-wave potentials are shifted to more negative values. For instance the values $E_{\frac{1}{2}} = -0.330, -0.346, -0.358, -0.367, -0.370, -0.372$ V corresponded respectively to gelatin concentrations of 0, 0.005, 0.01, 0.02, 0.035, 0.05%, with a $5 \cdot 10^{-4}M$ solution of Rh, 0.1M in thiourea, and 0.5 M in KCl. In Fig. 1 two waves, obtained with and without gelatin, are shown.

The half-wave potentials obtained at various thiourea concentrations are given in Table I. Because a rhodium complex is involved, the more thiourea present, the more $E_{\frac{1}{2}}$ is shifted to negative values. If the thiourea is less than 0.02M, a red-brown precipitate is formed on heating; the molecular ratio of this compound is not well defined and depends on the heating time: in fact, it was possible to observe, in the anodic step of thiourea, a decrease in agreement with any rhodium-thiourea ratio between 1:2 and 1:3.

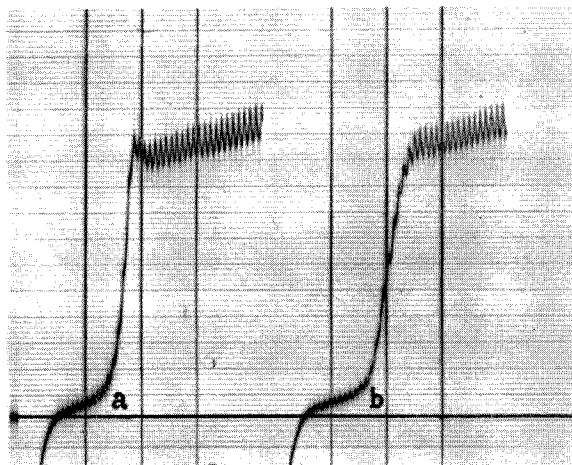


FIG. 1.—Polarograms of $5 \cdot 10^{-4} M$ Rh^{III} in $0.2 M$ thiourea : $0.5 M$ KCl: (a) without gelatin; (b) 0.01% gelatin. 0.3 , 0.4 and 0.5 V vs S.C.E. are indicated on each polarogram.

The limiting current proportional to the rhodium concentration is really a diffusion-controlled one: it is directly proportional to the square root of the height of the mercury column, corrected for the back-pressure at the Hg-solution interface. Experiments at various temperatures showed that the wave height increases by 1.2% for a 1° rise, as would be expected for a diffusion current. At the same time, $E_{\frac{1}{2}}$ is shifted about 5 mV per degree to more positive values, so that above 60° a composite anodic-cathodic wave is obtained, rhodium reduction taking place at the same potential at which the anodic step of thiourea is apparent. A large temperature coefficient constitutes fair evidence of the irreversibility of the reaction. In addition, the slope of E against $\log i/(i_d - i)$ along the wave is never lower than 35 mV per logarithmic unit, which also supports the irreversibility. Hence no attempt was made to draw any quantitative conclusion about the stability of complexes from the shift of $E_{\frac{1}{2}}$ at increasing thiourea concentration.

The diffusion current constant was found to be 5.10 in 0.2M thiourea solution. No significant difference was observed over the range of thiourea concentration shown in Table I. This value indicates that a three electron reduction is concerned, but millicoulometry was used to confirm the value for "n" of three.

On spectrophotometric examination, no maxima are noted in the absorption curves of rhodium-thiourea solutions, apart from the absorption of thiourea itself. The sensitivity around 400 m μ being small (rhodium must not be less than 10 μ g/ml), colorimetric determination is not very reliable, although Beer's law is followed. The behaviour of the other metals of the group is summarised below.

Platinum

A chloroplatinic acid solution turns nearly colourless on addition of an excess of thiourea. After several hours standing at room temperature, or a few minutes heating on a boiling water-bath, a turbidity is noted. Polarographic waves are never well-defined: immediately after thiourea is added, however, the limiting current, though ill-developed, is nearly as large as without thiourea, there being no reduction, but only complexing. After long standing, the solution becomes more and more turbid, and the diffusion current decreases, but is never reduced to zero.

Platinum^{II} is also complexed by thiourea, and no precipitation occurs. The resulting solution has a pale yellow colour. A cathodic diffusion current may be recorded at the end of the anodic wave of thiourea. Platinum therefore constitutes a serious interference when determining rhodium.

It is possible to identify the complex of platinum^{IV} present in solution, by determining free Pt^{IV} colorimetrically with potassium iodide while thiourea is added. A discontinuity is noted in Fig. 2, in the plot of optical densities against the thiourea-platinum ratio, at a value of the latter of nearly 2. The complex present is therefore probably bi-coordinated.

Palladium

A palladium solution, with an excess of thiourea, turns yellow, no maxima in the spectrum being noted apart from those arising from the absorbance of thiourea itself. A composite anodic-cathodic wave is recorded polarographically, the yellow complex not being sufficiently stable to give a true step. This behaviour allows simultaneous determination of rhodium and palladium when they are present together. In such a

case, as is shown in Fig. 3, there are two steps in the polarographic wave, the former being proportional to the palladium concentration, the latter to that of rhodium. Results of the determination of these two elements in the presence of one another are reported in Table II, showing the reliability of the method.

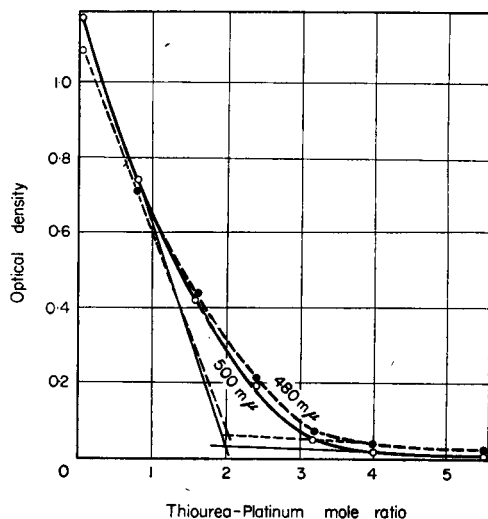


FIG. 2.— $1 \cdot 10^{-4}M$ Pt^{IV} in excess of KI: decrease of absorbance by adding thiourea.

With a very small amount of thiourea an orange-brown colour is developed, quite different from the yellow one obtained with an excess of complexing agent. A few minutes later a brown precipitate can be observed; the addition of gelatin

TABLE II. SIMULTANEOUS POLAROGRAPHIC DETERMINATION OF RHODIUM AND PALLADIUM, IN SOLUTIONS OF:
 $0.3M$ thiourea, $0.5M$ KCl , H^+ about $1 \cdot 10^{-3}M$, gelatin 0.002%

Taken		Found	
Rh, mg	Pd, mg	Rh, mg	Pd, mg
0.64	0.67	0.65	0.67
0.64	1.33	0.64	1.32
0.64	2.67	0.63	2.64
1.29	0.67	1.30	0.66
1.29	1.33	1.29	1.35
1.29	2.67	1.30	2.68
2.57	0.67	2.52	0.68
2.57	1.33	2.51	1.36
2.57	2.67	2.58	2.67

(0.05%), however, holds the compound in solution sufficiently long to permit of spectrophotometric measurement. This change of colour according to the amount of thiourea present produces an unusual optical density curve when studying the molecular ratios (Fig. 4) and when applying Job's method (Fig. 5). The most reliable interpretation appears to be the following: when thiourea is present at nearly the

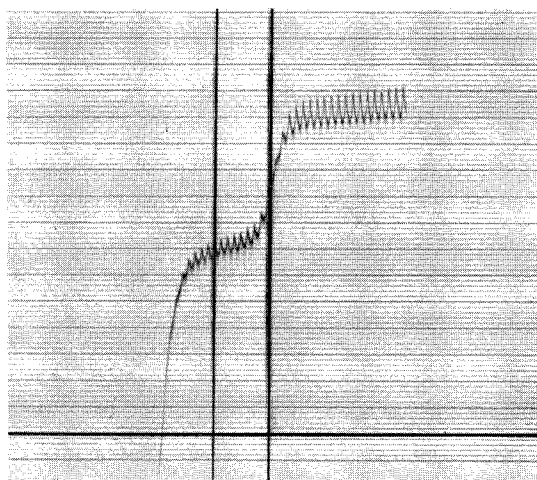


FIG. 3—Polarogram of $5 \cdot 10^{-4}M$ Rh^{III} and $1 \cdot 10^{-3}M$ Pd^{II} in $0.2M$ thiourea + $0.5M$ KCl, with 0.002% gelatin. -0.3 and -0.4 V vs S.C.E. are indicated.

same concentration as palladium, the red-brown, slightly-soluble 1:1 complex is formed. With an excess of thiourea, more molecules of the latter are coordinated and the yellow complex appears. From the position of the discontinuity in the curves of Figs. 4 and 5, this complex seems to be tetra-coordinated.

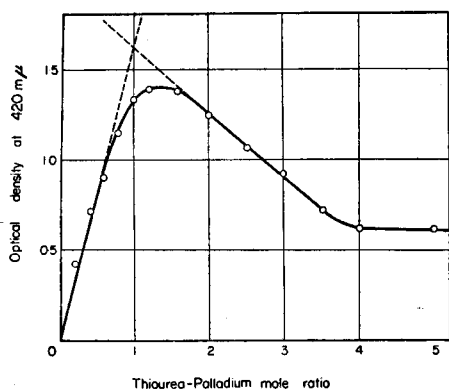


FIG. 4.—Variation of absorbance by adding thiourea to solutions of $5 \cdot 10^{-4}M$ Pd^{II}.

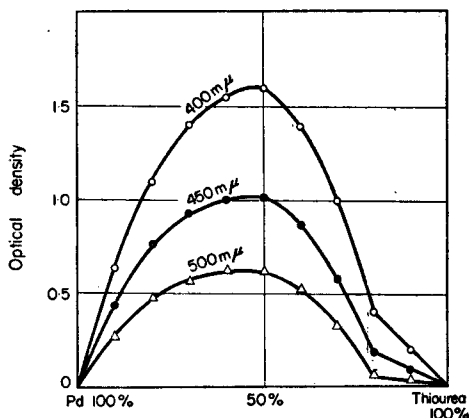


FIG. 5.—Variation of absorbance with molar fraction of palladium-thiourea: total concentration = $1 \cdot 10^{-3}M$.

Iridium

An iridium^{IV} solution turns colourless a few minutes after adding thiourea in a concentration at least as great as that of iridium. On standing, a white precipitate is observed. The colourless solutions give a polarogram exactly the same as the supporting electrolyte alone. Therefore determination of rhodium with sufficient accuracy is possible, even when an excess of iridium is present. From several polarograms of mixtures of rhodium and iridium, the latter being present up to 8 times the amount of the former, it was found possible to determine rhodium with a 2–3% error.

Zusammenfassung—Rhodium(III), durch Erhitzen in Thioharnstofflösung stabilisiert, gibt eine irreversible polarographische Stufe, die zur Bestimmung des Rhodiums verwertet werden kann. Der Einfluss von Grundlösung, Rhodium- und Thioharnstoffkonzentration, sowie pH und Gelatin wurde eingehend studiert. Platin stört, während Iridium ohne Einfluss ist. Palladium kann zugleich mit Rhodium bestimmt werden. Evidenz ist vorhanden für die Existenz eines bikoordinierten Platin- und eines mono- und tetrakoordinierten Palladiumkomplexes.

Résumé—Le rhodium III, stabilisé par chauffage dans une solution de thiourée, donne une vague polarographique irréversible, convenable pour son dosage. L'influence de l'électrolyte support, des concentrations de rhodium et de thiourée, ainsi que du pH et de la gélatine a été complètement étudiée. Le platine gêne, mais non l'iridium, le palladium peut être dosé en même temps que le rhodium.

La présence d'un complexe bicoordonné du platine et de complexes mono et tétracoordonnés du palladium est prouvée.

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SCINTILLATION RADIOAUTOGRAPHY OF TRITIUM-LABELLED COMPOUNDS ON PAPER CHROMATOGRAMS*

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Research Branch, Canada Department of Agriculture, Ottawa, Canada

(Received 21 April 1960)

Summary—A simple scintillation radioautographic method using ordinary fast photographic film has been developed for tritium-labelled compounds on paper chromatograms impregnated with anthracene. Tritium analysis can now be undertaken by any laboratory without the need for special equipment or controlled conditions.

INTRODUCTION

A SIMPLE, reliable and inexpensive analytical method to detect and determine tritium-labelled compounds was developed and proved useful in an investigation of nicotine metabolism in tobacco plants. The details for the paper chromatographic separation of tobacco alkaloids from tobacco extracts have been recorded,¹ but it was necessary to develop a method which would extend this for application of tritium autoradiography. A major obstacle in detection of the very soft tritium β -particle ($E_{\max} = 18$ keV) by radioautography is its absorption by the paper before it can enter the film. Wilson⁴ described a "scintillation autographic" technique to overcome this by using a liquid scintillator to convert weak β -particles into light quanta which produced an image on X-ray film. Because toluene is the primary solvent used for the scintillator, Wilson's method could not be applied in a study of nicotine, which is soluble in toluene.

In his study of steroid hormones, which are also soluble in toluene, Rogers² coated the paper chromatogram directly with melted photographic emulsion (Ilford K2). The strips were dried and placed in a desiccated light-proof box and exposed in a cold room at 5°. Although this technique avoids the use of toluene, it requires a nuclear emulsion, which is not generally available. In addition, considerable preparation is involved before exposure, and the chromatogram can be exposed only once.

Seliger and Agranoff³ incorporated anthracene as microcrystals to overcome the high degree of absorption by the paper. In their solid scintillation technique the photons produced are reflected from the paper and counted at 12° on the face of a phototube in a light-tight enclosure. The stability of the strips in this technique permits reproducible recounting, but considerable equipment involving special electronic circuits is needed.

Our simple procedure makes feasible the detection and determination of tritium-labelled compounds on paper chromatograms in any laboratory, and overcomes the drawbacks mentioned above. A paper chromatogram is dipped momentarily into a scintillation compound dissolved in a highly volatile solvent. The dry impregnated

* Contribution Nos. 67 and 10 of the Plant Research Institute and Analytical Chemistry Research Service respectively.

paper is placed in close contact with ordinary fast film and exposed for the desired time at room temperature. The developed spots can be compared with known amounts of activity either visually or by densitometer readings.

EXPERIMENTAL

Tritiated nicotine, prepared by the Wilzbach technique, was used as the best material. Various amounts of it, with activities of 6.20, 3.10, 1.55, 0.77, 0.38, 0.19 and 0.085 microcuries, were spotted on 1-cm² discs cut from Whatman No. 1 filter paper. The discs, after being allowed to dry, were dipped in the scintillation agent (a saturated solution of anthracene in benzene). The benzene evaporated almost instantly, leaving the discs impregnated with fine crystals of anthracene. Each disc was then given a second dip in the scintillator. Comparisons were made with discs spotted with the same

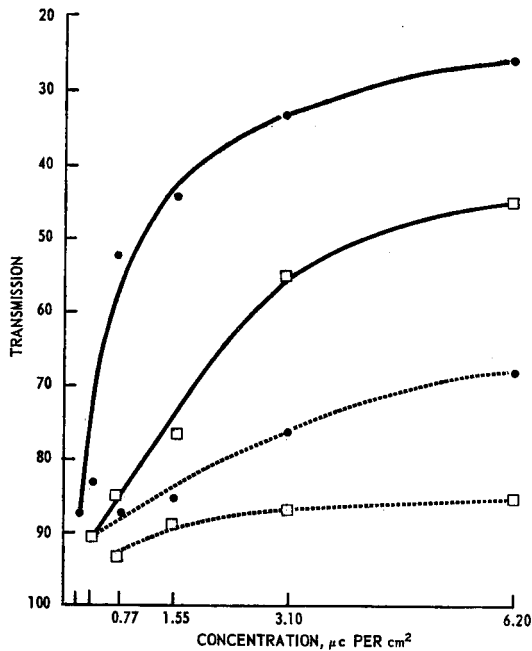


FIG. 1.—Variation of average densitometer readings with concentration of tritium. Solid lines represent 2-week exposures; dotted lines 1-week. ● with anthracene; □ without anthracene.

activities of tritiated nicotine, but without added scintillator. Blank discs, dipped either in benzene or in benzene with anthracene, were also prepared. The discs were attached with wire staples to a suitable thick paper backing, and were placed in contact with Kodak Royal-X Pan sheet film. Glass plates were placed on the outside, and pressure was applied to ensure close contact during the exposure time of 1–2 weeks. Five replicates were run for each exposure time. The film was developed in Kodak D-19 for 6 min at 20°. Although this developer is not usually recommended for this film, it was found to give extra contrast and a short development time. In some cases spots were formed even by the controls which had no scintillator added, showing the extreme sensitivity of the film to tritium emissions. Visual comparisons are satisfactory for many experiments, but a quantitative approach would be helpful for others. A Photovolt 525 densitometer was used to determine the darkening intensity of the exposed film.

RESULTS

No less than four readings were made on different portions of each spot. Fig. 1 is a plot of the average values, expressed as percentage transmission against concentration in microcuries. This figure shows that the presence of anthracene increases the

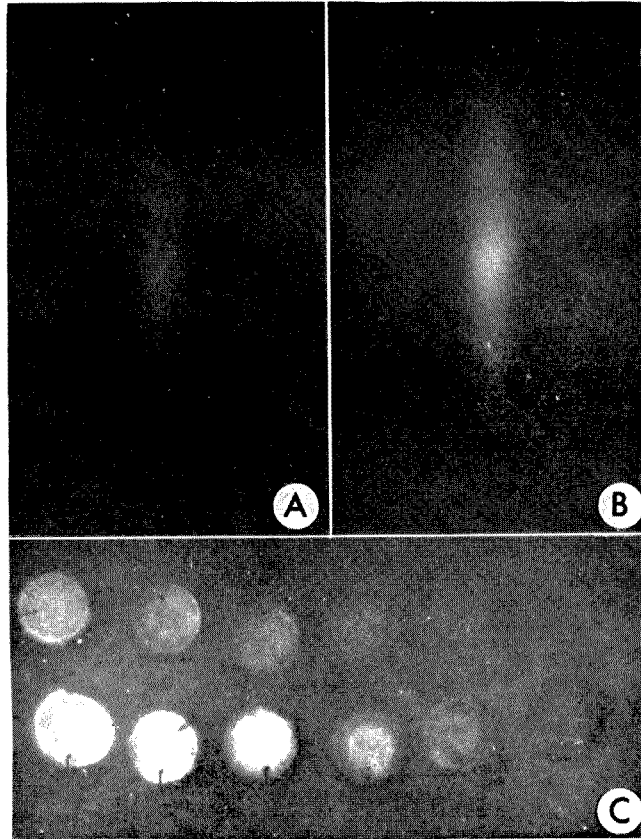


FIG. 2.—Autoradiograms of tritium-labelled nicotine. A—without scintillator; B—with scintillator. C—top row—without scintillator, bottom row—with scintillator.

darkening on the film to a marked degree during both the 1- and 2-week exposure times. Darkening of the film could be distinguished with 0.38 and 0.19 microcuries per cm^2 after exposures of 1 and 2 weeks, respectively. Exposure times beyond 2 weeks would tend to increase the sensitivity of the method. For the 2-week exposure period a near-linear relationship exists for levels of activity ranging from 0.19 to 1.51 microcuries per cm^2 . Similarly, 0.38 to 3.10 microcuries per cm^2 is the range for the 1-week exposure period.

In Fig. 2, photographs are shown displaying varying amounts of activity both with and without anthracene; and also the intensifying effect of anthracene added to actual chromatograms of nicotine made from extracts of a tobacco plant treated with tritiated nicotine.

Zusammenfassung—Eine einfache Scintillationsmethode zur radioautographischen Bestimmung von mit Tritium markierten organischen Verbindungen wurde entwickelt. Gewöhnlicher, hochempfindlicher Film wird in Verbindung mit Chromatogrammen auf, mit Anthracen imprägniertem, Papier verwendet. Tritiumanalysen können nun in jedem Laboratorium durchgeführt werden, ohne dass spezielle Einrichtungen oder Kontrollbedingungen nötig sind.

Résumé—Une méthode simple de "radioautographie" par scintillation utilisant un film photographique ordinaire rapide a été élaborée pour des composés marqués par du tritium sur des chromatogrammes de papier imprégnés d'anthracène. L'analyse du tritium peut être entreprise maintenant par tout laboratoire sans nécessiter un équipement spécial ou des conditions contrôlées.

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DETERMINATION OF CHLORIDE ION IN GLYCOL BY pCl MEASUREMENT*

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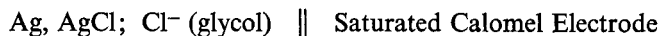
Summary—Measurement of pCl with a silver-silver chloride electrode affords a rapid means of detecting chloride in solution above the solubility limit of silver chloride in the solvent. The behaviour of the silver-silver chloride electrode in ethylene glycol was studied. A method was developed for rapidly analysing as little as 0.1 ppm of inorganic chloride in ethylene glycol.

INTRODUCTION

SEVERAL workers have investigated the measurement of chloride ion in aqueous solution using silver-silver chloride electrodes in concentration cells.^{1,3,6} Chanin² used a silver-silver chloride electrode and a mercury-mercury^I sulphate electrode to determine chloride in aqueous solution. Helmkamp *et al.*⁴ and Stern *et al.*⁸ used a silver-silver chloride electrode and a calomel electrode with a pH meter to determine the pCl of solutions.

This work was undertaken to develop an empirical method for determining small amounts of chloride ion in ethylene glycol using a silver-silver chloride electrode and a calomel electrode. The limit of detection of chloride ion should be lower in ethylene glycol than in water since silver chloride is less soluble in glycol than in water.

The cell used for chloride determination is:



The salt bridge in the above cell is of potassium nitrate to eliminate any chloride contamination. No theory is offered for the EMF of the above cell since no data on appropriate oxidation potentials in glycol are available. In addition, no estimate of the liquid junction potentials in the cell can be made.

The EMF of the above cell is given by the empirical equation:

$$\log C_{\text{Cl}^-} = k_1 + \frac{E}{k_2}$$

The constant k_1 would be a function of the activity coefficient of the chloride ion. At constant ionic strength the activity coefficient would be essentially constant. The Cl^- concentration of glycol solutions may be determined without first determining the constants k_1 and k_2 . Calibrations can be made on solutions of known Cl^- concentration over the range of interest.

APPARATUS AND REAGENTS

The Ag-AgCl electrodes were prepared by a modification of the fusion method of Owen⁷ and Keston⁸ followed by electrolysis in dilute hydrochloric acid. A paste was made of 7 parts of silver

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oxide, 1 part of silver chlorate and a little water. Platinum spirals (embedded in glass) were coated with the paste and placed in a furnace at 650° for 7 or 8 min. The electrodes were cooled and made anodes in a 0.2M hydrochloric acid solution for 1 hour with about 2 milliamps of current flowing. After the electrolysis, the Ag-AgCl electrodes were shorted to each other and soaked in a 0.01M potassium chloride solution for 1–2 days to eliminate any potential difference between them and to condition them for use.

The saturated calomel electrode used was a Beckman double-junction type calomel electrode (No. 4970-6). The outer chamber of this electrode, which is a salt bridge, was filled with saturated potassium nitrate solution. By this means possible chloride contamination from the calomel electrode was eliminated.

A Beckman Model G pH meter was used for the potential measurements. The silver-silver chloride electrode was plugged into the glass electrode jack on the meter.

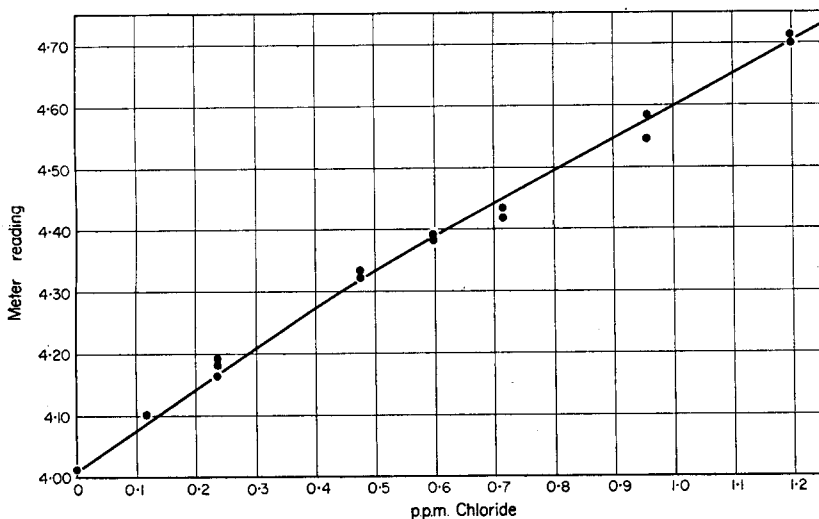


FIG. 1.

The 3.0M potassium nitrate solution was prepared from A.R. grade material.

The ethylene glycol used for preparation of the chloride solutions was a carefully distilled material which was chloride-free.

A glycol solution containing 1000 ppm chloride was prepared and this stock solution was used to prepare other standard chloride solutions by successive dilutions with the pure glycol.

EXPERIMENTAL

The pH meter was calibrated before each series of measurements. The electrodes were immersed in a glycol solution containing 1 ppm chloride and 5 drops of 3.0M potassium nitrate in 100 ml. The potassium nitrate was added to raise the conductivity of the solution so that the electrode system would not be sluggish. The meter was set at a reading (on the pH scale) of 4.60. This is an arbitrary number, which has no theoretical significance. The solution on the electrodes was stirred with a magnetic stirrer to attain equilibrium between the electrodes and the solution which required about 3–5 min. The zero adjuster was used to zero the meter.

A calibration curve was constructed for chloride in glycol. A series of solutions of different chloride concentrations (0–1.0 ppm) were prepared. Five drops of 3.0M potassium nitrate were added to 100 ml of each, and the EMF reading was determined on them in the same manner that the pH would be determined. A plot of this meter reading vs. ppm chloride is shown in Fig. 1.

Glycol samples with unknown chloride concentrations were analysed by this same technique. Five drops of 3.0M potassium nitrate are added to 100 ml of the sample. The EMF is read and the chloride concentration taken from the calibration curve (Fig. 1).

DISCUSSION

From repeated runs of standard samples of chloride in glycol the accuracy of the analysis is better than ± 0.1 ppm. As little as 0.1 ppm of chloride in glycol can be detected by this method.

The analysis was extended up to the 100-ppm range. These results are not given, because glycol usually does not contain such a high content of chloride.

The silver-silver chloride electrodes are stable in glycol for more than 6 months.

The usual impurities in commercial ethylene glycol are: aldehyde, 15 ppm; acid, 1-2 ppm; and iron, 0.02 ppm. No effect on the EMF was detectable when 30 ppm propionaldehyde, 10 ppm acetic acid, and 0.5 ppm iron were added to some samples of glycol. This is twice the aldehyde, 10 times the acid and 25 times the iron content of glycol.

Iron was added as an aqueous solution of iron^{III} sulphate. This produced an effect at higher concentrations of iron. The effect of 1 ppm of iron was equivalent to that of -0.1 ppm chloride. This concentration of iron is well above that found in glycol. Also, it is not known in what form iron occurs in glycol. In any case these common impurities do not interfere with the analysis.

Interference would be caused by materials which formed silver salts more insoluble than silver chloride or ligands which formed stable complexes with silver.

This technique should be applicable to the analysis of ionic chloride in any polar solvent, such as polyglycols, glycerine, etc.

Zusammenfassung—Die messung von pCl mit einer Silber-Silberchloridelektrode erlaubt rasches Nachweiss von Chlorid in Lösungen, die mehr Chlorid enthalten, als dem Löslichkeitsprodukt von Silberchlorid entspricht. Das Verhalten einer Silber-Silberchloridelektrode in Äthylenglycol wurde studiert. Eine Methode wurde entwickelt um bis hinab zu 0.1 ppm an anorganischem Chlorid in Äthylenglycol zu analysieren.

Résumé—La mesure de pCl avec une électrode argent-chlorure d'argent apporte un moyen rapide de détection du chlorure en solution au-dessus de la limite de solubilité du chlorure d'argent dans le solvant. Le comportement de l'électrode argent-chlorure d'argent dans l'éthylène glycol a été étudié. Une méthode a été élaborée pour l'analyse rapide de quantité aussi faible que 0,1 p.p.m. de chlorure minéral dans l'éthylène glycol.

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PRECIPITATION OF NICKEL DIMETHYLGLYOXIMATE FROM HOMOGENEOUS SOLUTION

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Summary—By reacting biacetyl and hydroxylamine in the presence of nickel^{II}, large, well-developed and readily filterable crystals of nickel dimethylglyoximate were precipitated from homogeneous solution. The needle-like crystals were frequently up to several mm in length. Large amounts of nickel—of the order of 200 mg—were easily handled. The usefulness of this method of precipitation from homogeneous solution is shown with results obtained for nickel in the presence of a few selected diverse substances, namely, cobalt, copper, iron, and in National Bureau of Standards steel samples.

INTRODUCTION

SINCE 1905, the reaction¹ of dimethylglyoxime with nickel^{II} has been used extensively for the quantitative determination of nickel. Many other dioximes were subsequently suggested, in some cases to increase the molecular weight of the dioxime and in other cases to overcome certain deficiencies, e.g. the slight solubility of dimethylglyoxime in water. One difficulty, namely, the voluminous and somewhat gelatinous character of nickel dimethylglyoximate, which has generally limited the quantity of nickel precipitated to less than 40 mg, was overcome by Bickerdike and Willard² who used urea to precipitate the chelate from homogeneous solution.

In the present paper, a method is described for the precipitation of large, well-developed, and readily filterable crystals of nickel dimethylglyoximate from homogeneous solution; dimethylglyoxime is generated in the presence of nickel^{II} by reacting biacetyl and hydroxylamine.³ The utility of the method is shown with results obtained for nickel in the presence of a few selected diverse substances, namely cobalt, copper, iron, and also in National Bureau of Standards steel samples.

REAGENTS AND APPARATUS

Unless otherwise specified, all chemicals were reagent grade.

Nickel, copper, cobalt and iron solutions: Appropriate amounts of reagent grade NiSO₄·6H₂O, CuCl₂(NH₄Cl)₂·2H₂O, Co(NO₃)₂·6H₂O, and FeNH₄(SO₄)₂·12H₂O were each dissolved in distilled water, filtered, and diluted so that each solution contained about 40 mg of metal per 25 ml of solution. The exact concentration of nickel was determined by precipitation as nickel dimethylglyoximate by the conventional method⁴ and checked by electrolytic deposition of nickel.⁵ The metal salts were obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J.

Biacetyl solution: Approximately 25 ml of biacetyl (Distillation Products Co., Rochester, N.Y.) was distilled through a small fractionating column packed with 0.25 in. glass helices. About 6 ml of the fraction which distilled between 87.5° and 90.2° (750 mm of Hg) was weighed, dissolved in distilled water, and diluted to 500 ml; the solution contained about 12 mg of biacetyl per ml.

Hydroxylamine hydrochloride: The reagent grade hydroxylamine hydrochloride used in the experimental work was obtained from the J. T. Baker Chemical Co., Phillipsburg, N.J.

All measurements were made with a Beckman Model 9600 pH meter calibrated with a Beckman pH 7 buffer solution (No. 3581).

PRECIPITATION OF NICKEL ALONE

Experimental

Preliminary investigations were conducted to determine the appropriate concentration of reagents, the temperature of reaction, and the pH which would result in quantitative precipitation of the nickel chelate in a readily filterable form but would not produce enough dimethylglyoxime to precipitate along with the nickel chelate.

The photomicrographs of Fig. 1 show the difference in the precipitates obtained by the conventional method of precipitation and by PFHS (precipitation from homogeneous solution). The needle-like crystals of nickel dimethylglyoximate precipitated from homogeneous solution are often up to several mm in length. They do not settle to the bottom of a solution as precipitates formed by the PFHS method ordinarily do because of their fine needle-like character. They can be filtered and washed quite easily, and are not characterised by the somewhat gelatinous nature of the conventionally prepared precipitate. The crystals exhibit a somewhat different reddish hue from that of the crystals obtained by conventional precipitation.

Procedure

Adjust the pH of the solution, containing no more than 200 mg of nickel, to 7.5 ± 0.1 with ammonium hydroxide. Add a quantity of biacetyl equal to 6 times the approximate weight of nickel to be precipitated, but never less than 0.12 g in any case. Next add, with stirring, 50 ml of a solution, adjusted to pH 7.5 ± 0.1 with ammonium hydroxide, containing a quantity of hydroxylamine hydrochloride equal to 4 times the weight of biacetyl added, but in no case less than 0.5 g. Adjust the final volume of the solution to 100 ml if 0.5–5 mg of nickel are present, to 200 ml for 5–50 mg, to 300 ml for 50–100 mg, or to 400 ml for 100–200 mg. Allow the solution to stand at room temperature for at least 1 hr (or longer) after precipitation begins, then heat to $80\text{--}90^\circ$ for 2 hr. Cool the solution, filter, wash the precipitate with water, and dry to constant weight at 140° .

Nickel content of filtrate and wash solution

In several instances, the filtrates and washings were evaporated to dryness, 10 ml of concentrated sulphuric acid added, and this solution evaporated to dense fumes and subsequently to dryness. Ten ml of concentrated nitric acid were then added twice to the residue and evaporated to dryness. The organic-free residues were dissolved in distilled water, and the nickel determined colorimetrically with 2:3-quinoxalinedithiol.⁶

Results

The above procedure was used to precipitate from 0.5 to 200 mg of nickel as shown in Table I. The results indicate quantitative precipitation of nickel. The amounts of nickel in the filtrates and washings from several determinations were found to coincide closely to those found in the filtrates from conventional determinations (*cf.* Table II).

PRECIPITATION OF NICKEL IN PRESENCE OF DIVERSE IONS

Experimental

Nickel dimethylglyoximate was precipitated from homogeneous solution in synthetic mixtures containing (a) copper, (b) cobalt, and (c) cobalt and iron. The procedure used was essentially that previously described with modifications as indicated.

After the precipitates were weighed, they were dissolved in concentrated hydrochloric acid, the solutions evaporated to dryness and the organic matter destroyed by treatment with nitric and sulphuric acids. The organic-free residues were dissolved in distilled water and the co-precipitated elements colorimetrically determined as follows:

(a) copper was separated from nickel by extraction with dithizone and determined with dithizone;⁷ (b) cobalt was separated from iron and nickel by extraction with ammonium thiocyanate solution and determined with nitroso-R-salt;⁷ (c) iron was separated from cobalt and nickel by chloroform extraction of the iron cupferrate and determined with *o*-phenanthroline.⁷

The general procedure was also used to precipitate nickel in National Bureau of Standards steel samples. The samples were dissolved in hydrochloric acid, the iron oxidised with nitric acid, then

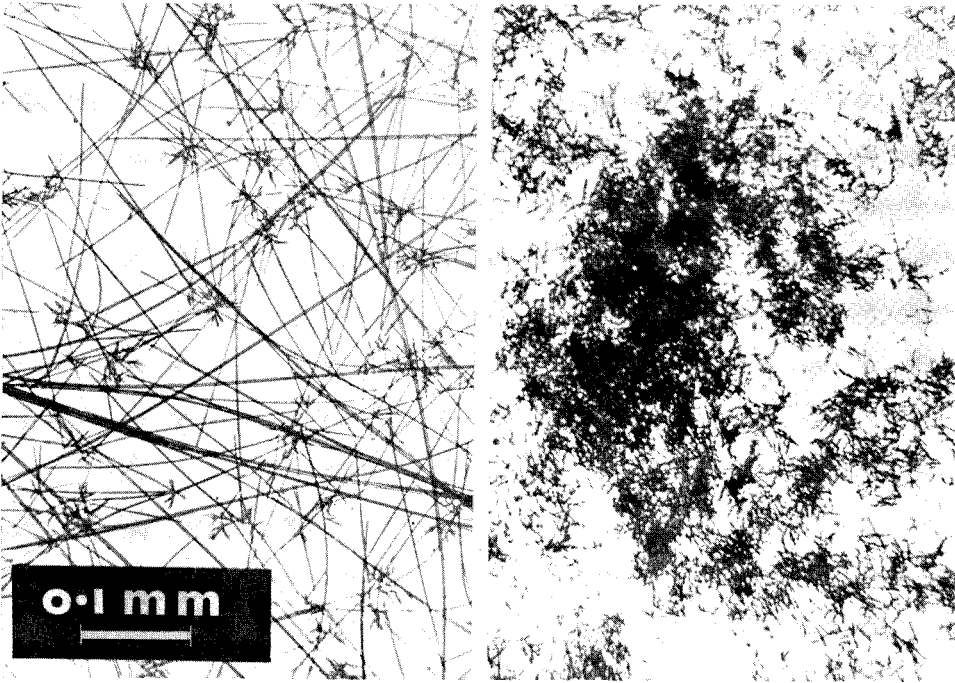


FIG. 1.—Photomicrographs of nickel dimethylglyoximate (both photomicrographs are at same magnification). a. left panel: method of PFHS. b. right panel: conventional method of precipitation.

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tartaric acid was added. The pH was adjusted to 7.5 ± 0.1 with ammonia and the solutions were filtered. Biacetyl and hydroxylamine were added as described in the general procedure. The solutions were allowed to react for 24 hr and were then heated to 80–90° for 2 hr.

Results

The results obtained in the presence of copper are shown in experiments No. 1–11

TABLE I. SEPARATION OF NICKEL BY PFHS

Nickel taken, <i>mg</i>	Nickel found (difference), <i>mg</i>		
0.49	–0.04,	–0.04,	–0.04
4.92	0.00,	+0.01,	+0.01
9.83	+0.05,	+0.03,	+0.01
39.3	0.0,	0.0,	0.0
98.3	–0.1,	–0.2,	–0.1
196.6	+0.4,	+0.5	

TABLE II. NICKEL IN FILTRATE AND WASHINGS^a

Nickel found (PFHS method), <i>mg</i>	Nickel found (conventional method), <i>mg</i>
0.050	0.040
0.050	0.043
0.063	0.050

^a 39.3 mg of nickel precipitated in all cases

of Table III. The superior separation of nickel obtained with the method of precipitation from homogeneous solution is clearly indicated by the comparatively negligible quantity of co-precipitated copper.

In the case of cobalt (No. 12–17) low results for nickel are obtained by conventional precipitation⁴ although the cobalt content of the precipitates was negligible. The reagent is apparently consumed by cobalt although this can be rectified by adding additional dimethylglyoxime. The gravimetric results obtained with the method of precipitation from homogeneous solution were excellent.

With both cobalt and iron present (No. 18–23) the method of PFHS gave satisfactory results only when the solution was allowed to stand at room temperature for a long period before being heated. Experiments No. 18 and 19 strikingly show the effect of a short standing period. It is likely that a shorter period of standing (less than 24 hr) will suffice but this was not investigated. The conventional method of precipitation gave excellent results, the only advantage of the PFHS method being that of easier handling of the precipitate along with the potential for handling larger quantities of nickel.

The results obtained for the National Bureau of Standards steel samples are shown in Table IV. The results clearly show the need here of a 24 hr standing period at room temperature before heating. The total time required to effect complete precipitation could possibly be reduced through the use of a shorter standing period followed by a period of heating of longer than 2 hr.

TABLE III. SEPARATION OF NICKEL FROM DIVERSE IONS BY PFHS AND

Number	1	2	3	4	5	6	7	8	9	10
Method of precipitation	PFHS ^{a,h}	PFHS ^{a,h}	PFHS ^{b,h}	PFHS ^{b,h}	PFHS ^{b,h}	PFHS ^{b,h}	PFHS ^{b,h}	Conv. ^{d,f,i}	Conv. ^{d,f,i}	Conv. ^{e,g,i}
Diverse element(s) taken, mg	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40	Cu, 40
Nickel taken, mg	39.3	39.3	9.83	9.83	9.85	9.85	9.85	9.83	9.83	9.83
Nickel found, mg	39.5	39.4	9.90	9.88	9.90	9.88	9.90	11.81	11.81	10.02
Difference, mg	+0.2	+0.1	+0.07	+0.05	+0.05	+0.03	+0.05	+1.98	+1.98	+0.19
Diverse element(s) in precipitate, mg				Cu, 0.057	Cu, 0.13	Cu, 0.12	Cu, 0.11	Cu, 2.03	Cu, 1.83	Cu, 0.18

^a Time before heating about 1 hr.

^b Time before heating about 24 hr.

^c Temperature about 70° when dimethylglyoxime was added.

^d Temperature about 25° when dimethylglyoxime was added.

^e One g each of anhydrous sodium sulphite and tartaric acid dissolved in the solution before precipitation.

No attempt was made to determine nickel in the presence either of the many other diverse ions or the various combinations of diverse ions with which it might conceivably be associated in practice. The present investigation was undertaken primarily to demonstrate the feasibility of precipitating nickel from homogeneous

TABLE IV. DETERMINATION OF NICKEL IN NICKEL STEELS

NBS sample number	Sample taken, g	Nickel found, g	% Nickel	
			Reported	Found
33b	1.3076	0.0454	3.48	3.47
	1.1652	0.0404		3.47
	1.4072	0.0488		3.47
101c	0.5667	0.0527	9.27	9.29
	0.5692	0.0529		9.29
	0.7063	0.0656		9.29
	1.1437	0.0986		8.62 ^a
	1.1693	0.1036		8.86 ^a
	1.0091	0.0922		9.14 ^a

^a Solutions allowed to stand for only 18 hr before heating for 2 hr at 80–90°.

solution by synthesis *in situ* of the chelate and to test the method with a limited number of diverse ions. It is hoped that the basic information presented herein will enable other investigators to apply the method to their particular problem of analysis.

Other oximes were also considered; nickel was precipitated from homogeneous solution with *cyclohexanedionedioxime* generated in a similar manner from *cyclohexanedione* and hydroxylamine. However, work with the other oximes was discontinued because it became quickly apparent that these offered no great advantage over the dimethylglyoxime method for nickel utilizing PFHS. It has also been found that palladium^{II} can be precipitated by the present method. This work will be subsequently reported in *Talanta*.

Acknowledgement—The authors acknowledge the partial assistance of the United States Atomic Energy Commission in supporting the investigation described herein under contract AT(11-1)-582.

Y CONVENTIONAL PRECIPITATION AS NICKEL DIMETHYLGLYOXIMATE

11	12	13	14	15	16	17	18	19	20	21	22	23
Conv. ^{c, g, i}	PFHS ^{b, h}	PFHS ^{b, h}	PFHS ^{a, h}	PFHS ^{a, h}	Conv. ^{c, f, i}	Conv. ^{c, f, i}	PFHS ^{a, e, h}	PFHS ^{a, e, h}	PFHS ^{b, e, h}	PFHS ^{b, e, h}	Conv. ^{c, e, f, j}	Conv. ^{c, e, f, j}
Cu, 40	Co, 40	Co, 40	Co, 40	Co, 40	Co, 40	Co, 40	Co, 40 Fe, 40	Co, 40 Fe, 40	Co, 40 Fe, 40	Co, 40 Fe, 40	Co, 40 Fe, 40	Co, 40 Fe, 40
9.83	39.3	39.3	39.3	39.3	39.3	39.3	39.3	39.3	39.3	39.3	39.3	39.3
10.89	39.4	39.4	39.2	39.3	38.7	38.6	20.2	19.4	39.4	39.4	39.5	39.5
+1.06	+0.1	+0.1	-0.1	0.0	-0.6	-0.7	-19.1	-19.9	+0.1	+0.1	+0.2	+0.2
Cu, 0.83					Co, 0.066	Co, 0.072			Co, 0.013; Fe, 0.10	Co, 0.005; Fe, 0.04	Co, 0.044; Fe, 0.05	Co, 0.061; Fe, 0.02

^f Solution acidified with 1 ml of 0.6N hydrochloric acid solution before addition of dimethylglyoxime. The solution was then made alkaline by the addition of ammonium hydroxide solution.

^g Like *f* except the solution was acidified with 3 ml of 6N hydrochloric acid solution before addition of dimethylglyoxime.

^h Approximately 0.3 g of biacetyl and 1.0 g of hydroxylamine hydrochloride used in the determination.

ⁱ Approximately 0.23 g of dimethylglyoxime used in the determination.

^j Approximately 0.33 g of dimethylglyoxime used in the determination.

Zusammenfassung—Wenn Diacetyl mit Hydroxylamin in Gegenwart von Nickel reagiert, werden wohlausegebildete und leicht filtrierbare Kristalle von Nickeldimethylglyoxim erhalten. Die nadel-förmigen Kristalle sind des öfteren mehrere Millimeter lang. Grosse Mengen von Nickel (bis hinauf zu 200 mg) können leicht gehandhabt werden. Die Nützlichkeit der Methode zur Bestimmung von Nickel neben anderen Elementen wird gezeigt indem Nickel in Gegenwart von Kupfer, Kobalt und Eisen, und in Standardstählen vom National Bureau of Standards gefällt wird.

Résumé—En faisant réagir du biacétyl et de l'hydroxylamine en présence de nickel (II), de grands cristaux de diméthylglyoximate de nickel bien développés et facilement filtrables sont précipités à partir d'une solution homogène. Les cristaux aciculaires ont fréquemment jusqu'à plusieurs millimètres de long. De grandes quantités de nickel—de l'ordre de 20 mg—sont facilement manipulées. L'utilité de cette méthode de précipitation à partir d'une solution homogène est montrée par les résultats obtenus pour le nickel en présence de quelques substances sélectionnées, telles que le cobalt, le cuivre, le fer et des échantillons d'acier du Bureau National des Standards.

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UNTERSUCHUNG DER KATIONENSORPTION AUS KOMPLEXANMEDIUM—I*

DAS VERHALTEN VON MANGAN UND ERDALKALIEN

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Zusammenfassung—Es wurde das Verhalten der Mangan- und Erdalkalikomplexe mit Äthylendiamin-tetraessigsäure (AeDTA) und mit 1.2-Diaminocyclohexan-N.N.N.'N'-tetraessigsäure (DCTA) an stark sauren Kationenaustauschern in Abhängigkeit von pH untersucht. Die durch entsprechende Sorptionskurven gegebenen Existenzbereiche der einzelnen Komplexe wurden mit dem Verlauf der pH-Abhängigkeit der scheinbaren Komplexbildungskonstante der einzelnen Komplexe verglichen. Es wurde eine selektive Trennung der Erdalkalien von grossen mittels DCTA komplex gebundenen Mengen Mangan ausgearbeitet.

METALLKOMPLEXE mit Reagenzien des Komplexantyps sind zur Verwendung in der Ionentechnik besonders geeignet. Wie bekannt, gehen die meisten Kationen solche Komplexe im einfachen stöchiometrischen Verhältnis (meist 1:1) ein; die Komplexe sind sehr stabil und untereinander durch ihre Komplexbildungskonstanten verschieden, was bereits bei komplexometrischen Titrationen und auf anderen Gebieten der analytischen Chemie bereits ausgenutzt wurde.¹

Eine der ersten Arbeiten, in der die Anwendung von AeDTA in der Ionenchromatographie behandelt wird, ist die Studie von Bovy und Duyckaerts² über die Trennung von Strontium und Barium an Katexen. Honda³ eluierte mit 0,01-m AeDTA das sorbierte Calcium bei pH 6,6 und Strontium bei pH 10. Fouarge und Fregar⁴ trennen Calcium und Strontium von Barium und Radium durch Auswaschen mittels AeDTA bei pH 7,4. Schwarzenbach⁵ bediente sich zur Trennung des Calciums von Magnesium der geringen Stabilität des AeDTA-Magnesiumkomplexes gegenüber Natronlauge. In stark alkalischer Lösung wird durch Titration gegen Murexid nur das Calcium komplex gebunden. Nach Herabsetzen der Alkalität bilden sich Magnesiumionen, die an Katex sorbiert werden, während der stabile Calciumkomplex durch die Katexsäule unverändert durchgeht. Die beiden sorbierten Elemente lassen sich auch durch selektives Auswaschen mittels AeDTA-Lösung bei pH 6,1 trennen;⁶ mit der gleichen Lösung wurde Mangan von Calcium bei pH 4,7 chromatographisch abgetrennt.⁷

In der vorliegenden Arbeit untersuchten wir systematisch das Verhalten von Mangan und den Erdalkalien nicht nur gegenüber AeDTA sondern auch gegenüber DCTA. Insbesondere widmeten wir unsere Aufmerksamkeit der Abhängigkeit der Kationensorption von pH. Wir knüpften hierbei an die Ergebnisse unserer früheren

* Auf der 20. IUPAC-Tagung in München in September 1959 wurde empfohlen, für Polyaminopolycarbonsäuren, die mit Metallen komplexe Anionen bilden, statt Komplexe, die Bezeichnung Komplexane zu verwenden.

Arbeit an⁷ und bedienten uns auch z.T. der von Fritz und Umbreit⁸ beschriebenen Methodik, mittels der die letztgenannten das Verhalten einiger Kationen an Ionenaustauschern in Gegenwart von AeDTA untersucht hatten. Das Verhalten der DCTA-Metallkomplexe an Ionenaustauschern wurde bisher nicht beschrieben.

VERSUCHSTEIL

Apparatur:

Es wurde mit stark saurem, Sulfongruppen enthaltendem Katex, Amberlite IR-120 (Röhm und Haas) der Korngrösse 0,1–0,3 mm gearbeitet. Der Ionenaustauscher wurde durch wiederholtes Dekantieren mit 3 m-Salzsäure und 3 m-Natronlauge gereinigt, dann mit Wasser bis zur neutralen Reaktion gewaschen und mittels 5% iger Kochsalzlösung in den Na-Cyclus übergeführt. Es wurde eine für die kinetische Methode⁹ übliche Säule verwendet. Zur Untersuchung der Sorption eine Säule von $15 \times 1 \text{ cm}^2$, zur Untersuchung der Trennung und zur praktischen Anwendung eine Säule von $25 \times 1 \text{ cm}^2$.

Das pH wurde potentiometrisch (Apparatur Typ K, Kovodružstvo, Prag) mit Hilfe der Glaselektrode gegen Normal-Kalomelektrode gemessen.

Reagenzien:

Die 0,05 m-AeDTA-Lösung wurde durch Lösen von 37,22 g des AeDTA-Dinatriumsalzes (Chelaton 3 der Firma Lachema, Brünn) in 2 Liter deionisiertem Wasser hergestellt.

Die 0,05 m-DCTA-Lösung wurde durch Neutralisieren von 19,4 g 1.2-Diaminocyclohexan-N.N.N.'N'-tetraessigsäure (J. R. Geigy, Basel, Schweiz) mit 10% iger Natronlauge zu pH 8 und durch Auffüllen mit deionisiertem Wasser zu 1 Liter hergestellt.

Die 0,05 m-Lösungen der untersuchten Metallsalze wurde aus Präparaten der Fa. Lachema, Brünn, CSR, bereitet. Auch die entsprechenden Pufferlösungen (s. Tab. 1) wurden aus analytisch reinen Substanzen hergestellt.

Verwendete Arbeitstechnik:

Zu 10 ml der 0,05 m-Lösung des untersuchten Metalls wurden 25 ml der 0,05 m-AeDTA oder DCTA-Lösung und 20 ml der entsprechenden Pufferlösung (Tab. 1) zugesetzt.

TAB. 1. ZUSAMMENSETZUNG DER VERWENDETEN PUFFERLÖSUNGEN. pH-BEREICH.

Zusammensetzung der verwendeten Pufferlösungen.	pH-Bereich
0,5 m Ameisensäure/Natronlauge	2–3,5
0,5 m Essigsäure/Natronlauge	3–6,2
0,2 m Borsäure/0,05 m Borax	7,1–8,5
0,2 m Borsäure/Natronlauge	8,0–10
0,2 m Borax/Natronlauge	9,5–12

(1) Unter potentiometrischen Kontrolle wurde das pH der Lösung mit Hilfe einer 10% iger Lösung der entsprechenden schwachen Säure oder mittels 10% iger Natronlauge auf den gewünschten Wert eingestellt. Nach Abspülen der Elektroden wurde die Lösung auf 70 ml verdünnt.

(2) Die mit dem Ionenaustauscher beschickte Säule wurde zunächst mit 20 ml des entsprechenden verdünnten Puffers (1:3) in der Weise ausgewaschen, dass die Katexsäule nach beendetem Auswaschen noch mit 5 ml der überstehenden Pufferlösung bedeckt war. Alsdann wurde die untersuchte Lösung durch die Säule mit einer Geschwindigkeit von 5 ml/min cm^2 durchgelassen und die ausfliessende Lösung wurde in einen Titrierkolben gefangen. Das Becherglas wurde zweimal mit 5 ml der verdünnten Pufferlösung ausgespült und die Katexsäule mit 50 ml deionisiertem Wasser nachgewaschen. In den vereinigten Eluaten wurde die freie AeDTA bzw. DCTA durch Rücktitration mit Masslösung des jeweils untersuchten Kations bestimmt. Bei der Bestimmung von Calcium, Strontium und Barium wurde als Indikator das Fluorescein Komplexon, bei der Bestimmung von Magnesium und Mangan

das Eriochromschwarz T verwendet. Das sorbierte Kation wurde aus der Säule mit 0,05 m-AeDTA-Lösung von pH-Wert 12 ausgewaschen. Nach dem Auswaschen mit 5% iger Natriumchloridlösung und mit Wasser war die Säule zur weiteren Verwendung bereit.

ERGEBNISSE UND DISKUSSION

Die Menge der durch Sorption zurückgehaltenen Kationen wurde titrimetrisch bestimmt und in Prozenten der Sorption ausgedrückt. Die Ergebnisse dieser sowohl mittels AeDTA als auch mittels DCTA durchgeführten Versuche in Abhängigkeit vom pH-Wert der Lösung sind in Abb. 1 wiedergegeben.

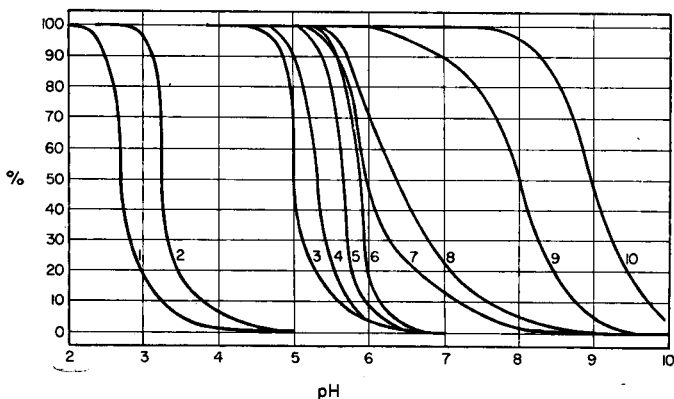


Abb. 1.—Sorption von Mangan und Erdalkalien an Amberlite IR-120 aus Komplextlösung in Abhängigkeit von pH. Konzentration Me^{II} : $7,2 \cdot 10^{-3}$ m; Konzentration des Komplexans: $1,8 \cdot 10^{-2}$ m. Ordinate: % der Sorption, 1 MnDCTA, 2 MnAeDTA, 3 MgDCTA, 4 CaDCTA, 5 CaAeDTA, 6 MgAeDTA, 7 SrAeDTA, 8 SrDCTA, 9 BaAeDTA, 10 BaDCTA.

Aus den erhaltenen Ergebnissen tritt der wesentliche Unterschied im Verhalten beider Komplexbildner bei der Einstellung des Gleichgewichtes zwischen dem Komplex und dem Ionenaustauscher klar hervor. Dieser Unterschied ist in erster Linie durch die Werte der thermodynamischen Komplexbildungskonstanten und ferner durch verschiedene Affinität der betreffenden Ionenart zum Austauscher gegeben. Die Konzentration des freien Kations in der Lösung seines Komplexes ist nicht nur durch die entsprechende thermodynamische Konstante K gegeben, sondern sie wird auch durch die in die scheinbare Komplexbildungskonstante in Form der H -Funktion einbezogene Wasserstoffionenkonzentration beeinflusst. Um die Bedingungen der Verteilung zwischen dem Komplex und dem Ionenaustauscher vergleichen zu können, berechneten wir die scheinbare Komplexbildungskonstante bei einem solchen pH-Wert, bei dem der Verteilungskoeffizient zwischen dem Kation und dem Ionenaustauscher gleich 1 ist. Bei der graphischen Darstellung der Funktion $\log K' = f(\text{pH})$ für AeDTA wurden die von Körbl und Přibil¹¹ berechneten α_H -Werte verwendet. Die analogen Werte für DCTA wurden nach dem gleichen Verfahren¹⁰ berechnet. Alle Werte der Dissoziations- und Komplexbildungskonstanten wurden den Bjerrumschen Tabellen¹² entnommen. Die Abhängigkeit des K' -Wertes einiger Kationen vom pH veranschaulicht Abb. 2. In Tab. 2 sind die Werte von thermodynamischen Konstanten, scheinbaren Komplexbildungskonstanten und diejenigen pH-Werte verglichen, bei denen die Verteilung des Kations gleich 1 ist. Die Reihenfolge einzelner Spalten in der Tabelle ist durch die Reihenfolge der Sorptionskurven aus der Abb. 1 bestimmt. Aus diesen Abhängigkeiten geht hervor, dass die Lage

jeder Sorptionskurve im pH-Abhängigkeitsbereich durch die Differenz der scheinbaren Komplexbildungskonstanten bestimmt ist. Ausserdem macht sich hier auch der Einfluss der Komplexstärke und der Sorbierbarkeit einzelner Ionenarten bemerkbar. Die Sorptionskurven von Mangan aus AeDTA- bzw. CDTA-Lösungen nehmen

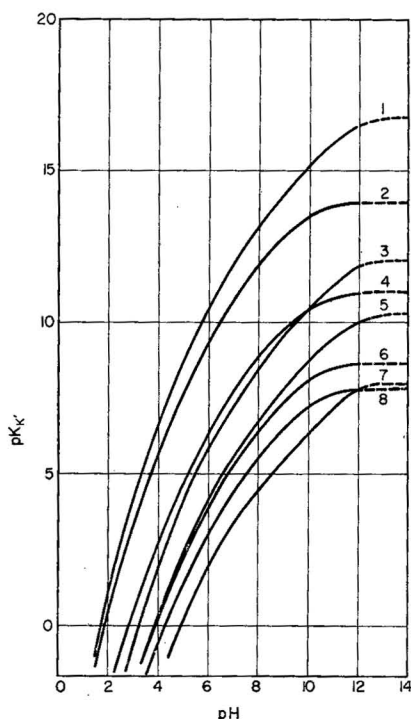


ABB. 2.-Abhängigkeit einiger scheinbaren Konstanten K' von Komplexen einiger Metalle mit Komplexanen von pH. 1. MnDCTA, 2 MnAeDTA, 3 CaDTA, 4 CaAeDTA, 5 MgDCTA, 6 MgAeDTA, 7 BaDCTA, 8 BaAeDTA.

TAB. 2. WERTE VON SCHEINBAREN KOMPLEXBILDUNGSKONSTANTEN K' UND VON pH, BEI DEM DIE VERTEILUNG DES METALLS ZWISCHEN DEM AUSTAUSCHER UND DEM KOMPLEX GLEICH 1 IST.
C=DCTA: Y=AeDTA

Komplex	MnC	MnY	MgC	CaC	CaY	MgY	BaY	BaC
pH	2,90	3,35	5,15	5,35	5,55	5,85	8,00	8,90
K	16,8	14,0	10,3	12,1	11,0	8,7	7,8	8,0
K'	4,2	3,7	2,7	4,6	5,5	3,8	5,5	5,2

bezüglich der Sorptionskurven anderer Metallionen eine Sonderstellung ein (Abb. 1, Kurve 1, 2). Ihre Stellung zueinander stimmt mit dem Verlauf der pH-Abhängigkeit ihrer Konstanten K' (Abb. 2, Kurven 1, 2) gut überein. Die beiden in Abhängigkeit von pH veranschaulichten Kurven des Bariums (Abb. 1, Kurven 9, 10) unterscheiden sich von den Kurven anderer Erdalkalien durch Verschiebung des pH zu höheren Werten. Diese Verschiebung ist nicht nur durch die Differenz der Komplexbildungskonstanten verursacht, sondern ist auch auf die durch Bildung von schwerlöslichen Bariumverbindungen mit der Funktionsgruppe des Ionenaustauschers bedingte

betrachtliche Sorbierbarkeit der Bariumionen zurückzuführen. Die scheinbar anomale Sorption des Bariums aus dem thermodynamisch stabileren Komplex mit DCTA ist im guten Einklang mit dem Verlauf der scheinbaren Komplexbildungskonstanten K' (Abb. 2, Kurven 7, 8).

Die unterschiedliche Lage der einzelnen Sorptionskurven ermöglicht einige analytische Trennungen. In dieser Arbeit wird die Bestimmung von Calcium und Magnesium bei Gegenwart grosser Mengen Mangan beschrieben.

Arbeitsanleitung: Eine schwach saure, Mangan, Calcium und Magnesium enthaltende Lösung versetzt man im einem 250 ml Becherglas mit einem auf den Mangangehalt bezogenen, etwa 10% igen Überschuss von 0,05 m-DCTA-Lösung.

TAB. 3. TRENNUNG DER ERDALKALIEN VON MANGAN IM DCTA-MEDIUM BEI pH 4,0–4,4.
IN ALLEN FÄLLEN WURDE MIT 140 MG Mn GEARBEITET.

Gegeben, mg		Gefunden, mg Mg(Ca)	Differenz, mg	Abweichung, rel %	Mn:Mg(Ca)
Mg	Ca				
2,49		2,63	0,14	105,6	56:1
6,23		6,24	0,01	100,2	22:1
12,45		12,39	–0,06	99,5	11:1
24,90		24,98	0,08	100,3	5,6:1
	4,01	4,40	0,39	111	35:1
	10,00	10,00	—	100,0	14:1
	20,04	20,34	0,30	101,5	7:1
	40,08	40,10	0,02	100,1	3,5:1

(Die Trennung kann ohne Verluste an Erdalkalien auch bei einem 200% igen DCTA-Überschuss durchgeführt werden.) Man fügt 25 ml 0,5 m-Acetatpuffer hinzu, stellt das pH unter potentiometrischer Kontrolle auf den Wert von 4,0–4,4 ein und verdünnt auf 150 ml. Die Lösung lässt man nun mit einer Geschwindigkeit von 5 ml/min cm^2 durch die Säule durchfliessen und wäscht alsdann mit Prufferlösung und deionisiertem Wasser wie in der Anleitung unter 2 angegeben ist, nach. Nach der Abtrennung von Mangan wäscht man die sorbierten Ionen mit abgemessenen mengen 0,05 m-AeDTA-Lösung bei pH 11,5 aus und bestimmt den AeDTA-Überschuss durch Rücktitration mit 0,05 m-Zink- oder Mangesiumsalz. Wie aus Tab. III ersichtlich ist, stimmen die Ergebnisse dieser Trennung mit den kannten Werten gut überein.

Die Trennung an Ionenaustauschern ist unvergleichbar schneller als die bisherigen klassischen Trennverfahren. Die obige Arbeitsvorschrift ermöglicht eine schnelle Bestimmung von Calcium und Magnesium im Material mit hohem Mangangehalt wie z.B. in Manganschlacken, in Flüssen für Schweissautomate und in zahlreichen Mineralen.

Auf einem ähnlichen Prinzip beruht auch die Trennung des Calciums von Barium, bzw. die Trennung der Erdalkalien. Einzelheiten darüber werden demnächst veröffentlicht. Die weitere Anwendung von DCTA in der Ionen-Technik bildet den Gegenstand der nächsten Mitteilungen.

Summary—The behaviour of manganese and of alkaline earth complexes with ethylenediaminetetraacetic acid and with 1:2-diaminocyclohexane-N:N':N':N'-tetra-acetic acid (DCTA) has been studied on strongly acid cation-exchangers in respect of pH-dependence. The actual range of existence of

individual complexes indicated by sorption curves has been correlated with the pH dependence of the apparent stability constants of the complexes. A procedure has been developed for the separation of alkaline earths from large amounts of manganese complexed by DCTA.

Résumé—Le comportement des complexes du manganèse et des alcalinoterreux avec l'acide éthylène diamine tétracétique et l'acide 1-2 diamino cyclohexane N-N'-N'-N' tétracétique (DCTA) a été étudié sur des échangeurs de cations fortement acides au point de vue de sa variation avec le pH. Le domaine réel d'existence des complexes particuliers indiqué par les courbes de sorption a été reliée à la manière dont les constantes de stabilité apparente des complexes dépendent du pH. Un procédé a été développé pour séparer sélectivement les alcalino-terreux de grandes quantités de manganèse complexé par le DCTA.

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NEW REDOX SYSTEMS—III

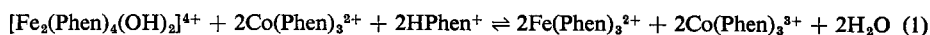
INDIRECT CERIMETRIC DETERMINATION OF COBALT

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Summary—The previously studied redox reaction:



is utilised for the indirect cerimetric determination of cobalt. The determination is based on the titration of the resulting ferroin with potentiometric or visual control.

RECENTLY we studied the oxidation of cobalt^{II} salts with a solution of iron^{III} chloride in the presence of 1:10-phenanthroline.^{1,2} It was proved that the reaction takes place according to equation (1). The equilibrium of this reaction in solutions of pH 2-4 is shifted in practice to the right. It was found further that highly diluted solutions of cobalt^{II} salts can, under optimal pH, be titrated directly with 0.01M iron^{III} chloride. The potential jump at the equivalent point is 250 mV per 0.05 ml of iron^{III} chloride solution. The direct titration is limited to solutions in which iron is not present or is suitably removed or is reduced to its bivalent form. Experiments towards solving this problem are still being carried out, and these will be published in a future paper.

The reaction described above for the determination of cobalt could be utilised in another way. The intensely coloured ferroin resulting from this reaction could be determined colorimetrically. This fact enables the indirect determination of cobalt to be made.³ At higher concentrations of cobalt, the ferroin coloration is too intense to be suitable for colorimetry. Therefore, oxidimetric titration of ferroin to ferriin was studied. Cerium^{IV} sulphate was found to be most suitable for this purpose. This titration is easily followed potentiometrically, or, after sufficient dilution, even visually (intensely red ferroin turns to weakly blue ferriin).

EXPERIMENTAL

Reagents and solutions

0.1M 1:10-phenanthroline solution was prepared by dissolving 18.022 g of reagent grade substance in redistilled water acidified with hydrochloric acid. After adjusting the pH to 3, the solution was diluted to 1 litre with water. Other solutions—0.01M and 0.05M Co(NO₃)₂, 0.01M and 0.05M FeCl₃ and 0.075M Ce(SO₄)₂—were prepared from the reagents of highest purity.

Apparatus

Potentiometric measurements were carried out with a Trüb and Täuber potentiometer (Switzerland). A platinum electrode and a saturated calomel electrode were used. The control of pH was carried out potentiometrically using a glass electrode and pH-meter (Kovodružstvo, Praha).

RESULTS AND DISCUSSION

Cerimetric determination of ferroin

Oxidation of red ferroin to blue ferriin was applied for the visual indication of some cerimetric titrations. In all cases only small amounts of ferroin indicator were used. In this particular case, when ferroin functions as a reducing agent, it was important to study the conditions of its quantitative oxidation, particularly at higher concentration. Due to the instability of ferroin in a strongly acidic medium, especially

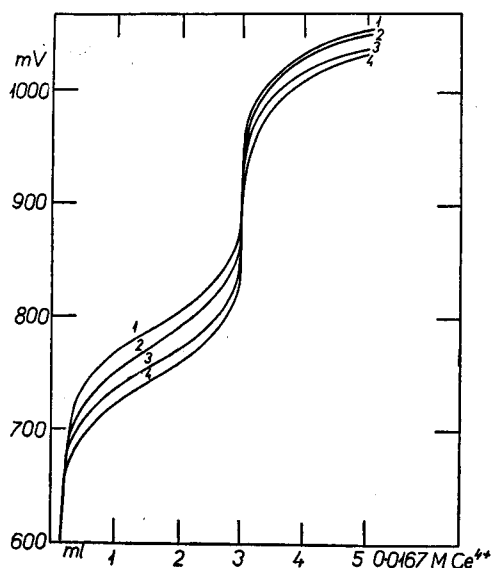


FIG. 1.—Cerimetric determination of ferroin at various molarities of H_2SO_4 . Curves: (1) 0.5M, (2) 1M, (3) 2M, (4) 4M.

at higher temperatures, the effect of acidity at room temperature was particularly studied. Experiments were carried out as follows:

5 ml of 0.01M cobalt^{II} nitrate solution were mixed with 2 ml of 0.05M iron^{III} chloride solution and 5 ml of 0.1M 1:10-phenanthroline solution. The pH of the solution was adjusted to 2–4 by appropriate addition of sodium hydroxide or hydrochloric acid. After 15 min a suitable volume of 9N sulphuric acid was added, and the solution diluted to 100 ml and titrated potentiometrically with 0.0167M cerium^{IV} sulphate using a 5-ml microburette.

From the shape of the curves in Fig. 1, representing the titrations in 0.5–4M sulphuric acid medium, it is evident that during the 30 min in which the titrations took place, the determination was not effected by acidity. A similar condition of acidity had to be kept also for the proper determination of cobalt. It is necessary to emphasise that the basic reaction (1) has its optimum at pH 2–4. The subsequent cerimetric oxidation of the resulting ferroin takes place in a strongly acidic medium. That is why reaction (1) was carried out in a non-buffered solution at pH 2–4.

Visual titration

Cerimetric determination of ferroin, as well as the indirect titration of cobalt, can be observed very exactly visually when the titration is carried out sufficiently

slowly. The colour change at the end-point is from orange-red to distinct blue. Thus relatively low concentrations of cobalt may be determined. At higher concentrations it is necessary to dilute the solution to render the colour change more distinct. In Table I some results of visual and potentiometric determinations of cobalt are given.

TABLE I. INDIRECT CERIMETRIC DETERMINATION OF COBALT.

Co taken, mg	Co found, mg	
	potentiometrically	visually
1.45	1.48	1.47
2.90	2.90	2.92
5.80	5.77	5.78
14.50	14.56	14.60
29.00	28.95	29.13

Selective determination

The effect of other cations on reaction (1) and on the subsequent cerimetric determination of the resulting ferroin was studied in some detail. The procedure was the same as described above.

1. *Effect of iron.* From the colorimetric measurements³ it was obvious that an excess of iron^{III} in comparison with 1:10-phenanthroline has such an effect on reaction (1) that either the reaction does not proceed quantitatively or it does not proceed at all. The explanation is that, under the given conditions, the complex $[\text{Fe}_2(\text{Phen})_4(\text{OH})_2]^{4+}$ is not formed. The resulting complex of different constitution is not readily reduced by cobalt. The effect of iron was studied potentiometrically in detail. It was found that, for example, in the presence of 5 ml of 0.1M 1:10-phenanthroline, 3 mg of cobalt could be reliably determined in the presence of 90 mg of iron (Co:Fe = 1:30). This ratio could be higher if the iron was masked with a suitable complex-forming compound. This problem will be discussed in a subsequent paper dealing with the colorimetric determination of cobalt.³

2. *Effect of other metals.* From a series of experiments it was obvious that none of the common cations is capable of reducing iron^{III} in the presence of 1:10-phenanthroline, but cobalt^{II}, under the same conditions, is able to reduce copper to its univalent form which combines with 1:10-phenanthroline to form a very stable complex. This reaction proceeds more slowly than reaction (1) and, from this point of view, it may be considered as a specific reaction for cobalt. Strong reductants (hydroxylamine, ascorbic acid) and strong oxidants have a comprehensibly interfering effect. Some bivalent cations in higher concentrations interfere because they form stable complexes (soluble or insoluble) with 1:10-phenanthroline. This effect could be suppressed by the addition of 1:10-phenanthroline in excess. But at present the use of 1:10-phenanthroline is somewhat limited because of its high cost. Some interfering cations could be screened by the addition of EDTA.³ Unfortunately, EDTA is not suitable for potentiometric titrations because it is oxidised by cerium^{IV} sulphate. Metals which do not form complexes with 1:10-phenanthroline, e.g. alkaline earths and rare earths,

thorium, beryllium, titanium, uranium, chromium, aluminium, lead and zirconium, do not interfere in this reaction.

The maximum permitted concentration of interfering elements was determined as follows:

The definite amount of cobalt solution was mixed with 5 ml of 0.05M 1:10-phenanthroline solution and 5 ml of 0.05M iron^{III} chloride solution, then the cerimetric titration was carried out as described above.

The experiments showed that, for example, it is possible to determine 2.9 mg of cobalt with an error of up to 1% in the presence of 110 mg of Ni, 25 mg of Cd, 65 mg of Zn, 20 mg of Cu, 30 mg of Mo, 45 mg of V (as VO₃) and 50 mg of W. Silver, mercury and thallium^I made this determination impossible, even when present in low concentration, because of the formation of insoluble precipitates, and they must, therefore, be removed.

Analytical application

The proposed method was used for the determination of cobalt in steels, ferrous and non-ferrous alloys containing moderate amounts of cobalt (about 2-40%). As an example, this method was applied to the cerimetric determination of cobalt in an alloy used for the manufacture of permanent magnets (procedure 1), and for a special cobalt-chromium alloy (procedure 2).

Procedure 1. About 0.5 g of sample is treated with *aqua regia*, partly evaporated, then diluted. Any insoluble residue is filtered off and washed with hot dilute hydrochloric acid. The filtrate is accurately diluted to 250 ml. Twenty-five ml of this solution are neutralised with 5% sodium hydroxide to the formation of a precipitate, which is then dissolved in the minimum amount of hydrochloric acid. The pH is adjusted to a value of 2-4 (glass electrode, universal indicator paper), and 10 ml of 0.1M 1:10-phenanthroline of pH 3 are added. After 15 min the solution is acidified with 50 ml of 9N sulphuric acid, diluted to 200 ml with water and titrated with 0.05-0.1M cerium^{IV} sulphate solution from a suitable microburette, with potentiometric control.

With this procedure cobalt was determined in permanent magnet alloy BCS No. 233 (11.22% Ni, 6.98% Al, 0.78% Ti, 0.23% Mn and 23.7% Co). The average of 3 determinations was 23.78% of cobalt. (0.35% error).

Procedure 2. This was the same as for procedure 1. With regard to the fact that the sample contained a small amount of iron, after dissolving the alloy, a sufficient amount of iron^{III} chloride was added to make its concentration in the solution higher than that of the cobalt.

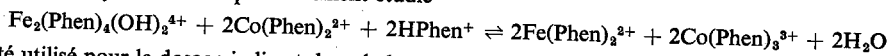
The special cobalt-chromium alloy has the following composition: 0.58% C, 0.23% Si, 1.67% Fe, 57% Cr and 39.21% Co. With the modified method the average of 3 determinations was 39.10% of cobalt (0.25% error).

Zusammenfassung—Das früher studierte Redoxsystem:



wurde zur indirekten cerimetrischen Bestimmung von Cobalt herangezogen. Die Bestimmung beruht auf der potentiometrischen oder visuellen Titration des entstehenden Ferriions.

Résumé—Le système rédox préalablement étudié



a été utilisé pour le dosage indirect du cobalt par cérimétrie. Le dosage est basé sur le titrage de la ferroïne formée avec contrôle potentiométrique ou visuel.

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ANALYTICAL USES OF BROMINE MONOCHLORIDE DETERMINATION OF HYDROXYLAMINE. CONTRIBUTIONS TO THE BROMIC ACID-HYDROCHLORIC ACID REACTION

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Summary—The oxidation of hydroxylamine by bromine monochloride, by elementary chlorine in hydrochloric acid medium, and by bromate and bromic acid has been investigated. Oxidation by bromine monochloride is utilised for the analytical determination of hydroxylamine.

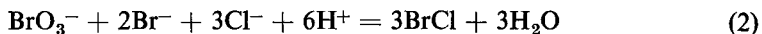
Detailed examination of the reaction of bromate with hydrochloric acid proves that, in the presence of excess of hydrochloric acid, these compounds quickly react forming bromine monochloride and elementary chlorine. The proportions of the reaction products have been determined. On the basis of the results of these investigations, it is possible to present an interpretation of the analytical method suggested by Kurtenacker for the determination of hydroxylamine.

THE conventional analytical determination of hydroxylamine is based on determination of the acid component of its sulphate or hydrochloride. Rupp and Mäder¹ were the first to use oxidation by bromine for the determination of hydroxylamine, and they found that hydroxylamine is oxidised by bromine to nitric acid. Kurtenacker and co-workers,^{2,3} however, pointed out that this method is only suitable for minute amounts of hydroxylamine. With greater quantities of hydroxylamine, nitrogen oxides are also formed. In the opinion of Kurtenacker and Wagner² the best method for the determination is to oxidise hydroxylamine with bromate in strong hydrochloric acid medium. According to these authors, hydroxylamine is then oxidised to nitric acid by nascent chlorine which is formed by the reaction of bromate with hydrochloric acid.

During our investigations into the analytical uses of bromine monochloride, we studied the oxidation of hydroxylamine by bromine monochloride. It was found that hydroxylamine is quantitatively oxidised to nitric acid by an excess of bromine monochloride:



In our attempts to utilise this reaction for the analytical determination of hydroxylamine, we used a 0.1*N* standard solution of bromate which contained an equivalent amount of bromide according to the equation:



This standard solution was added in excess to a weighed amount of hydroxylamine in a bromination flask. On acidification with hydrochloric acid, reaction (2) takes place and hydroxylamine is oxidised according to (1). The excess of bromine monochloride is determined iodometrically. In this reaction, the equivalent weight of hydroxylamine is $M/6$.

On examining the reaction between bromine monochloride and hydroxylamine in detail under the conditions mentioned later it was found that:

1. When bromine monochloride is present in an excess greater than 100%, hydroxylamine is quantitatively oxidised to nitric acid in 3 min.
2. The results are not affected by using longer reaction periods.
3. It is practical to use 5–10 ml of 20% hydrochloric acid.
4. On varying the excess of bromine monochloride (greater than 100%), no change was observed in the results. The use of excesses of bromine monochloride greater than 100% is necessary because, during the oxidation, bromine monochloride is reduced to bromide which latter itself reduces bromine monochloride to elementary

TABLE I

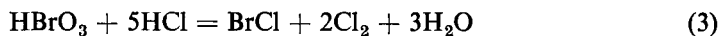
NH ₂ OH·HCl taken, mg	0·1N BrCl added, ml	0·1N Na ₂ S ₂ O ₃ consumed, ml	0·1N BrCl consumed, ml	Reaction time, min	20% HCl used, ml	NH ₂ OH·HCl found, mg	Δ mg	Δ %
2·971	9·96	7·40	2·56	5	5	2·965	−0·006	−0·2
5·010	9·96	5·63	4·33	5	5	5·015	+0·005	+0·1
9·862	20·00	11·48	8·52	5	5	9·869	+0·007	+0·1
9·862	20·00	11·50	8·50	5	10	9·846	−0·016	−0·2
9·862	20·00	11·50	8·50	10	10	9·846	−0·016	−0·2
9·862	20·00	11·46	8·54	10	5	9·892	+0·030	+0·3

bromine. Because of this fact the reaction is slowed down, since the elementary bromine oxidises the hydroxylamine more slowly.

By utilising the afore-mentioned observations, 3–12 mg of hydroxylamine hydrochloride could be determined with an error of $\pm 0\cdot5\%$ (cf. Table I).

The bromatometric method suggested by Kurtenacker² for the determination of hydroxylamine was also examined.

First, in the reaction between bromate and hydrochloric acid it was found that, on pouring only 5 ml of 20% hydrochloric acid* into 10 ml of 0·1N bromate solution in a volume of 20 ml, no bromate is present in the solution after 5 min. To disclose this fact we used the method suggested by us⁴ for the eventual bromate content of a bromine monochloride standard solution. By raising the concentration of hydrochloric acid, the rate of reaction was increased. The proportions of reaction products were established as well. Thus, bromine monochloride and elementary chlorine formed in the reaction were converted into halogen cyanides, and the amount of cyanogen bromide measured by iodometry in the presence of the iodometrically inactive cyanogen chloride. According to our investigations, the following reaction takes place quantitatively between bromate and an excess of hydrochloric acid:



By raising the concentration of hydrochloric acid the rate of reaction increases. The kinetics of the reaction will be discussed in another communication.

* In his determination Kurtenacker used 40 ml of 20% hydrochloric acid.

The oxidation of hydroxylamine by chlorine and bromic acid, respectively, were studied too. It was found that hydroxylamine is oxidised to nitric acid by elementary chlorine at approximately the same rate as by bromine monochloride. In our studies of the oxidation by bromic acid, it was necessary to maintain conditions which exclude the possibility of formation of bromine monochloride, elementary bromine or elementary chlorine. Therefore, oxidation was carried out in a medium containing sulphuric acid, in the presence of mercury^{II} ions, which are capable of preventing interference from halide ions binding them as poorly dissociating mercury halides. Under these conditions the reaction is extremely slow and ambiguous. No equation can be given for this process.⁵

Accordingly, as proved by our investigations, in the oxidations by bromate carried out in a medium of hydrochloric acid, bromine monochloride and elementary chlorine are always the oxidising reagents. The situation is the same in the method suggested by Kurtenacker.²

EXPERIMENTAL

Determination of hydroxylamine by oxidation with bromine monochloride

Reagents

0.1N bromate solution: 2.7835 g of potassium bromate and 3.9670 g of potassium bromide dissolved in water and diluted to 1000 ml in a standard flask.

Hydrochloric acid: 20%.

Potassium iodide.

0.1N solution of sodium thiosulphate.

Potato starch solution: 1%, decomposed and preserved by 0.1% of salicylic acid.

All the reagents were of analytical grade. The hydroxylamine hydrochloride was Merck analytical grade.

Procedure

An aliquot of solution, containing 3–12 mg of hydroxylamine hydrochloride was, transferred to a Schulek bromination flask and treated with sufficient 0.1N standard solution to maintain, on acidification with hydrochloric acid, an excess of bromine monochloride greater than 100%. Subsequently, the volume of the reaction mixture was diluted with distilled water to 30–40 ml. Then 5–10 ml of 20% hydrochloric acid were poured into the cup-shaped, broadened neck of the bromination flask. On loosening the stopper, the liquid flowed into the flask. After 5 min, 10 ml of a freshly prepared 5% solution of potassium iodide were added to the reaction mixture in a similar way. The amount of iodine liberated was determined, without allowing the mixture to stand, with 0.1N standard sodium thiosulphate solution using potato starch solution as indicator.

1 ml of 0.1N solution corresponds to 1.1583 mg of hydroxylamine hydrochloride (equivalent weight is $M/6$ in this reaction).

The error of the results is $\pm 0.5\%$.

Investigation of the reaction between bromate and hydrochloric acid

Reagents

0.1N bromate solution.

Hydrochloric acid: 20%, distilled, free from bromide.

Potassium cyanide.

Potassium iodide.

Sodium hydroxide: 20%.

Potato starch solution: 1%, decomposed and preserved by 0.1% of salicylic acid.

All the reagents were of analytical grade.

Procedure

10.00 ml of 0.1N standard bromate solution were diluted with distilled water to 20 ml, and acidified with 5 (10 and 20) ml of 20% hydrochloric acid. On allowing the mixture to stand for 5 min, 0.5 g

of potassium cyanide was dissolved in the mixture and then 20% sodium hydroxide was added to attain an alkali excess of about 2 ml. Bromine monochloride and elementary chlorine reacted with cyanide forming cyanogen bromide and cyanogen chloride and, in the alkaline medium, both hydrolysed to cyanate and bromide or chloride ions, indifferent to iodometry. Accordingly, the bromate content of the solution could be measured iodometrically after 5 min.

Results

Our results showed that, after a reaction period of 5 min, no bromate could be detected.

In order to determine the proportion of the reaction products, about 0.20 g of potassium cyanide was dissolved in the acidic solution when the reaction between bromate and hydrochloric acid was already completed. In a period of about 10 min, bromine monochloride was quantitatively converted into cyanogen bromide and chloride ions even in an acidic solution, while cyanogen chloride and chloride ions developed from elementary chlorine. In the solution containing an excess of cyanide, cyanogen chloride is present as a complex, $[\text{Cl}(\text{CN})_2]^-$, which is iodometrically inactive due to its high stability. Thus, it is possible to measure cyanogen bromide iodometrically in the presence of cyanogen chloride.

According to our results, one third (33.35%) of the products formed in the reaction of bromate and hydrochloric acid consists of bromine monochloride, while two thirds (66.65%) consist of elementary chlorine (*cf.* equation (3)).

Oxidation of hydroxylamine by elementary chlorine

In these experiments, aliquots of chlorine water containing exactly known amounts of chlorine were added to the solution of hydroxylamine hydrochloride with the aid of the bromine monochloride apparatus suggested by Schulek.⁶ Excess chlorine was determined iodometrically.

With oxidation by elementary chlorine for 5 min, 98.7% of the weighed amount is recovered. On considering that, under the applied experimental conditions, a deviation of 1–2% in the results is hardly avoidable, oxidation by chlorine can be accepted as quantitative.

Oxidation of hydroxylamine by bromic acid

The aqueous solution of hydroxylamine hydrochloride was allowed to flow into a mercury^{II} sulphate solution (0.2 g of mercury^{II} oxide dissolved in a few ml of 50% sulphuric acid) and the necessary amount of 0.1*N* standard bromate solution was added. Excess bromate was determined by iodometric titration after 5 (in another experiment after 30) min.

The results obtained showed a marked deviation, and it was impossible to evaluate them from an analytical point of view. On calculating with the equivalent weight of the oxidation by bromine monochloride, only about 25% of the weighed substance could be recovered after 30 min oxidation.

Zusammenfassung—Die Oxydation von Hydroxylamin durch Bromchlorid, elementarem Chlor sowie in salzsaurem Medium durch Bromat und Bromsäure wurde untersucht. Die Oxydation durch Bromchlorid wurde zur Bestimmung von Hydroxylamin gebraucht.

In Gegenwart von Säureüberschuss reagiert Bromate rasch mit Salzsäure unter Bildung von Bromchlorid und elementarem Chlor. Das Verhältnis der entstehenden Produkte wurde bestimmt. Auf Grund der erhaltenen Resultate war es möglich die von Kurtenacker ausgearbeitete Metlische zur Bestimmung von Hydroxylamin zu interpretieren.

Résumé—L'oxydation de l'hydroxylamine par le chlorure de brome, le chlore élémentaire et, en milieu acide chlorhydrique par le bromate et l'acide bromique, a été étudiée. L'oxydation par le chlorure de brome a été utilisé pour le dosage de l'hydroxylamine.

En présence d'un excès d'acide, le bromate réagit rapidement avec l'acide chlorhydrique formant du chlorure de brome et du chlore élémentaire. Les proportions des produits ont été déterminées. En se basant sur ces résultats, il a été possible de donner une interprétation de la méthode analytique suggérée par Kurtenacker pour le dosage de l'hydroxylamine.

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POTENTIOMETRISCHE UNTERSUCHUNG EINIGER FÄLLUNGS-UND KOMPLEXIERUNGSREAKTIONEN DES SILBERS IN STARK ALKALISCHEM MEDIUM

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Zusammenfassung—Es wurde die potentiometrische Titration des Silbers in stark alkalischer Lösung der 4-Sulfonamidobenzoesäure untersucht. Als Titriermittel wurden Kaliumchlorid, Kaliumbromid, Kaliumjodid und Kaliumcyanid verwendet. Weiterhin wurden die Fehlerquellen geprüft und einfache Mittel zu ihrer Ausschaltung gezeigt.

Die Abtrennung des Silbers mit Hilfe der 4-Sulfonamidobenzoesäure in alkalischem und karbonathaltigem Medium, gefolgt von einer potentiometrischen Titration mit Kaliumcyanid oder Kaliumjodid bildet eine schnelle und genaue Bestimmungsmethode des Silbers.

DIE 4-Sulfonamidobenzoesäure ist eine seit langem synthetisierte Substanz, aber eine analytische Bedeutung fand sie erst in neuester Zeit. Die Löslichkeit des Silber-salzes der 4-Sulfonamidobenzoesäure in alkalischem Medium, wie auch seine leichte Reduzierbarkeit aus dieser Lösung, wurde erstmals von Gh. Ciuhandu zum Nachweis und zur Bestimmung des Kohlenoxyds in der Luft^{1,2} und anderen Gasen³ verwendet. Dieses spezifische Verhalten des Silbers wurde auch zum Erkennen und Bestimmen des Silbers ausgenutzt.⁴

Da sich das Silber mit Hilfe einer alkalischen Lösung der 4-Sulfonamidobenzoesäure, mit oder ohne Zugabe eines Alkalikarbonats, von den anderen Metallen leicht trennen lässt, haben wir die Möglichkeit einer direkten potentiometrischen Titration des Silbers in dieser Lösung geprüft. Zu diesem Zweck wurden einige der bekanntesten Fällungs bzw. Komplexbildungsagenten des Silbers verwendet: Cl^- , Br^- , I^- und CN^- . Diese Reagentien ergeben beim Titrieren in neutraler Lösung eine hohe Genauigkeit⁵ so dass sie zur Überprüfung der in alkalischem Medium erhaltenen Ergebnisse verwendet werden konnten.

Bei unseren Untersuchungen in alkalischem Medium wurde folgenderweise vorgegangen: zu 5 cm³ AgNO_3 0,1N wurde ein gleiches Volumen einer 0,1N Lösung des Natriumsalzes der 4-Sulfonamidobenzoesäure hinzugefügt, der erhaltene Niederschlag in einem Überschuss an 0,1N NaOH aufgelöst und schliesslich mit Wasser bis zu einem Gesamtvolumen von 70–80 cm³ verdünnt.

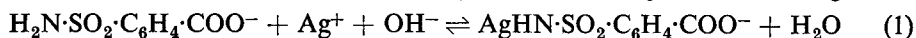
Als Indikatorelektrode wurde ein Silberdraht verwendet, während als Bezugslektrode eine gesättigte Kalomelektrode. Ein mit gesättigter Kaliumnitratlösung gefüllter Heber diente als Stromschlüssel.

Um das an der Kontaktstelle des Hebers mit der zu titrierenden alkalischen Lösung auftretende Diffusionspotential auszuschalten, wurde in einer Versuchsserie an Stelle der Kalomelektrode eine Bezugslektrode mit Quecksilberoxyd(II) und 0,1N Natriumhydroxyd als Elektrolyt, verwendet. Wie zu erwarten war, konnten keine Unterschiede gegenüber den anderen Titrationen festgestellt werden.

EXPERIMENTELLE ERGEBNISSE

Wenn das Potential einer Silberelektrode in alkalischer Lösung der Silberverbindung der 4-Sulfonamidobenzoesäure als Funktion der Alkalinität verfolgt wird, ergibt sich die in Abb. 1 dargestellte Kurve. Aus ihrem Verlauf geht hervor dass die

Konzentration der freien Silberionen mit steigender Alkalinität stark zurückgeht, was die Existenz folgenden, schon früher vorausgesetzten, Gleichgewichts⁴ bestätigt:



Aus diesem Verhalten lässt sich der Einfluss der Alkalinität auf die Grösse des

ABB. 1.—Potential der Silberelektrode (bezogen auf die gesättigte Kalomelektrode) als Funktion der Alkalinität.

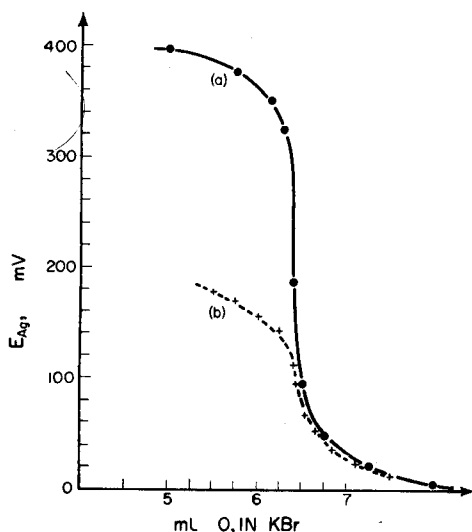
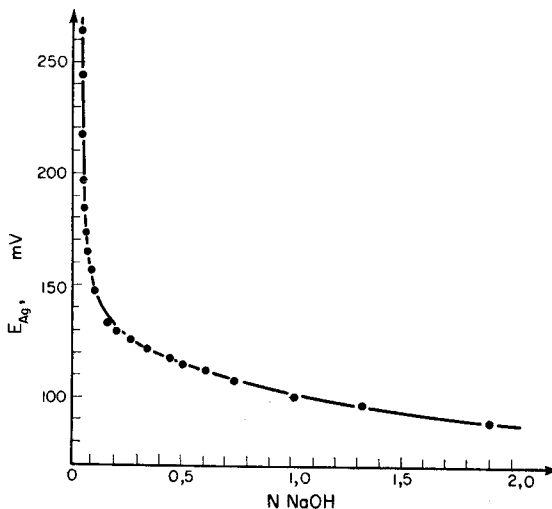


ABB. 2.—Titrationskurven mit KBr 0,1N; (a) in neutralem Medium; (b) in alkal. Medium.

Potentialsprunget im Äquivalenzpunkt abschätzen: der Potentialsprung wird um so kleiner, je grösser die Alkalinität der zu titrierenden Lösung ist.

Beim Titrieren mit Kaliumchlorid (sämtliche Titriermittel wurden in 0,1N Lösung verwendet), war der Potentialsprung selbst bei kleinster Hydroxydkonzentration die ein Auflösen des Silberniederschlags eben noch ermöglicht, äusserst flach, so dass der Äquivalenzpunkt nicht mit genügender Genauigkeit zu bestimmen war.

Mit Kaliumbromid ist der Sprung ausgeprägter, so dass der Abschnitt grösster Neigung leicht zu finden ist (Abb. 2). Trotzdem, waren die Ergebnisse im Vergleich mit jenen aus neutraler Lösung, systematisch um 1% bis 1,5% zu hoch.

Benützt man Kaliumjodid als Titriermittel, erhält man einen noch grösseren Potentialsprung (Abb. 3). Aber auch in diesem Fall wurden immer zu hohe Werte gefunden, die bis zu 1,8% über dem aus neutraler Lösung ermittelten Gehalt lagen.

Beim Arbeiten mit Kaliumjodid konnte überraschenderweise festgestellt werden dass erst nach dem Äquivalenzpunkt ein Ausfallen des Silberjodids beginnt, aber auch

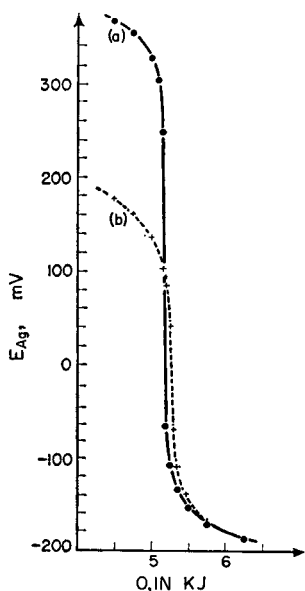


ABB. 3.—Titrationskurven mit KJ 0,1N; (a) in neutralem Medium; (b) in alkalischem Medium.

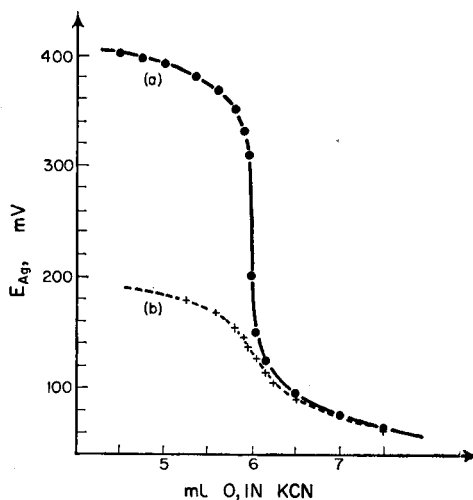


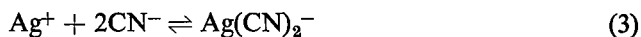
ABB. 4.—Titrationskurven mit KCN 0,1N; gemäss Reaktion (a) in neutralem Medium; (b) in alkalischem Medium.

dann nur als schwache Opaleszenz. Dieses Verhalten könnte auf eine hohe Stabilität des Silberjodid-Sols im benützten Medium hinweisen.

Die besten Ergebnisse konnten mit Kaliumcyanid erhalten werden. In diesem Fall benützt man, je nach Alkalinität der Lösung, den ersten Potentialsprung entsprechend der Reaktion:



oder den zweiten Potentialsprung, der im Äquivalenzpunkt folgender Reaktion auftritt:



Der erste Sprung ist relativ klein (Abb. 4). Trotzdem sind die Ergebnisse besser als beim Titrieren mit Kaliumjodid, obzwar auch hier immer um 0,4-0,6% zu viel gefunden wurde.

Um entsprechend der Reaktion (3) zu titrieren, muss die zu titrierende Lösung stark alkalisch sein, damit die Konzentration der freien Silberionen soweit zurückgedrängt wird, dass ein Ausfällen von Silbercyanid nicht mehr eintritt. Das erreicht man sobald die Alkalinität höher als 1N ist, was einem Anfangspotential der Silber- elektrode von annähernd +100 mV gegenüber der Kalomelektrode entspricht (Abb. 1).

Wenn man in diesen Bedingungen titriert, erhält man die besten Resultate, die praktisch gleich sind mit jenen die sich beim umgekehrten Titrieren (Cyanid mit Silber) in neutraler Lösung ergeben (Abb. 5).

Bekanntlich ist beim Titrieren einer neutralen Silbersalzlösung mit Kaliumcyanid, der zweite Potentialsprung, entsprechend der Reaktion:



unsicher, da sich das Gleichgewicht sehr langsam nach rechts verschiebt. Beim

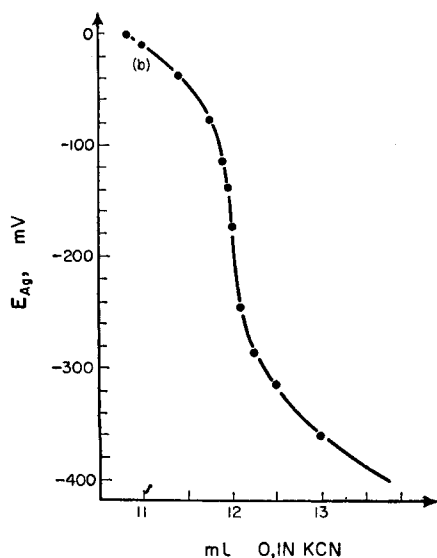


ABB. 5.—Titrationkurve mit KCN 0,1N in alkalischem Medium, gemäss Reaktion (3).

Titrieren in alkalischem Medium hingegen wird ein Ausfällen von Silbercyanid verhindert und daher ist auch der Potentialsprung, bei kürzester Einstellzeit, am richtigen Platz.

BESPRECHUNG DER ERGEBNISSE

Aus den Titrationskurven ist zu ersehen dass die geprüften Titriermittel zu hohe Werte ergeben, wobei die Abweichungen beim Kaliumbromid und Kaliumjodid besonders gross sind.

Es könnten folgende Quellen systematischer Fehler in Betracht kommen: Beim Titrieren sinkt die Alkalinität der zu titrierenden Lösung, was zu einem Ansteigen des Potentials der Indikatorelektrode (Abb. 1) und damit zu einer Verspätung des Potentialsprunges führt.

Es gibt zwei Möglichkeiten diesen Effekt auszuschalten:

(a). Alkalinisierung des Titriermittels, damit die Alkalinität der zu titrierenden Lösung konstant bleibt;

(b). Alkalinisierung der zu titrierenden Lösung bis zu einem Wert für den der Verdünnungseffekt vernachlässigbar ist (Abb. 1).

Beide Methoden haben beim Titrieren mit Kaliumcyanid zu richtigen Werten geführt. Für Kaliumbromid und Kaliumjodid konnten die Fehler zwar vermindert aber nicht ganz ausgeschaltet werden (Abb. 6).

Daraus kann man auf das Bestehen einer weiteren Fehlerquelle schliessen.

Eine solche könnte die Oxydation der Halogenide in alkalischem Medium auf Kosten gelösten Sauerstoffs sein. Zu dieser Vermutung leitet die Feststellung dass die ersten Tropfen beim Titrieren mit Kaliumjodid eine starke Gelbfärbung der Lösung hervorrufen (freies Jod in alkalischem Medium). Die Farbe verschwindet aber nach einiger Zeit, wahrscheinlich gemäss einer Gesamtreaktion folgender Form:

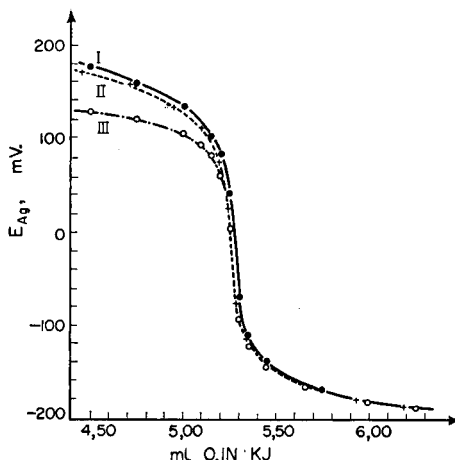
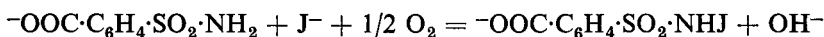


ABB. 6.—Titrationskurven mit KJ 0,1N bei verschiedenen Alkalinitäten der zu titrierenden Lösung. I- 0,05N NaOH; II- 0,05N NaOH mit alkalisiertem Titriermittel. III- 0,1N NaOH.

Um diese Voraussetzung zu prüfen wurden Titrationsen mit Kaliumjodid in Gegenwart von Natriumsulfit durchgeführt. Tatsächlich konnten in diesem Fall die gleichen Werte wie beim Titrieren in neutraler Lösung erhalten werden.

Beim Titrieren mit Kaliumcyanid finden die Oxydationsreaktionen durch gelösten Sauerstoff nicht statt und daher sind die Fehler wesentlich kleiner und können durch Verhindern des Verdünnungseffektes ausgeschaltet werden.

Abschliessend kann man sagen, dass beim Titrieren des Silbers in alkalischem Medium, von den untersuchten Titriermittel die besten Ergebnisse mit Kaliumcyanid zu erhalten sind, wenn bis zum zweiten Potentialsprung, entsprechend Reaktion (3) titriert wird.

Mit Kaliumjodid sind ebenfalls gute Werte zu erhalten, aber nur in Gegenwart von Natriumsulfit.

Auch auf diesem Weg danken wir Herrn Dr. Gh. Ciuhandu für das freundliche Überlassen von 4-Sulfonamidobenzoesäure sowie auch für einige Hinweise über noch unveröffentlichte Eigenschaften dieses Reagens.

Summary—The potentiometric titration of silver in strongly alkaline solutions of 4-sulphoamido-benzoic acid has been investigated. Potassium chloride, bromide, iodide and cyanide were used as titrants. Sources of error were investigated and means indicated for their elimination. The separation of silver by means of 4-sulphoamidobenzoic acid in alkaline or carbonate-containing media, followed by a potentiometric titration with potassium cyanide or iodide promises a rapid and accurate method for the determination of silver.

Résumé—Les auteurs ont étudié le titrage potentiométrique de l'argent dans des solutions fortement alcalines d'acide 4-sulfoamidobenzoïque. Les chlorure, bromure, iodure et cyanure de potassium ont été utilisés comme agents titrants. Les causes d'erreurs ont été étudiées et les moyens de les éliminer indiqués. La séparation de l'argent au moyen de l'acide 4-sulfoamidobenzoïque en milieu alcalin ou carbonate, suivie d'un titrage potentiométrique par le cyanure ou l'iodure de potassium est une méthode rapide et précise de dosage de l'argent.

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ÜBER DIE ANFÄNGE DER KOLORIMETRISCHEN ANALYSE

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Zusammenfassung—Es wird ein historischer Überblick der ersten kolorimetrischen und photometrischen Bestimmungen gegeben.

Die Fachbücher, die über einen Zweig der analytischen Chemie verhandeln, geben in den ersten Seiten meistens einen kurzen, mehr oder weniger richtigen historischen Rückblick der betreffenden Methode. Es ist mir jedoch kein Buch über die Kolorimetrie bekannt, in dem man einen derartigen, wenn auch noch so kurzen Rückblick auffinden könnte.

Die kolorimetrische Methode ist ein der verbreitetsten Verfahren der analytischen Chemie. Es schien mir deshalb der Mühe wert die Pioniere dieses Verfahrens aus der Vergessenheit herauszugraben.

Schon bevor irgend einer in Form eines exakten Gesetzes es proklamiert hätte, nahm man an, dass zwischen der Farbenstärke von färbigen Lösungen und der Konzentration der die Farbe liefernden Substanz eine direkte Proportionalität besteht. Diese Annahme entstand offensichtlich aus der alltäglichen Beobachtung des praktischen Lebens.

Ich fand aus dem Jahre 1845 die erste Beschreibung einer auf Farbenvergleich beruhenden Bestimmung. Sie stammt von Heine¹ und verhandelt über die Bromidbestimmung in Mineralwassern. Er benützte hiezu die braungelbe Färbung die Brom mit Äther gibt.

Im folgenden Jahr (1846) veröffentlichte Jacquelin² ein Verfahren zur Kupferbestimmung auf Grunde einer Titration bis Farbgleichheit mit Hilfe einer ammoniakalischen Kupferlösung von bekanntem Kupfergehalt.

Herapath bestimmte mit Hilfe von Vergleichslösungen 1852 Eisen auf Grunde der mit Rhodanid gebildeten Färbung³. Der Vergleich erfolgte ebenfalls in Epruvetten vor einem weissen Papier. Er wendete bald das Verfahren zu verschiedenen praktischen Bestimmungen an, z.B. zur Bestimmung des Rhodanids in Speichel.⁴

Man findet aus dem Jahre 1853 das erste turbidimetrische Verfahren, das ebenfalls von Herapath entworfen war. Mit Hilfe von Vergleichslösungen bestimmte er Jodid auf Grunde der dunklen Färbung die der suspendierte Niederschlag des Palladiumjodids in den Lösungen erzeugt⁵.

1853 konstruierte Müller ein Gerät, mit dessen Hilfe die Auswertung von kolorimetrischen Bestimmungen seiner Meinung nach genauer erfolgen kann. Er nannte das Gerät Komplementer-Kolorimeter⁶.

In einer folgenden Veröffentlichung⁷ berichtete Müller über gewisse Modifikationen des Gerätes. Er empfahl zur Auswertung statt farbigen Glasplatten, die auf ein

für allemal einen Standardvergleich ermöglichen, die Anwendung von Vergleichslösungen, die dieselbe Substanz in bekannter Konzentration enthalten. Er untersuchte derart das Verhalten von Eisenrhodanid, Kupferammoniak und Chromatlösungen und stellte z.B. fest, dass die Eisenrhodanidfärbung zwischen den Konzentrationsgrenzen von 0,00075–0,003 g Fe/100 ml zur Bestimmung geeignet ist und dass die Färbung von der Säure- und Rhodanidkonzentration abhängig ist.

Dehm⁸ konstruierte 1864 einen neuartigen Kolorimeter, bei welchem schon zwei Zylinder nebeneinander standen in welchen ebenfalls Röhre beweglich und die Flüssigkeitsschichten biplan begrenzt waren. Man konnte von oben durch eine Linse beide Röhre auf einmal betrachten. In dem einen Zylinder befand sich Wasser auf einer blauen Glasplatte, in dem anderen die zu bestimmende Kupferammoniaklösung. Die Höhe der wässrigen Lösung regelte man solange bis die Farbe in beiden Zylindern gleich wurde. Die Ermittlung der Konzentration erfolgte ebenfalls durch Vergleichslösungen.

Auf diesem Weg schritt Duboscq⁹ weiter, der 1870 direkt mit der Vergleichslösung die Färbung der unbekanntenen Lösung verglich und das Licht durch Glasprismen führte, so dass die eine Hälfte des Sehkreises von dem durch den einen Zylinder, die andere von dem durch den zweiten Zylinder kommenden Licht beleuchtet wurde.

Soviel über die Anfänge der Kolorimetrie. Jetzt folge noch einiges über die Anfänge der Photometrie. Bei der sogenannten Photometrie erfolgt die Bestimmung nicht durch Konzentrations- oder Schichthöheänderung der farbigen Lösungen, sondern man schwächt oder erhöht die Intensität eines monochromatischen Lichtes im notwendigen Masse.

Theoretisch beruht die Photometrie auf dem Lambert-Beer-schen Gesetz. Lambert veröffentlichte 1760 ein Werk mit dem Titel *Photometria*. Das Buch ist von reinem optischem Inhalt. In diesem Werk berichtete er über seine Untersuchungen bezüglich des Verhältnisses zwischen der Lichtabsorption und der Schichtbreite von festen Stoffen, in erster Linie von Glas. Er fand, dass wenn ein Licht von Intensität I eine Glasschicht von einer gewissen Längeneinheit durchschreitet, seine Intensität auf $I \cdot \frac{1}{n}$, im Falle des Fortpflanzens durch eine zweite Schicht von gleicher Länge auf $I \cdot \frac{1}{n} \cdot \frac{1}{n}$ sinkt. Beträgt die Breite in Längeneinheiten m , so ist die Intensität des austretenden Lichtes

$$I = \frac{I}{n^m}$$

Es soll jedoch erwähnt werden, dass schon vor Lambert, im Jahre 1729 Bouguer¹⁰ dasselbe Gesetz feststellte.

Beer untersuchte dann 1852 die Lichtabsorption in färbigen Lösungen, stellte das Verhältnis zwischen der Dicke der durchstrahlten Lösung und deren Konzentration fest und führte den Begriff des Absorptionskoeffizienten ein: "Unter dem Absorptionskoeffizienten wollen wir den Coefficienten der Schwächung verstehen, welche die Amplitude eines Lichtstrahls erleidet, wenn dieser durch die Längeneinheit eines absorbierenden Stoffes sich fortpflanzt."¹¹ Er berechnete den Absorptionskoeffizienten von verschiedenen färbigen Lösungen wie von Kupfer- und Chromsalzen. Der Ausdruck des Extinktionskoeffizienten stammt von Bunsen und Roscoe. Sie nannten

in ihren photochemischen Versuchen den Reciproken derjenigen Schichtdicke so, bei deren Durchschreiten die Lichtintensität auf $\frac{1}{10}$ des ursprünglichen Wertes sinkt. Es lag jedoch bei dieser Gelegenheit kein analytisches Problem vor.¹² Den Bunsen-schen Koeffizienten zog zur Konzentrationsbestimmungen zuerst Vierordt heran.

Absorptionsspektroskopie benützten zuerst Bahr und Bunsen¹³ zu quantitativen Bestimmungen.

Der Vergleich erfolgte nicht auf Grunde von Lichtintensitätsregelung, sondern mit Hilfe von Konzentrationsänderung. Lichtintensitätsänderung benützten zuerst Govi und Vierordt. Bei dem Spektralapparat von Govi befanden sich vor dem Spalt zwei Prismen übereinander, die das aus zwei Quellen kommende Licht auf eine halbdurchsichtige Platte projizierten. Ein schmaler Spalt diente dazu um das zur Untersuchung geeignete Gebiet vom übrigen Spektrum zu separieren. Die gleiche Lichtintensität wurde durch geeignete Regelung der Entfernungen der Lichtquellen gesichert. Govi benützte seine Apparatur jedoch nur zu physikalischen Messungen.¹⁴ Später trat er gegenüber Vierordt mit Prioritätsansprüchen auf.¹⁵ Diese waren jedoch ganz unberechtigt, da es zweifellos ist, dass zu analytischen Zwecken eine derartige Apparatur zuerst Vierordt konstruierte und benützte.

Bei Vierordts erstem Apparat bestand der Spalt aus einem unteren und oberen Teil. Die Breite beider konnte durch eine Mikrometerschraube geregelt werden. Vor dem Spalt setzte er einen planparallelen Glastrog, den er bis zur Hälfte mit der zu untersuchenden Lösung füllte. Ein Teil des aus einer Petroleumlampe kommenden Lichtes durchschritt die Lösung und den unteren Spalt, der andere Teil pflanzte sich über die Lösung und durch den oberen Spalt durch. Das durch das Fernrohr betrachtete spektrale Sehfeld gab somit im oberen Teil das reine Spektrum, im unteren Teil das durch das vorgelegte Medium veränderte Spektrum der Lichtquelle. Bei gleicher Spaltbreite war das Spektrum des Lichtes, das durch die Lösung kam, natürlich dunkler. Durch Regelung der entsprechenden Spaltbreite machte er die beiden Spektren gleich. Die Regelung der Spaltbreite erfolgte durch eine Trommel, die gemäss der Durchlassung in 100 Teilen eingeteilt war. Die zu den einzelnen Durchlassungswerten gehörenden Extinktionswerte gab er tabellarisch an, mit Hilfe dieser konnte man leicht die Konzentrationen ermitteln. Um das Spektrum auf das gewünschte Gebiet zu verengen wandte er in dem Okularrohr verschiebbare Blendungen an, welche ausser den zu untersuchenden, sämtliche Teile des Spektrums abblendeten. Vierordt bestimmte derart Permanganat, Chromat, Kupferammoniak, Fuchsin, Blutfarbstoff und weitere Substanzen¹⁶ (1870).

Um den durch einseitige Regelung der Spalte hervorgerufenen Fehler, nämlich dass dadurch nicht nur die Lichtintensität, sondern auch im gewissen Masse die Qualität des Lichtes geändert wird, zu beseitigen, konstruierten Glan,¹⁷ weiterhin zu gleicher Zeit Hüfner¹⁸ Photometer bei denen nicht durch Spaltregelung, sondern durch Polarisierung die Lichtintensitäten geregelt wurden.

Bis zu 1880 verfügte also die analytische Chemie über beide Typen der Photometer (Spaltregelung und Polarisierung) aus denen dann alle weitere Apparatypen abstammten.

Zur lichtelektrischen Auswertung soll Berg das erste Patent im Jahre 1911 erhalten haben.¹⁹

BIOGRAPHISCHE DATEN

- Bahr, Jöns Fridrik (1815–1875): Adjunkt an der Universität Upsala.
 Beer, August (1825–1863): Professor der Mathematik an der Universität Bonn.
 Bougouer, Pierre (1698–1758): französischer Astronom und Mathematiker.
 Bunsen, Robert Wilhelm (1811–1899): Professor der Chemie an der Universität Heidelberg.
 Duboscq, Jules (1817–1886): Inhaber einer optischen Werkstätte zu Paris.
 Glan, Paul (1846–1898): Professor an der Universität Berlin.
 Govi, Gilberto (1826–1889): Physiker, Professor der Physik an den Universitäten in Florenz, Turin und Neapel.
 Heine, Carl (1808–?): Direktor von Berg- und Hüttenwerken in Böhmen.
 Herapath, Thornton John (1830–1858): Chemiker in der Industrie in England u. Südamerika.
 Hüfner, Carl Gustav (1840–1908): Professor der organischen und physiologischen Chemie an der Universität Tübingen.
 Jacquelin, Augustin (1804–1885): Chemiker in der Industrie in Frankreich.
 Lambert, Johann Heinrich (1728–1777): Zuerst Buchhalter, dann Hauslehrer, endlich Oberbaurat zu Berlin.
 Müller, Alexander (1828–1906): Professor an der höheren Gewerbeschule zu Chemnitz, nachher Professor der Agrikulturchemie an der Universität Stockholm.
 Vierordt, Carl (1818–1884): Arzt, Professor der Physiologie an der Universität Tübingen.

Summary—A historical account of the earliest colorimetric and photometric determinations is presented.

Résumé—L'auteur présente un compte-rendu historique des dosages colorimétriques et photométriques les plus récents.

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UV SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF SELENIUM WITH *o*-PHENYLENEDIAMINE*

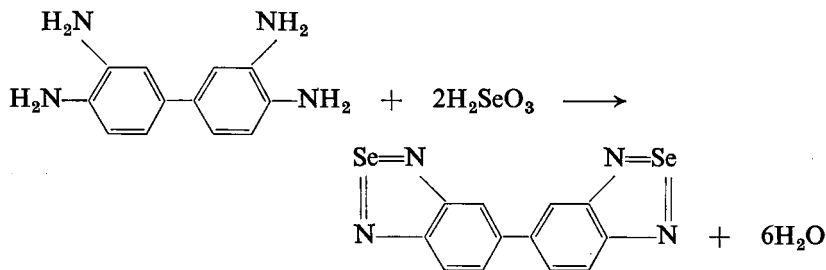
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(Received 14 March 1960)

Summary—3:3'-Diaminobenzidine is an excellent reagent for selenium and the semi-molecule of the reagent, *o*-phenylenediamine, is found to be even better. This forms piaselenol with selenous acid over the pH range of 1.5 to 2.5, which may be extracted with toluene. From the absorbance at 335 $m\mu$ of the toluene extract, selenium is determined. Of many different ions tested only iron^{III}, tin^{IV} and iodide ions interfere. But iron^{III} can be masked with EDTA.

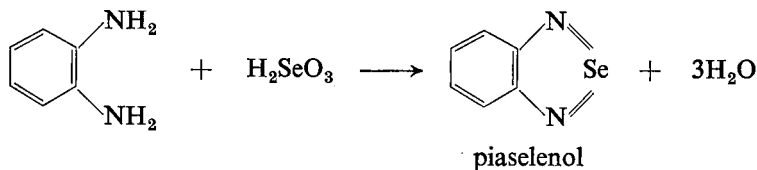
INTRODUCTION

A SELECTIVE colorimetric reagent for selenium^{IV}, 3:3'-diaminobenzidine, was first introduced by Hoste and Gillis.^{1,2} The reagent forms an intense yellow product, piaselenol, with selenium in an acidic medium. Cheng³ recently reported that the piaselenol could be extracted with toluene between pH 6 and 7, and the quantity of selenium could be determined from the absorbance at 420 $m\mu$. The following reaction scheme was presented:



The functional group of 3:3'-diaminobenzidine reacting with selenium is the diamine at the ortho position. The semi-molecule of the reagent, *o*-phenylenediamine, could also react with selenium.

Hinsberg⁴ described in 1889 the reaction of *o*-phenylenediamine with selenium^{IV} as follows:

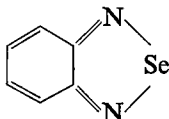


* Read at the 8th annual meeting of Japan Analytical Chemistry Society held in Okayama, September 1959.

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Piaselenol was easily prepared by mixing the aqueous solutions of *o*-phenylenediamine hydrochloride and selenous acid. It was recrystallised from the alcoholic solution as white needles which melt at 76°. He also stated that aromatic ortho-diamine derivatives could react with selenium but that the aromatic meta- or para-diamines and the aliphatic diamines could not.

According to Luzzati⁵ the structural formula was found by X-ray analysis to be as follows:



In this paper, the determination of selenium was studied with *o*-phenylenediamine as in the procedure described by Cheng³ for 3:3'-diaminobenzidine.

REAGENTS AND APPARATUS

o-Phenylenediamine hydrochloride solution: 0.2% aqueous solution, freshly prepared, although the solution could be stored for a few days in a refrigerator.

Standard selenium solution: 1.4053 g SeO₃ dissolved in 1 litre of water (1.001 mg of Se in 1 ml). A Se solution 1.001 µg per ml was prepared by diluting the stock solution.

Standard piaselenol solution: 43.5 g piaselenol dissolved in 250 ml toluene. A piaselenol solution, 3.48 µg per ml (as selenium, 1.5 µg) was prepared by diluting the stock solution with toluene.

Formic acid: 80% and 2.5M.

EDTA solution: 0.1M.

Other reagents were of analytical reagent grade.

Shimadzu Model QB-50 spectrophotometer with 1-cm quartz cell.

Horiba Model M-3 Glass-electrode pH meter.

EXPERIMENTAL AND DISCUSSION

Spectral properties

An aliquot containing 25 µg of selenium was placed in a 100-ml beaker. The solution was diluted to approximately 50 ml with water after adding 2 ml of 2.5M formic acid. The pH was adjusted to between 2 and 3. Two ml of 0.2% *o*-phenylenediamine was added to the solution, and it was then allowed to stand for 2 hours. The absorbance curves of this solution and of a blank without selenium were measured. After the solutions were neutralised with 7M ammonium hydroxide to a pH between 6 and 7, the absorbance curves were measured again (Fig. 1).

The same maximum at 335 mµ was found in the absorbance curves of those different pH solutions containing 25 µg of selenium. The above-mentioned solutions were transferred into 125-ml separatory funnels and exactly 10 ml of toluene were added to each. The funnels were shaken vigorously for 30 sec, and the toluene portions were centrifuged for a few min. Their absorbance curves were measured over the range of 300-400 mµ (curves 1, 2, 3 and 4 in Fig. 2). The absorbance curve of the standard piaselenol solution was also measured (curve 5 in Fig. 2).

The curves containing selenium have the same absorption maximum at 335 mµ. This result indicates the formation of piaselenol.

Time required for the formation of piaselenol

On the toluene extract, curve 1 in Fig. 3 shows that at pH 1.8 a constant absorbance value was obtained after standing for 30 min at room temperature. Curve 2 shows

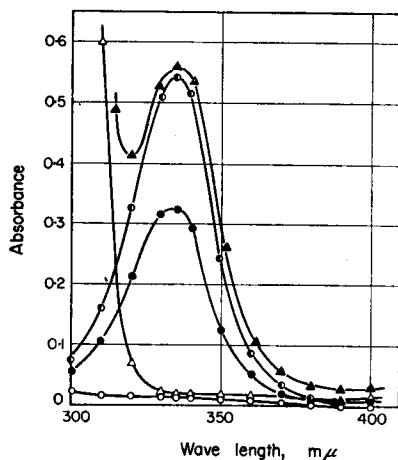


FIG. 1.—Absorbance curves of aqueous solution.
 ○ *o*-phenylenediamine in water at pH 2-3. (Curve 1)
 ● 25 μg of Se in 50 ml of water at pH 2-3. (Curve 2)
 △ *o*-phenylenediamine in water at pH 6-7. (Curve 3)
 ▲ 25 μg of Se in 50 ml of water at pH 6-7. (Curve 4).
 Water as blank.

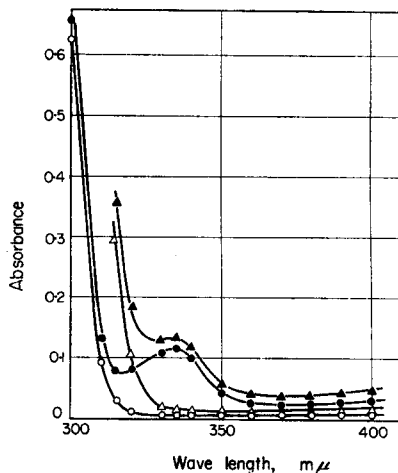


FIG. 2.—Absorbance curves of toluene solution.
 ○ *o*-phenylenediamine in toluene at pH 2-3. (Curve 1)
 ○ 25 μg of Se in 10 ml of toluene at pH 2-3. (Curve 2)
 △ *o*-phenylenediamine in toluene at pH 6-7. (Curve 3)
 △ 25 μg of Se in 10 ml of toluene at pH 6-7. (Curve 4)
 ● piaselonol (15 μg of Se) in toluene. (Curve 5).
 Toluene as blank.

that at pH 0.05 (adjusted by 2*N* hydrochloric acid instead of formic acid) a better value was not obtainable even after standing for 4 hours.

On standing for 24 hours the aqueous solution turned deep brown, because the reagent was decomposed by air.

Though heating hastens the formation of piaselonol, it is not recommended under ordinary conditions, because the reagent decomposes at the same time.

Effect of pH

Piaselenol was formed only in acid medium. After 2 hours to allow the formation of piaselenol at various pH values, 10 ml of toluene were added. The absorbances of toluene extracts were measured at 335 m μ (Fig. 4). Between pH 1.5 and 2.5, a constant value was obtained.

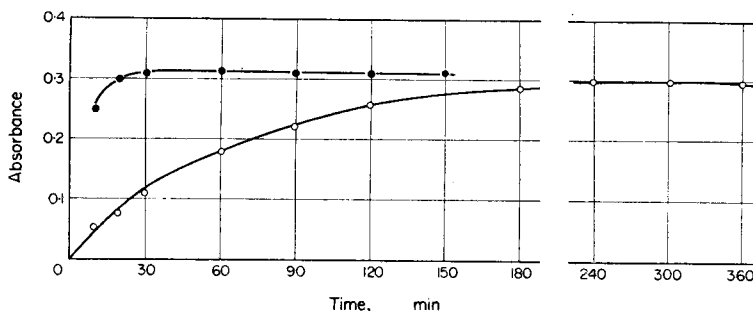
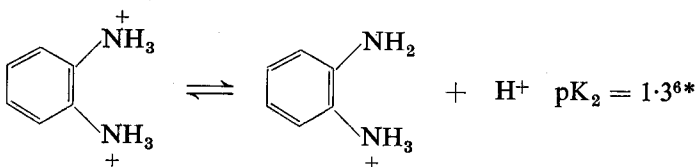
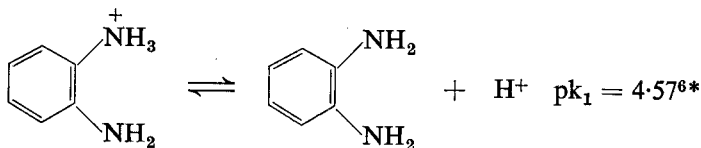


FIG. 3.—Effect of time of standing on maximum formation of piaselenol.

● 15 μ g of Se in 10 ml of toluene pH 1.8. (Curve 1)

○ 15 μ g of Se in 10 ml of toluene pH 0.05. (Curve 2)

The following explanation may be proposed for this phenomenon. In the acid medium, selenous acid and *o*-phenylenediamine behave as follows:



At pH below 2.6, selenous acid will be predominantly in the undissociated form, whereas *o*-phenylenediamine will be in the singly protonated form. Below pH 1.3, *o*-phenylenediamine exists in the doubly protonated form. Since the optimum reactivity observed is in the range of pH 1.5 ~ 2.5, we can conclude that the reactive species are the undissociated selenous acid and the singly protonated *o*-phenylenediamine.

Solvent extraction

In each extraction, 10 ml of toluene was used for approximately 50 ml of the solution containing selenium. The toluene extract from the acid medium was colourless, but that from the medium neutralised with ammonium hydroxide was coloured pale pink. When the absorbance curve of the neutralised solution was measured, a new absorption

* In 50% alcoholic solution.

maximum appeared at $420\text{ m}\mu$, which influenced the absorbance at $335\text{ m}\mu$. The absorbances at $335\text{ m}\mu$ and $420\text{ m}\mu$ of the reagent alone were measured over various pH ranges. Though the absorbance at $420\text{ m}\mu$ was not directly connected with pH, it was related closely to the absorbance at $335\text{ m}\mu$ (Fig. 5). After the formation of piaselelol, the aqueous solution was adjusted to various pH values and extracted with toluene. The absorbance at $335\text{ m}\mu$ was measured and corrected by the value at $420\text{ m}\mu$ according to Fig. 5. The results are shown in Fig. 6.

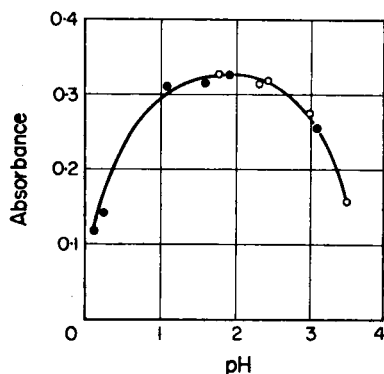


FIG. 4.—Effect of pH on colour development of piaselelol.

○ formic acid. ● hydrochloric acid.

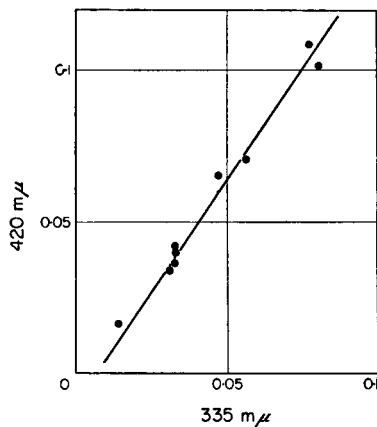


FIG. 5.—Correction curve for colour development in an alkaline medium.

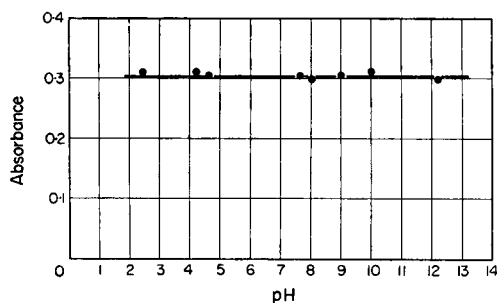


FIG. 6.—Effect of pH on extraction of piaselelol with toluene. $15\text{ }\mu\text{g}$ of Se in 10 ml of toluene.

From Fig. 6, a constant value was obtained whether or not the aqueous solution was neutralised before the extraction. This implies that the neutralisation is not essential and that the extraction can be carried out without it after standing for 2 hours.

Back extraction of standard piaselelol with solution of varying pH

Ten ml of standard piaselelol solution were added to 50 ml of each of the aqueous solutions, adjusted to various pH values. The back extraction was carried out by the same procedure as the extraction. The absorbances at $335\text{ m}\mu$ were plotted against pH (Fig. 7). The absorbances are constant from pH 0 to 13 and this indicates that the neutralisation before the extraction is not necessary. The recoveries are about 97%

and the absorbance values are somewhat higher than those of Fig. 6. The extractability from the solution in which piaselelol is formed is about 95%.

Procedure

Place an aliquot containing not more than 30 μg of selenium in a 100-ml beaker. Dilute to approximately 50 ml with water after adding a few ml of 80% formic acid. Adjust the pH to between 1.5 and 2.5. Add 2 ml of 0.2% *o*-phenylenediamine solution and set aside for 2 hr at room

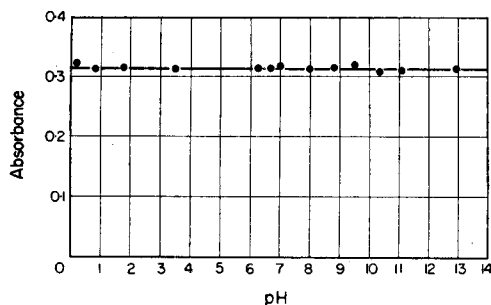


FIG. 7.—Back extraction of standard piaselelol with solutions of varying pH.

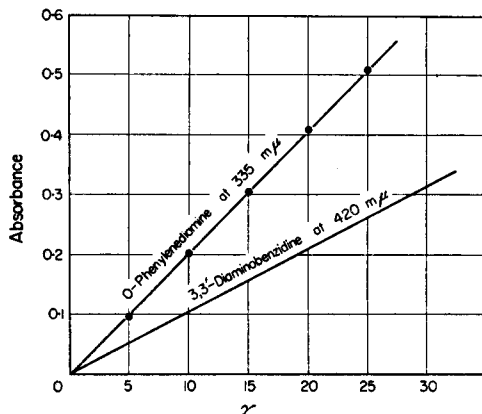


FIG. 8.—Calibration curves for selenium.

temperature. Transfer to a 125-ml separatory funnel, add exactly 10 ml of toluene, and shake vigorously for 30 sec. Centrifuge the toluene portion for a few min. Separate, and determine the absorbance at 335 $m\mu$, using a reagent as blank.

The calibration curve follows Beer's law up to 25 μg of selenium per 10 ml of toluene. For comparison with 3,3'-diaminobenzidine, the calibration curve at 420 $m\mu$ is also shown in Fig. 8.

Interference studies

The effects of the presence of many different ions are summarised in Table I. 15 μg of selenium were added to aqueous solutions containing different salts. The determination was made by the above-mentioned procedure.

Aluminium, ammonium, antimony, arsenic, barium, cadmium, calcium, chromium cobalt, copper, lead, magnesium, manganese^{II}, nickel, potassium, sodium and zinc ions do not interfere. An aqueous solution containing bismuth should be adjusted to pH 0, because the ion precipitates as bismuthyl hydroxide even at pH 1. Thus in the presence of bismuth, the pH must be very low to obtain the correct value for selenium. Iron^{III} and tin^{IV} also interfere.

Chloride, nitrate, sulphate, phosphate and tartrate ions do not interfere, but iodide ion disturbs the formation of piaselenol.

The interference of iron^{III} may be effectively eliminated by the addition of EDTA to the sample solution³. The excess of EDTA may deposit in acid solution, but the

TABLE I. ABSORBANCES OF 15 μg OF SELENIUM IN PRESENCE OF VARIOUS SALTS

Salt, 0.1M	ml	Absorbance	Salt, 0.1M	ml	Absorbance	
CuSO ₄	1	0.310	(NH ₄) ₂ SO ₄ *	2g	0.315	
	5	0.310		5g	0.314	
	30	0.312		5	0.307	
ZnSO ₄	1	0.312	Ni(NO ₃) ₂	30	0.306	
	5	0.308	MnSO ₄	30	0.304	
	30	0.305	KAl(SO ₄) ₂	30	0.298	
MgCl ₂	1	0.311	KCr(SO ₄) ₂	30	0.306	
	5	0.299	SbOC ₆ H ₄ O ₆	30	0.303	
	30	0.302	CaCl ₂	30	0.305	
Pb(NO ₃) ₂	5	0.305	Ba(NO ₃) ₂	30	0.302	
	30	0.305	CdCl ₂	5	0.310	
	5	0.313	30	0.308		
Co(NO ₃) ₂	5	0.162	CdSO ₄	30	0.306	
	BiCl ₃	30	0.283	KNaC ₄ H ₄ O ₆	30	0.301
		10		(NH ₄) ₂ HPO ₄	30	0.297
			AsCl ₃	30		
SnCl ₄	30	0.004	FeNH ₄ (SO ₄) ₂	5	0.043	
KI	30	0.044				

* Added as solid.

determination can be carried out by extraction and centrifugation without any difficulty.

Acknowledgement—The authors wish to express their sincere thanks to Professor Koichi Emi for his encouragement.

Zusammenfassung—3,3'-Diaminobenzidin ist ein ausgezeichnetes Reagens auf Selen; das Semimolekül, o-Phenylendiamin, wurde als noch besser gefunden. Es bildet Piaseleol mit seleniger Säure im pH-Bereich 1.5–2.5. Dieses kann mit Toluol extrahiert werden. Durch Messung der Absorption des Extraktes bei 335 $m\mu$ kann das Selen bestimmt werden. Von vielen untersuchten Ionen stören nur Fe(III), Zinn(IV) und Jodid. Eisen kann mit EDTA maskiert werden.

Résumé—La 3-3' diaminobenzidine est un excellent réactif du sélénium, et la semi-molécule du réactif, l'o-phénylènediamine se trouve même être meilleure. Celle-ci forme avec l'acide sélénieux le piaseleol dans le domaine de pH 1,5–2,5, et celui-ci est extrait par le toluène. L'absorption du corps extrait par le toluène à 335 $m\mu$, permet de doser le sélénium. Parmi les nombreux ions essayés, seuls le fer(III), l'étain(IV) et l'iodure gênent. Le fer(III) peut être dissimulé par l'EDTA.

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PRELIMINARY COMMUNICATION

Precipitation of metal cupferrates from homogeneous solution

(Received 23 June 1960)

THE ammonium salt of nitrosophenylhydroxylamine, known as cupferron, is one of the most important and versatile reagents used in analytical separations. Although more than fifty years have passed since its introduction by Baudisch¹, considerable interest still centres around its use, as shown by recent publications. The method of precipitation from homogeneous solution has not yet been applied to cupferron precipitates.

Heyn and Brauner² devised a method for the generation of α -nitroso- β -naphthol from β -naphthol and sodium nitrite in acetic acid medium. This method of generating the precipitant from an organic parent compound by nitrous acid appeared to be appropriate for the synthesis of cupferron also. Copper, iron and titanium have been determined by this method.

When acidic solutions of appropriate cations are mixed with solutions of β -phenylhydroxylamine and sodium nitrite, the cupferrate of the metal is generated and precipitated. Cupferron itself, however, is not precipitated in the reaction mixture and the reagents produce the cupferrate directly. This is an advantage because cupferron is not very soluble in water, and in the conventional procedure it precipitates along with the cupferrate. Moreover, cupferron decomposes in acidic medium, in which the precipitation is almost universally carried out. The decomposition products tend to contaminate the precipitate. In the present method the precipitate is obtained from water-soluble substances which are not precipitated under the conditions of precipitation. It is only necessary to filter off the precipitate after digestion, if desired. The precipitates thus obtained are not curdy, and are more easily filtered than those obtained by direct precipitation.

The β -phenylhydroxylamine required for precipitation can be prepared easily³ and then recrystallised from benzene. This substance is not very stable at room temperature, but can be stored in a refrigerator for more than a month.

For carrying out the precipitation, the cation solution is diluted to about 100 ml and cooled well in an ice-bath. Phenylhydroxylamine and sodium nitrite are also dissolved separately and cooled. When the solutions are cold (0–5°), phenylhydroxylamine is filtered, and the clear solution is added to the cation solution. The mixture is stirred and sodium nitrite solution is added quickly. Precipitation begins after a few sec and stirring is continued for about 5 min. The precipitate is filtered off after 15 min, washed with 1:20 HCl, followed by 1:3 NH₄OH, and finally with water. It is then dried, ignited and weighed as oxide.

In order to establish the composition of the precipitate and to prove its identity with the precipitate obtained with cupferron, C, H and N analyses were run, which showed good agreement with the theoretical values.

Further proof of the identity of the precipitates was obtained by X-ray diffraction patterns, which proved to be identical with those obtained from the corresponding cupferrates prepared by the conventional procedures.

Work is in progress with a number of cations.

Summary—A method has been devised to synthesise metallic cupferrates in homogenous solutions. Sodium nitrite and β -phenylhydroxylamine solution are added to a cold acidic solution of the cations and generate and precipitate the metallic cupferrate. Good results have been obtained for iron, titanium and other metals. This method produces more easily filtered precipitates than are obtained by direct precipitation.

Zusammenfassung—Eine Methode zur Fällung von Metallkupferonaten aus homogener Lösung wurde beschrieben. Natriumnitrit und 2-Phenylhydroxylaminlösung werden zur sauren, kalten Lösung des Metallions zugegeben und erzeugen so den Niederschlag. Gute Ergebnisse wurden bei Eisen, Titan und anderen Metallen erzielt. Die Methode führt zu Niederschlägen die leichter filtrierbar sind, als die durch direkte Fällung erhaltenen.

Résumé—Les auteurs ont établi une méthode de synthèse des cupferrates métalliques en solution homogène. Du nitrite de sodium et une solution de β phénylhydroxylamine sont ajoutés à une solution acide froide des cations, produisent et précipitent le cupferrate métallique. De bons résultats ont été obtenus pour le fer, le titane et d'autres métaux. Cette méthode produit des précipités plus facilement filtrables que ceux obtenus par précipitation directe.

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SHORT COMMUNICATIONS

The ultraviolet spectra of some inorganic solids*

(Received 15 February 1960)

Summary—The ultraviolet spectra of nine sulphates, three chromates, and two nitrates have been investigated in the solid state using the KBr disc technique. The sulphate samples show absorption in the 260 $m\mu$ and 300 $m\mu$ regions; the chromates at both 270 $m\mu$ and 370 $m\mu$; and the nitrates absorb slightly in the 290 $m\mu$ region. Qualitative identification of these ions in artificial samples has been demonstrated.

INTRODUCTION

THE measurement of ultraviolet spectra of solutions has long been a recognised analytical tool, especially for the characterisation and analysis of organic samples. Similar investigations involving inorganic materials have not been as abundant and many of the inorganic systems examined have involved co-ordination complexes in which the ligands are organic in nature. In attempting to identify or assign observed absorption bands, it is frequently of value to study the role of the solvent. In such studies it is convenient, even necessary, to have the corresponding spectrum of the "anhydrous" material.

The ultraviolet spectra of solids can be obtained by studying single crystals, by examining the powder sublimed or otherwise deposited onto a quartz plate, or by measuring the optical properties of a compacted sample in which the absorbing substance has been diluted with another material which is transparent in the particular spectral region being investigated. This latter method is the basis of the widely used potassium bromide disc technique of Stimson and O'Donnell¹ which, although originally proposed for both I.R. and U.V. work, has been most extensively employed in the infrared range with organic samples.

This investigation was undertaken, therefore, to determine the applicability of the KBr disc technique to the study of simple inorganic compounds in the 220–400 $m\mu$ region.

EXPERIMENTAL

Apparatus

Spectrophotometer: A line-operated Beckman spectrophotometer, Model DU, was used for all absorbance measurements.

Sample die: A standard Perkin-Elmer KBr evacuable die, part number 021-106, was used for all disc preparations. Sample discs thus prepared were approximately 0.5 inch in diameter.

Sample holders: Matched 1-cm silica cells were used for all solution measurements. For the solid samples a special holder was constructed. This holder accommodates four discs at one time and replaces the usual cuvette holder in the DU without modification of the cell compartment. Construction details for this holder have been described by Waggoner².

Reagents

Potassium bromide: Reagent-grade potassium bromide was ground to approximately 100-mesh in an agate mortar and then dried in a vacuum oven at 100° for 24 hr before disc preparation. Blanks of equal weight were made from this same material to be used with the disc samples.

Other reagents: All other reagents were analytical grade and were used without further purification. Distilled water was used in the preparation of all solutions and as a blank for all solution measurements.

Sample preparation

Solutions: Aqueous solutions were prepared by standard volumetric techniques using the same reagents as were employed in making the solid samples. The concentrations finally employed varied considerably from solute to solute but were generally chosen after examination of several different concentrations.

Solid samples: Both the potassium bromide and the sample compounds were separately ground in an agate mortar to approximately 200-mesh particle size before being pressed. For the preparation of a disc, the appropriate weight of potassium bromide was taken and the desired weight of sample added directly, its weight being determined by difference from the weight of the mixture. The mixture was then thoroughly blended by further grinding together, placed in the die, and pressed under

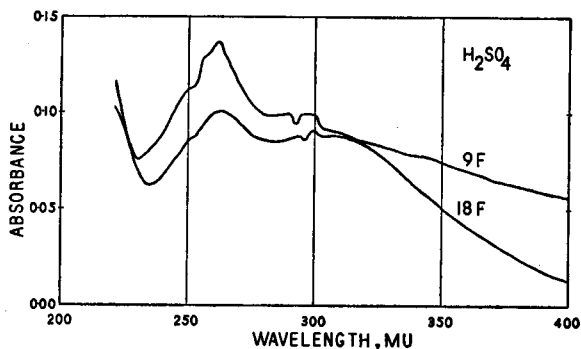


FIG. 1.—Absorbance curves for sulphuric acid solutions.

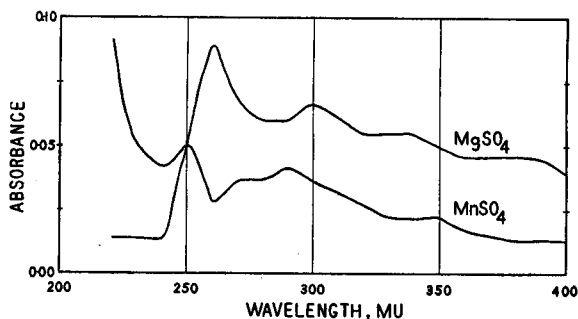


FIG. 2.—Absorbance curves for Mn^{II} and Mg sulphate solutions.

approximately 25,000 psi for 3 min. Discs thus prepared were quite transparent and faintly coloured if the sample material was coloured. For all sulphate samples, the final composition of the discs was 0.1 mg of metal sulphate in 500 mg of KBr; for the chromate samples, 0.2 mg of metal chromate in 400 mg of KBr. The nitrate samples were more concentrated, containing 2.1 mg of $Ni(NO_3)_2 \cdot 6H_2O$ and 1.7 mg $Co(NO_3)_2 \cdot 6H_2O$, respectively, each in 400 mg of potassium bromide.

DISCUSSION

The absorbance curves obtained with aqueous solutions of sulphates were rather disappointing. Sulphuric acid samples (9F and 18F) gave the spectra shown in Fig. 1. The more prominent peak occurs at 260 $m\mu$ and the smaller shoulder at 290–300 $m\mu$.

With the solutions of metallic sulphates the spectra varied considerably in appearance. Fig. 2 shows the curves obtained with $MnSO_4 \cdot H_2O$ (ca. 5F) and $MgSO_4 \cdot 7H_2O$ (ca. 5F) and Fig. 3 those for $CoSO_4 \cdot 7H_2O$ (ca. 0.5F) and $NiSO_4 \cdot 6H_2O$ (ca. 0.5F). The other salts examined (Cd^{++} , K^+ , VO^{++} , UO_2^{++}) gave curves which generally decreased in absorbance as the wavelength increased, with no significant maxima.

Bastian, Weberling and Palilla³ have reported that a solution of $\text{Fe}_2(\text{SO}_4)_3$ has a peak at 300–305 $m\mu$. Buck, Singhadeja and Rogers⁴ found a peak at 267 $m\mu$ for a solution of NiSO_4 in dilute KCN.

The absorbance curves obtained with 0.001*F* aqueous chromate solutions are given in Fig. 4. The two maxima occur at approximately 270 $m\mu$ and 370 $m\mu$. These results are in good agreement with the results reported by Schaumann⁵, Davies and Prue⁶ and Griffiths, Lott and Symons⁷, all of whom reported peaks at 270 $m\mu$ and 370 $m\mu$.

Inconclusive results were obtained with the two nitrate solutions examined. A slight increase in absorbance in the 300 $m\mu$ region was noted but it was not sufficiently pronounced to permit a definite assignment. Past workers, notably Morton and Riding⁸, von Halban⁹, Buck, Singhadeja and Rogers⁴, have reported that the nitrate ion absorbs in solution at 300–302 $m\mu$.

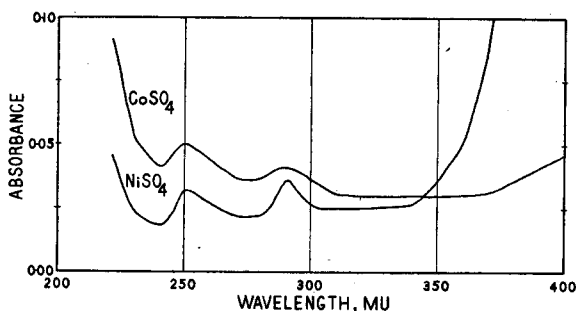


FIG. 3.—Absorbance curves for Co^{II} and Ni^{II} sulphate solutions.

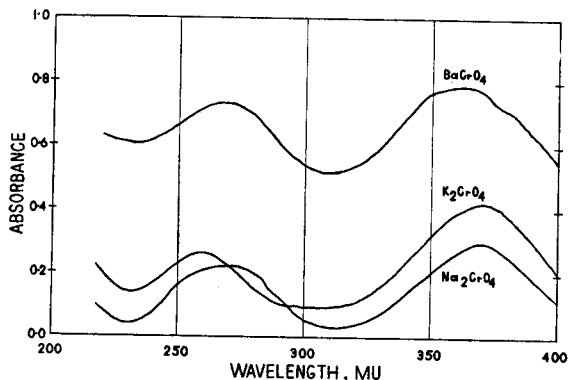


FIG. 4.—Absorbance curves for chromate solutions.

Figs. 5 and 6 show the absorbance curves obtained with the metallic sulphates in potassium bromide discs. In every case, a maximum or at least a levelling effect, was noted in both the 260 $m\mu$ and 300 $m\mu$ regions.

The curves obtained with the three solid chromate samples are shown in Fig. 7. Maxima at approximately 275 and 375 $m\mu$ are evident. Griffiths, Lott and Symons⁷ have reported that crystals of BaCrO_4 and K_2CrO_4 absorb at 275–280 $m\mu$ and at 360–375 $m\mu$.

The curves obtained with the two solid nitrate samples examined are shown in Fig. 8. A maximum at 280–295 $m\mu$ was reported by Maslakowicz¹⁰ for crystalline KNO_3 . Schaumann⁵ reported that crystals of NaNO_3 absorbed at 2915 Å.

In order to test the practicality of utilising this technique for the qualitative detection of individual inorganic ions, two synthetic mixtures were prepared and examined. The first mixture contained 0.4 mg CdSO_4 and 0.2 mg K_2CrO_4 in 400 mg KBr. The absorbance curve for this mixture is shown in Fig. 9 with the tentative assignments indicated. The second mixture contained 0.4 mg K_2SO_4 , 0.2 mg K_2CrO_4 and 0.9 mg KNO_3 in 400 mg KBr. The curve for this mixture is shown in Fig. 10, also with the tentative assignments as to the causes of the maxima noted. In both of these mixture curves, no explanation is offered for the extraneous peaks.

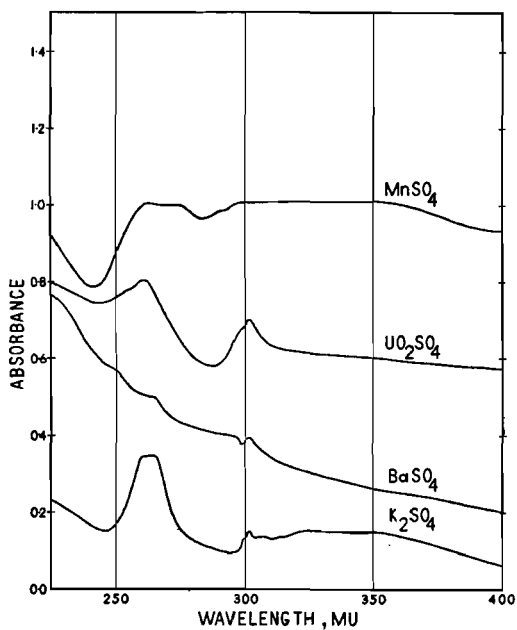


FIG. 5.—Absorbance curves for sulphates in potassium bromide.

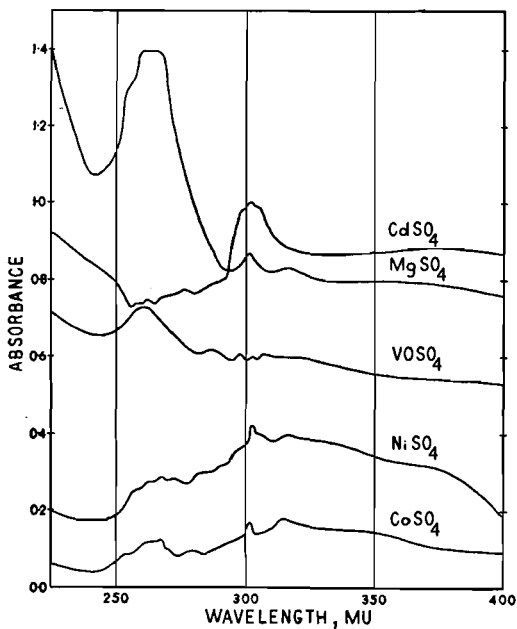


FIG. 6.—Absorbance curves for sulphates in potassium bromide.

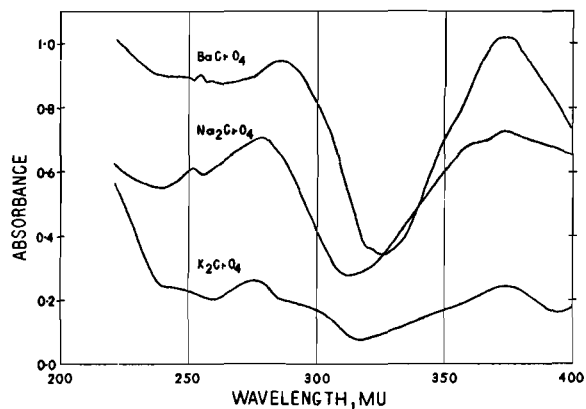


FIG. 7. Absorbance curves for chromates in potassium bromide.

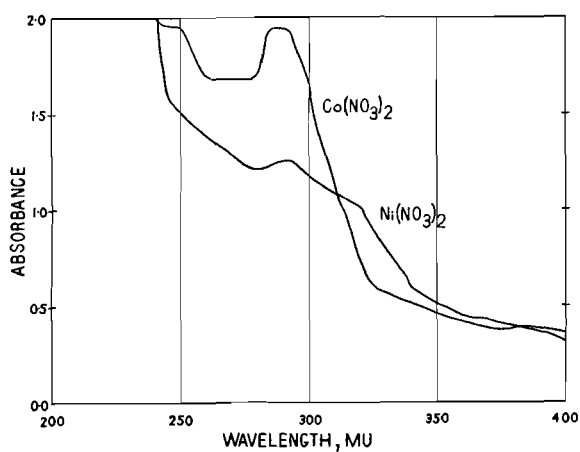


FIG. 8. Absorbance curves for nitrates in potassium bromide.

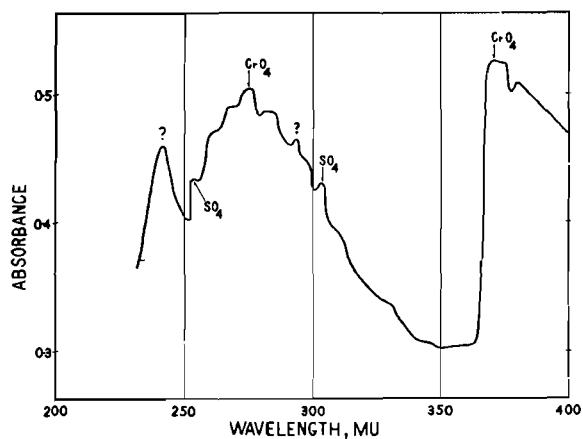


FIG. 9. Absorbance curve for sulphate-chromate mixture in potassium bromide.

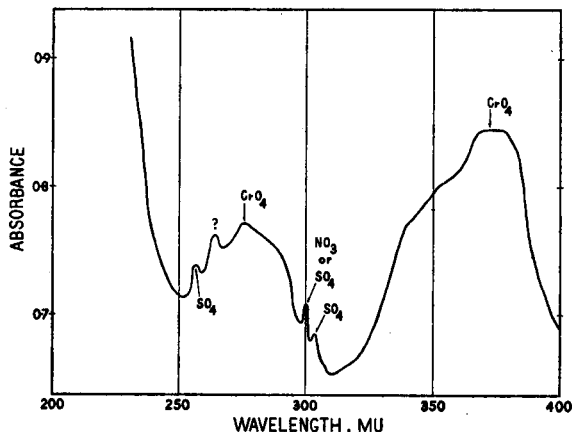


Fig. 10. Absorbance curve for sulphate-chromate-nitrate mixture in potassium bromide.

CONCLUSIONS

On the basis of this preliminary study it appears that the potassium bromide method of sampling inorganic materials for examination in the ultraviolet spectral region does give promising results. Solvent effects are eliminated and the procedure is more rapid than those employed with single crystal samples. The existence of definite absorption bands, apparently attributable to specific ionic groups, recommends this technique to the qualitative analysis of solid mixtures.

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Zusammenfassung—Das Ultraviolettenspectrum von neun Sulfaten, drei Chromaten und zwei Nitraten in festem Zustande wurde untersucht, unter Verwendung der Scheibentechnik. Die Sulfatproben wiesen Absorption im Bereiche 260 und 300 $m\mu$, die Chromate sowohl bei 270 und 370 $m\mu$. Die Nitrate absorbierten bei 290 $m\mu$, aber nur sehr wenig. Der qualitative Nachweis dieser Substanzen in kunstlichen Probemischungen wurde demonstriert.

Résumé—Les spectres ultra-violetts de neuf sulfates, trois chromates et deux nitrates à l'état solide ont pu être étudiés par la méthode du disque de KBr. Les échantillons de sulfate montrent une absorption dans les régions 260 et 300 $m\mu$; les chromates à la fois à 270 et à 370 $m\mu$; et les nitrates absorbent faiblement à 290 $m\mu$. L'identification qualitative de ces ions dans des échantillons artificiels a été démontrée.

A new spot test for auric gold with *N:N'*-di-2-naphthyl-*p*-phenylenediamine

(Received 7 July 1960)

THE alkyl derivatives of *p*-phenylenediamine are widely used in qualitative microanalysis. These compounds, known as Wurster reagents¹, react with some oxidising ions and substances to give intensively coloured compounds of the merquinoidal type. Free halogens², vanadium³, manganese⁴ and copper⁵ are detectable owing to their reaction with dimethyl-*p*-phenylenediamine.

It was found in our laboratory that auric gold and some of the platinum metals—platinum, iridium and ruthenium ions—also oxidise dimethyl-*p*-phenylenediamine to Wurster Red.

In order to find a reagent with more selective analytical properties, we studied the redox behaviour of some alkyl and aryl derivatives of *p*-phenylenediamine. In the course of this investigation we found that *N:N'*-di-2-naphthyl-*p*-phenylenediamine is a highly selective and sensitive reagent for auric gold.

EXPERIMENTAL

Reagent solution: a saturated acetone solution of *N:N'*-di-2-naphthyl-*p*-phenylenediamine (an Eastman Organic Chemical product purified by recrystallisation in an acetone–water mixture).

Gold solution: $\frac{1}{1000}$ *M* HAuCl₄ standard solution prepared by diluting 1 g of HAuCl₄·3H₂O (a B.D.H. product) in 500 ml of H₂O containing 2.5 ml of conc HCl.

Procedure

One drop of the neutral or slightly acid (pH value 3–8) test solution is mixed in a depression of a white spot plate with one or two drops of a freshly prepared solution of the reagent. In the presence of auric gold a red-brown precipitate or coloration is formed. The reagent solution itself is faintly yellow-brown; hence with small amounts of auric gold, the colour should be compared with that of a blank test.

Limit of identification: 0.1 μg of gold.

Limit of dilution: 1:500,000.

Interfering ions

Only iron^{III}, cerium^{IV} and osmium^{VIII} cations interfere with the reaction. The interference of cerium^{IV} and iron^{III} ions can easily be eliminated by the addition of some crystals of potassium fluoride, which precipitate Ce^{IV} and mask Fe^{III}. In the presence of the extremely volatile osmium tetroxide, the solution should be boiled before the test.

Most of the anions and even most of the oxidising anions do not interfere with this test. Nevertheless, the ferricyanide and permanganate ions oxidise the reagent similarly to auric gold. Also sulphite and sulphide ions prevent the reaction between gold ions and the reagent owing to their reducing action.

These interferences can be prevented as follows:

(i) In the presence of ferricyanide or of sulphite ions, the test solution should be boiled with H₂O₂ (6%).

(ii) In the presence of permanganate ions, 1 or 2 drops of a 0.1% solution of As₂O₃ and 1 or 2 drops of a 10% solution of Na₂CO₃ (to adjust the pH) should be added.

(iii) The sulphide ions, if present, should be precipitated with zinc carbonate.

Summary—A new selective and sensitive spot test for the detection of auric gold is proposed, based on the redox reaction between the latter and *N:N'*-di-2-naphthyl-*p*-phenylenediamine.

Zusammenfassung—Eine neue selektive und empfindliche Tüpfelprobe für dreiwertiges Gold wurde angegeben. Die Probe beruht sich an die Redoxreaktion zwischen dreiwertiges Gold und *N:N'*-di-2-naphthyl-*p*-phenylenediamine.

Résumé—Un nouvel essai à la goutte sensitif et sélectif pour la détection de l'or(III) est proposé. L'essai est basé sur la réaction d'oxyréduction entre l'or et le N:N'-di-2-naphthyl-*p*-phénylènediamine.

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Interference of iron in the determination of 12-tungstophosphoric acid with tri-*n*-butylamine

(Received 6 July 1960)

In a recent paper on the determination of tungsten as tris(tributylammonium)12-tungstophosphate¹ we mentioned that the presence of iron complicated the analysis. The nature of the complications is now outlined.

EXPERIMENTAL

Reagent and standard solutions were prepared, and tungstophosphate precipitates formed and separated under the same conditions as before, except that 50% more tributylamine was used for precipitations. Unless otherwise indicated, precipitates were left overnight before filtration.

When solutions containing sodium tungstate and disodium hydrogen phosphate were acidified with hydrochloric acid and iron^{II} sulphate and tributylammonium chloride then added, the onset

TABLE I. EFFECT OF IRON SALTS ON PRECIPITATION OF TUNGSTOPHOSPHATE WITH TRIBUTYLAMINE
100 ml of 0.25*N* hydrochloric acid solution contain 200 mg of tungsten^{VI}
and 85 mg of phosphate (PO₄)

	Fe ^{II}				Fe ^{III}		
	25	150	700	1400	25	280	1400
Iron added, <i>mg</i>	25	150	700	1400	25	280	1400
Precipitate obtained at 140°, <i>mg</i>	337	347	357	356	355	354	352
Ignition product (750°), <i>mg</i>	263	266	267	267	267	266	264
Ratio of weights obtained at 140° and at 750°, R ₁	1.28	1.31	1.34	1.33	1.33	1.33	1.33
Iron in ignition product, <i>mg</i>	2.4	3.9	4.9	5.6	5.1	—	5.9
Phosphorus in ignition product, <i>mg</i>	2.6	3.4	(4.1)	3.2	3.2	—	2.8
Tungsten (approx.) in filtrate, <i>mg</i>	0.5	0.5	0.5	0.5	0.5	—	4

of precipitation was usually retarded. As the amount of iron^{II} was increased, the weights of precipitates obtained after drying at 140° increased to a maximum. A much smaller amount of iron^{III} gave a similar result. Ignition products of the heaviest precipitates (Table I) appeared to be Fe₂O₃·P₂O₅·24WO₃ (200 mg of tungsten = 265.9 mg, including 5.1 mg of iron and 2.8 mg of phosphorus), which suggested that the amine had been co-ordinated about the iron ion in the original precipitates. The precipitate obtained in the experiment with 280 mg of iron^{III} was weight-constant from 105°-150° and contained 18.3, 3.57 and 1.75% of carbon, hydrogen and nitrogen, respectively. The corresponding values for [Fe(H₂O)(C₁₂H₂₇N)₃]PW₁₂O₄₀·2H₂O, which might conceivably

represent the composition, are 18.4, 3.63 and 1.79%. The use of very large excesses of the amine increased the weights of precipitates by only 1 mg.

The same general effects were observed when 2:4-dimethylquinoline, 8-hydroxyquinoline or cinchonine replaced tributylamine. The cinchonine complex was weight-constant from 105°-200°.

TABLE II. EFFECT OF VARYING AMOUNTS OF ACID AND PHOSPHATE ON PRECIPITATION OF TUNGSTOPHOSPHATE WITH TRIBUTYLAMINE IN PRESENCE OF IRON SALTS

200.0 Mg of W = 354.7 mg of $[\text{Fe}(\text{H}_2\text{O})(\text{C}_{12}\text{H}_{27}\text{N})_3]\text{PW}_{12}\text{O}_{40}\cdot 2\text{H}_2\text{O}$ (heated at 140°) = 265.9 mg of $\text{Fe}_2\text{O}_3\cdot\text{P}_2\text{O}_5\cdot 24\text{WO}_3$; R_1 , the ratio of these weights, is 1.334.

200.0 Mg of W = 311.5 mg of $(\text{C}_{12}\text{H}_{27}\text{N}\cdot\text{H})_3\text{PW}_{12}\text{O}_{40}$ (heated at 210°) = 258.6 mg of $\text{P}_2\text{O}_5\cdot 24\text{WO}_3$; R_2 , the ratio of these weights, is 1.204.

X is the weight of ignition product in mg.

Hydrochloric acid	Phosphate (PO_4)	Weight of iron ^{III} present, mg											
		25			100			280			700		
N	mg	X	R_1	R_2	X	R_1	R_2	X	R_1	R_2	X	R_1	R_2
0.2	85	267*	1.33										
	425	266†	1.34		264†	1.34		265*	1.33		262*	1.34	
0.5	850				265	1.34		260†	1.34		255†	1.34	
	85				257	1.33					248	1.34	
	425	264†	1.31		265†	1.34		265†	1.34		265†	1.34	
1.0	850	266	1.33		264	1.34		263†	1.34		261†	1.34	
	425										259	1.34	
2.0	850	263	1.28	1.22	260	1.27		263	1.32		264†	1.33	
	1700							251	1.31	1.25	258	1.33	
	850				259	1.26	1.20	259	1.26		251	1.32	1.26
	1700										258	1.27	
											261	1.26	1.20
					Iron ^{II}						Iron ^{II}		
2.0	850				260	1.25	1.20				260	1.25	1.20

* Filtration after 1 hr. All other precipitates were filtered the following day.

† 12-Tungstophosphoric acid used.

analyses for nitrogen and carbon showed that 2.59 molecules of dibasic cinchonine were associated with 12 of tungsten, and the ignition product was apparently $\text{Fe}_2\text{O}_3\cdot\text{P}_2\text{O}_5\cdot 24\text{WO}_3$.

In further experiments with tributylamine (see Table II) the amounts of acid and phosphate were varied. Results, except those indicated by †, relate to a standard solution prepared by *gradually* acidifying a solution containing sodium tungstate and a 10-fold excess of disodium hydrogen phosphate. Additional phosphate, as orthophosphoric acid, and iron salts were added to acidified solutions, the volumes of which were made 100 ml before precipitation.

Although 12-tungstophosphoric acid that had been degraded by means of an excess of sodium hydroxide solution and then re-formed in presence of additional phosphate by slow or rapid addition of acid, gave with tributylamine the weight of precipitate expected for undegraded material,¹ it was now found that *rapidly* acidified solutions of degraded tungstophosphate, to which ferric chloride and tributylamine were then added, gave variable lower weights of precipitates and values of R_1 than *slowly* acidified solutions, which alone gave the results expected for 12-tungstophosphoric acid plus ferric chloride.

With reference to Table II, R_1 values of 1.33–1.34 allied with values of $X < 265$ mg denoted incomplete precipitation of tungsten. This was associated with high concentrations of iron and phosphate and counteracted somewhat by a higher acid concentration. As a rule, supernatant solutions yielded a little more precipitate after further standing. R_2 values of 1.20 for 2*N* hydrochloric acid solutions indicated, however, that tris(tributylammonium)tungstophosphate was the product of reaction. Here, ignition products contained $< 70 \mu\text{g}$ of iron when 100 and 700 mg of iron^{II} were present during precipitation of tungstophosphate but 0.4 and 0.9 mg, respectively, when iron^{III} was used.

A silver reductor column² (length 14 cm, diameter 1 cm) containing 18 g of silver was suitable for reduction of at least 100 mg of iron^{III} in a solution containing 12-tungstophosphoric acid. Fifty ml of sample solution (1*N* hydrochloric acid) and appropriate washings were passed through the reductor, and the acid concentration of the blue effluent, which gradually lost its colour on heating in air, was raised to 2*N* before precipitation and separation of tris(tributylammonium)-tungstophosphate as usual. Two hundred mg of tungsten, alone and in presence of 100 mg of iron, yielded 311.6 ± 0.1 mg of the complex. About 0.4 mg of tungsten found in filtrates was balanced by a little silver chloride in the precipitates.

CONCLUSION

Satisfactory determination of 12-tungstophosphate as the tris(tributylammonium) complex is possible in solutions containing iron^{II}, provided that acid concentration is fairly high. A silver reductor is suitable for reducing iron^{III}. With reference to Table II, determination as the aquopentakis(tributylamine)iron^{III} complex might be feasible if the amounts of phosphate, iron and acid present in the solution before precipitation could be so regulated as to ensure values for R_1 and X of 1.33–1.34 and at least 265 mg, respectively.

When tungsten is precipitated as tungstic acid in presence of iron and phosphate, by digestion with acids and addition of cinchonine,³ contamination with iron may *not* be entirely due to coprecipitation associated with a single precipitation.

Acknowledgement—We thank Dr. R. A. Chalmers of Aberdeen University for recording the thermal behaviour of some precipitates.

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D. H. THOW

Summary—When 12-tungstophosphoric acid reacts with tri-*n*-butylammonium chloride in presence of iron salts, a precipitate of apparent composition, $[\text{Fe}(\text{H}_2\text{O})(\text{C}_{12}\text{H}_{27}\text{N})_5]\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$, may form. Reduction of iron^{III} to iron^{II} and precipitation in 2*N* hydrochloric acid solution prevent its formation.

Zusammenfassung—Wenn 12-Wolframphosphorsäure mit Tri-*n*-butylammoniumchlorid in Gegenwart von Eisen(III)salzen zur Reaktion gebracht wird, resultiert ein Niederschlag der scheinbaren Zusammensetzung $[\text{Fe}(\text{H}_2\text{O})(\text{C}_{12}\text{H}_{27}\text{N})_5]\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$. Reduktion des Eisen(III) zu Eisen(II) und Arbeiten in 2 *n* Salzsäure verhindert die Fällung.

Résumé—Quand l'acide 12-tungstophosphorique réagit avec le chlorure de tri-*n*-butylammonium en présence de sels de fer, il peut se former un précipité de composition apparente $[\text{Fe}(\text{H}_2\text{O})(\text{C}_{12}\text{H}_{27}\text{N})_5]\text{PW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$. La réduction du fer(III) en fer(II) et le précipitation en solution acide chlorhydrique 2*N* empêchent sa formation.

REFERENCES

- 1 C. C. Miller and D. H. Thow, *Analyst*, 1959, **84**, 440.
- 2 G. H. Walden, L. P. Hammett and S. M. Edmonds, *J. Amer. Chem. Soc.*, 1934, **56**, 350.
- 3 W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, Chapman and Hall, London, 2nd. Ed., 1953, p. 689.

LETTER TO THE EDITOR

SIR,

I AM sorry that Mr. Greenfield (*Talanta*, 1960 4, 147) should think fit to rebuke me for using part of a sentence from his paper to illustrate poor presentation in a paper describing an analytical method. It should have been evident from the incomplete reference I gave, that I was anxious not to appear discourteous. Furthermore, I had no intention of criticising Mr. Greenfield's method: I merely wanted to set down the actual words used by an author.

Since, however, Mr. Greenfield has chosen to defend the type of wording to which I object, I must reply that his instructions quoted in my letter (*Talanta*, 1960, 3, 272) are not only difficult to carry out, but that they are unnecessarily precise. Since the sodium peroxide is to be added to a solution containing 55 ml (no limits given) of hydrochloric acid (4*N* "accurately" adjusted within unspecified limits) it is difficult to see how the use of even double the quantity of sodium peroxide would have much effect on the normality of the final solution.¹ In any case, a direction such as "between 0.4 and 0.6 grams of sodium peroxide" would have been adequate, more realistic, and therefore, more likely to inspire confidence in the reader.

In answer to Mr. Greenfield's final paragraph I would say that no matter how good a method is, if the directions for carrying it through are in any way inaccurate or obscure the method cannot be expected to work. If, therefore, an author cannot present his method in a manner that an analyst can easily follow and obtain results with the accuracy the author has claimed, he must get someone else to write it for him.

A. A. Moss

Department of Mineralogy
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Cromwell Road, London, S.W.7

24 June 1960

¹ 1 drop (0.05 ml) 4*N* HCl \equiv 8 mg Na₂O₂.

BOOK REVIEWS

Methods of Analysis for Petrochemicals. Edited by E. R. LITTMAN. Chemical Publishing Co. Inc., New York, 1958. pp. 384. \$12.00.

To a comparatively new industry, such as the petroleum chemical industry, a comprehensive collection of analytical methods applicable to its products would be a very valuable aid. A book of that type would fill the need of many laboratories and would be welcome to most chemists working in this field.

The present volume does not fill this need. It is not a comprehensive collection of analytical methods used in the petroleum chemical industry, since it leaves out whole areas of vital importance. For instance there is hardly a mention of the analysis of hydrocarbon gases, whether by low temperature distillation, by gas-liquid chromatography, or by spectrographic methods. Analysis of ethylene products, with the exception of that of ethyl alcohol, is not dealt with. Such important products as ethylene oxide and its numerous derivatives, polymers of ethylene or propylene, cannot be found amongst the chemicals with which the book is concerned.

The book contains in effect a collection of analytical methods at present in use at the Enjay laboratories. These methods are necessarily confined to the products handled by the Enjay organisation, which is a subsidiary of the Standard Oil of New Jersey group. This is the reason for the very partial coverage of the field.

On the other hand, there are numerous methods of analysis of petroleum, as distinct from petroleum chemical products, such as determinations of flash points, viscosities, aniline points etc. These methods are of relatively minor interest for the analysis of petroleum chemicals.

Within these limitations, which are not clear from its misleading title, the book gives a good number of sound and well tried methods of analysis for a restricted range of petroleum chemicals and also petroleum products. It deals largely with derivatives of propylene, butylenes and aromatics. Many of the methods are the standard procedures of A.S.T.M. with the additional experience and added details, gathered over many years, by the Enjay laboratories. There are many hints and references to small points, so essential in analytical work, revealing the considerable body of experience available to the author of the book. In the description of practical details, very little, if anything, is omitted. This is not so with regard to theoretical background. For instance, in the description of the determination of water in hydrocarbon gases using the Karl Fischer reagent and the dead stop-method, full experimental details are given, but the electrochemical background to the method is not mentioned. Generally there is also a dearth of literature references.

The book is well produced but the price may be considered high by British readers.

H. STEINER

Heterometry. MORDECHAI BOBTELSKY. D. Van Nostrand Company, Ltd., London: Elsevier Publishing Co., Amsterdam, 1960. Pp. vii + 229. 42s.

HETEROMETRY is the study of the formation of precipitates from solution by measuring the light absorbancy of the heterogeneous medium at different ratios of reactants. The method has been devised and developed exclusively by the author and his pupils, as a glance down the list of references at the end of this book will show.

The work is split up into ten chapters, the first four of which outline the development and scope of heterometry, its relationship to other physico-chemical methods (turbidimetry, conductimetry, and potentiometry), technique and instrumentation and analytical aspects. The remaining chapters

provide examples of the application of the method; analysis by virtue of normal salt and chelate formation, the study of the composition of complexes, and of chemical reactions including so called heterogeneous chain reactions, and intermediates and final compounds in the study of polymers and lakes.

There is little that can be said in favour of this book. The main faults, apart from a number of obvious inconsistencies, lie in the immoderate claims made for the method and the amount of space devoted to experimental detail and speculative discussion based on the results. Most of these claims are made in the chapters (VII—X) dealing with the properties of precipitates. From the ratios of one reactant to another which make up precipitates the reader is often presented with reaction mechanisms and detailed structures of the products without reference to supporting evidence from other sources. It is even claimed (p. 187) in discussing dye complexes that a critical point on the heterometric curve, from which the ratio is derived, provides a "deep insight into the electronic structure of the compound".

Heterometric titrimetry would appear to have definite potentialities in chemical analysis, particularly in the rapid determination of minor constituents in mixtures. While the two chapters (V and VI) dealing directly with chemical analysis are probably the best in the book, even here important aspects tend to be obscured by the detail presented.

Many of the faults of this book may be attributed to the author's difficulty with the language in spite of the fact that he had assistance in correcting it. Accordingly there can be little doubt that greater justice would have been done to heterometry if it had been produced under the guidance of an experienced scientific editor.

S. J. LYLE

Monographs on the Radiochemistry of Elements. The Sub-Committee on Radiochemistry, National Academy of Sciences. National Research Council, U.S.A.

THIS is a series of monographs on the radiochemistry of the elements produced by the sub-committee on radiochemistry of the National Research Council, U.S.A. The series has grown out of a need for up-to-date and specialised information and procedures. Each monograph is written by an authority on the radiochemistry of the particular element, and has been written to a standard format. Contents include general reviews of the inorganic, analytical and radiochemistry of the element, a table of its isotopes, a review of properties of particular interest to radiochemists, counting techniques pertinent to the element under consideration, and a collection of detailed radiochemical procedures.

In the latter section, which occupies the major part of the monograph, there is ample evidence that a careful selection of the known radiochemical techniques for each element has been made. Many originated in Atomic Energy Establishments and it is possible that their appearance in these monographs marks their first open publication. The literature has been covered up to 1959.

Undoubtedly this series will be of particular interest and value to the radiochemist or the analytical chemist. It has, however, also much to offer to the biochemist and physicist who often use radiochemical techniques in the solution of specific problems.

The following monographs in the series are now available:

- ¹ The Radiochemistry of Arsenic. Harold C. Beard. January 1960 \$0.50.
- ² The Radiochemistry of Cadmium. James R. DeVoe. January 1960 \$0.75.
- ³ The Radiochemistry of Francium. Earl K. Hyde. January 1960 \$0.50.
- ⁴ The Radiochemistry of Thorium. Earl K. Hyde. January 1960 \$0.75.
- ⁵ The Radiochemistry of Fluorine, Chlorine, Bromine and Iodine. Jacob Kleinberg and G. A. Cowan. January 1960 \$0.50.
- ⁶ The Radiochemistry of Americium and Curium. R. A. Penneman and T. K. Keenan. January 1960 \$0.75.
- ⁷ The Radiochemistry of Chromium. J. Pijck. January 1960 \$0.50.
- ⁸ The Radiochemistry of Rhodium. G. R. Choppin. January 1960 \$0.50.
- ⁹ The Radiochemistry of Molybdenum. E. M. Scadden and N. E. Ballou. January 1960 \$0.50.

R. J. MAGEE

Principles and Practice of Gas Chromatography. Edited by ROBERT L. PECSOK. John Wiley and Sons, Inc., New York: Chapman and Hall, Ltd., London, 1959. Pp. xii + 226, 54s.

THIS book has its origins in a first course in gas chromatography given at the University of California, Los Angeles in 1959. All important aspects of gas chromatography are touched upon in 150 pages of text divided into thirteen chapters, of which twelve are contributed separately by four authors and one by the editor. There is also a bibliography which is virtually complete up to 1958 and includes some early 1959 references.

Notwithstanding that the book aims at being an introduction to the subject, nowhere is there given a general introduction to technique, and a reader new to the subject would have difficulty in orienting himself. The real value of the book is for the practitioner of the technique who wishes to acquire a clear understanding of the basic elements on which the method is founded. These are very clearly set out, and are always closely related to practical operation. In consequence, the book contains much general information concerning the choice and control of operating conditions which even experienced and well informed gas chromatographers will find of value. It is on this score that the book justifies its existence and enables the reviewer to give it his recommendation. However, it must be said that the present device of having four independent contributors is an inefficient way of achieving this objective. There is much wasteful repetition of material and, with a high-cost book such as this, one becomes rather sensitive about paying a number of times over, as it were, for the same information. Especially irritating in this connection is the fact that some of the chapters are cut short at a point where they promised to become distinguished contributions, presumably because of the lack of space. Again, it is felt that more space could well have been devoted to recent developments such as ionisation detectors and capillary columns, about which very little indeed is said.

The bibliography consists of the titles of publications, listed in alphabetical order of the authors, and classified by the year of publication; it is a striking illustration of the explosive growth of the subject. Unfortunately, the absence of a subject index related to the bibliography greatly limits the value of the compilation of references.

In order to facilitate rapid publication, the book has been reproduced from typescript by the photo-offset method, but the layout is good and the page appearance pleasing.

DESMOND BRENNAN

NOTICES

Wednesday–Friday 2–4 November 1960: 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 and 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. The exhibition will consist of 65 manufacturers of scientific apparatus and supplies.

For further information about the meeting contact the Publicity Chairman: E. WYNNE, Fisher Scientific Co., P.O. Box 375, Fair Lawn, N.J., U.S.A.

Monday 27 February–Friday 3 March 1961: Analytical Chemistry Group, Pittsburgh Section, **American Chemical Society and Spectroscopy Society of Pittsburgh: Twelfth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy**. Penn-Sheraton Hotel, Pittsburgh, Penna., U.S.A.

A symposium entitled *New Frontiers in Optics and Spectroscopy* will be sponsored jointly by the **Pittsburgh Conference and the Optical Society of America**.

In addition to the programme of technical papers, there will be an exhibition of the newest instrumentation for analysis.

Original papers are invited on all phases of analytical chemistry, spectroscopy, and nucleonics applied to analysis. The final date for receipt of abstracts is 15 October 1960.

All correspondence should be addressed to: Dr. WILLIAM F. HARRIS, Programme Chairman, The Twelfth Annual Pittsburgh Conference, Research Laboratories, Westinghouse Electric Corporation, Pittsburgh 35, Penna., U.S.A.

The B.S.I. News announces, amongst others, the following amendment slips to British Standards:
B.S. 1672: Methods of testing rubber latex: Part 2: 1954. Chemical and physical tests. Amendment No. 2: PD 3683 (Price 2s.)

B.S. 2782: Methods of testing plastics: Part 4: 1958. Analytical methods and viscosity in solution. Amendment No. 4: PD 3709. (Gratis); Part 5: 1958. Miscellaneous methods. Amendment No. 3: PD 3708. (Gratis).

PAPERS RECEIVED

- Fundamental principles of titrations with potassium bromate.** E. SCHULEK, K. BURGER and J. LASZ-LOVSKY. (20 June 1960).
- The estimation of vanadium and ash in vanadium-sodium bearing residual fuel oils.** R. BASKERVILLE and V. S. GRIFFITHS. (20 June 1960).
- A study of some solvents as media for the high-frequency titration of weak acids.** E. L. GROVE and W. S. JEFFERY. (21 June 1960).
- Precipitation of metal cupferrates from homogeneous solution.** ARNO H. A. HEYN and NATWAR C. DAVE. (23 June 1960).
- Determination of oxygen in zirconium by the platinum flux method.** CH. VENKATESWARLU and MANLEY W. MALLETT. (27 June 1960).
- Analytical applications of Xylenol Orange—V: A spectrophotometric study of the bismuth-Xylenol Orange complex.** K. L. CHENG. (28 June 1960).
- A note on the iodate-iodide (Andrews) titration.** J. J. KIPLING and G. GRIMES. (28 June 1960).
- Microdetermination of chloride in water.** WIKTOR KEMULA, ADAM HULANICKI and ANDRZEJ JANOWSKI. (30 June 1960).
- Applications of infrared spectroscopy—II: Observations on some aspects of the Zeisel alkoxy determination.** D. M. W. ANDERSON and J. L. DUNCAN. (30 June 1960).
- Interference of iron in the determination of 12-tungstophosphoric acid with tri-*n*-butylamine.** C. C. MILLER and D. H. THOW. (6 July 1960).
- The colorimetric determination of trace amounts of aluminium in steel.** D. BLAIR, K. POWER, D. L. GRIFFITHS and J. H. WOOD. (6 July 1960).
- A new spot test for auric gold with N:N'-di-2-naphthyl-*p*-phenylenediamine.** JACQUES C. SORIANO and ERWIN JUNGREIS. (7 July 1960).
- Applications of complementary tri-stimulus colorimetry—I: Analysis of binary and ternary colorant systems.** HERMANN FLASCHKA. (9 July 1960).

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 unbiased 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. 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 re-drawing 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 lettering should be sufficiently large and bold to permit this reduction. 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.

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