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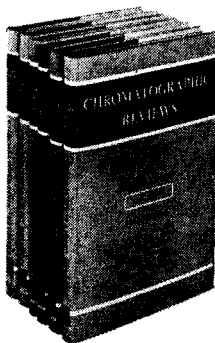
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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 32, No. 6, June 1965

A SIMPLE SEMIMICRO CELL FOR THE MEASUREMENT OF
SPECTRAL REFLECTANCE

The construction and method of employment of a simple cell suitable for the measurement of the spectral reflectance of semimicro samples, such as those removed from chromatoplates, are described. An attempt is also made to correlate the performance of the cell with current theories of reflectance spectroscopy using data obtained with a system consisting of Merck silica gel G and McCormick blue, a food dye.

R. W. FREI AND M. M. FRODYMA,
Anal. Chim. Acta, 32 (1965) 501-507

PHOTOMETRIC DETERMINATION OF BORON WITH OXA-
ZINE DERIVATIVES

Eight oxazine derivatives were examined for their ability to form extractable complexes with boron fluoride. Brilliant cresyl blue, Capri blue and Nile blue form such complexes and can be used as sensitive photometric reagents for boron. Capri blue can even be more sensitive to boron than methylene blue.

O. B. SKAAR,
Anal. Chim. Acta, 32 (1965) 508-514

THE PHOTOMETRIC TITRATION OF MERCURY WITH
TRIEN

A mercury(II) solution containing copper ion can be titrated photometrically at pH 4.7 with triethylenetetramine solution (trien) after the addition of iminodiacetic acid (IDA); IDA causes a reversal of the effective formation constants of Hg-trien and Cu-trien and permits the titration. Copper-trien which absorbs at 580 m μ serves as the indicator for the titration. Mercury can be determined in presence of many other metals with an accuracy of about 1%; the main interferences are iron(III), nickel, bismuth and chloride ion.

D. J. PIETRZYK AND J. BELISLE,
Anal. Chim. Acta, 32 (1965) 515-520

ห้องสมุด กรมวิทยาศาสตร์
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ANALYSIS FOR AROMATIC COMPOUNDS ON PAPER AND THIN-LAYER CHROMATOGRAMS BY SPECTROPHOTOPHOSPHORIMETRY

APPLICATION TO AIR POLLUTION

A technique is introduced in spectrophosphorimetric analysis by means of which spectra can be obtained directly on an adsorbent after chromatography. Spectra of the phosphorescent compound, its salts, its reduced or oxidized forms, or its derivatives can be obtained in all types of solvents. Examples of this simple technique are given; detection limits range from 0.1 ng to μg amounts. A new system for the circular paper chromatographic separation of aza heterocyclic hydrocarbons using aqueous formamide is described. Many of these heterocyclic compounds can be separated from each other as can the parent compounds from their alkyl derivatives.

Air pollution mixtures separated by column and paper chromatography are analyzed with the phosphorimetric technique. Spots obtained on the paper chromatograms are analyzed directly in the phosphorimeter. With these techniques benzo(f)quinoline, benzo(h)quinoline, benz(a)acridine, benz(c)acridine, and hydrocarbons such as phenanthrene and benzo(e)pyrene are readily characterized.

E. SAWICKI AND J. D. PFAFF,
Anal. Chim. Acta, 32 (1965) 521-534

COMPLEX FORMATION OF IRON(III) WITH ERIOCHROME CYANINE R

The complex formation of iron(III) with the trisodium salt of 5-[α -(3-carboxy-5-methyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2-sulfo-benzyl]-3-methylsalicylic acid (eriochrome cyanine R) was studied by spectrophotometry. The pure tetrabasic acid of the ligand (H_4ER) was prepared and used in the investigation. In the pH range 2.7-4.2 three complexes were detected: a ring-formed dimer $\text{Fe}_2(\text{ER})_2$, $\text{Fe}_2(\text{ER})$ and $\text{Fe}(\text{ER})$; the absolute stability constants (at an ionic strength of 0.1 M and at room temperature ($20 \pm 3^\circ$)) were $\log k = 37.9$, $\log k = 22.5$ and $\log k = 17.9$, respectively.

F. J. LANGMYHR AND T. STUMPE,
Anal. Chim. Acta, 32 (1965) 535-543

SOME METALLOFLUORESCENT DERIVATIVES OF 2,2'-DIAMINODIPHENYL-N,N,N',N'-TETRAACETIC ACID

The N,N,N',N'-tetraacetic acid derivatives of five 4,4'-disubstituted 2,2'-diaminodiphenyls have been prepared and their fluorescent properties examined. 2,2'-Diaminodiphenyl-4,4'-dicarboxylic acid-N,N,N',N'-tetraacetic acid exhibits intense fluorescence in aqueous solution above pH 4, and forms stable non-fluorescent 1 : 1 complexes with copper(II) and nickel(II) ions at pH 7.5. The quenching of the fluorescence of the compound by nickel(II) may be used in the fluorimetric determination of nickel.

G. F. KIRKBRIGHT AND W. I. STEPHEN,
Anal. Chim. Acta, 32 (1965) 544-551

THE ANALYSIS OF ANHYDROUS TITANIUM TRICHLORIDE

Titrimetric determinations of titanium and chloride were examined for their suitability in establishing the stoichiometry of titanium trichloride. Aluminium metal reduction of titanium(IV) to titanium(III) in aqueous sulphuric acid solution gave higher precision than the Jones Reductor procedure; in both cases exceptional care was necessary before titration in order to prevent some reoxidation of reduced titanium by dissolved oxygen in the titrant. Deaerating the ferric alum titrant and delivering it under nitrogen made it possible to obtain a virtually complete titanium recovery. A convenient apparatus is described. A procedure is also described for the elimination of interference in the Volhard chloride determination due to the presence of high concentrations of titanium sulphate and of gelatin used for sample encapsulation.

E. S. PILKINGTON AND P. R. SMITH,
Anal. Chim. Acta, 32 (1965) 552-558

DETERMINATION OF SILICA IN GLASSES, CERAMICS AND REFRACTORIES

A rapid method for the determination of silica in glasses, glass ceramics and refractories is described. The utilization of direct coulometric titration of the excess of 8-quinolinol employed to precipitate the silico-12-molybdate complex, enables duplicate determinations in the presence of diverse ions to be completed in about 3 h. Studies of the optimum conditions indicated that the acidity and choice of acid were critical. For greatest versatility, a sulfuric acid medium was better than hydrochloric or perchloric acids. The addition of glycerol allowed analysis of titanium-containing refractories. The accuracy of the method for a wide variety of materials is similar to that of the conventional acid-dehydration method.

YAO-SIN SU, D. E. CAMPBELL AND J. P. WILLIAMS,
Anal. Chim. Acta, 32 (1965) 559-567

ISONITROSOACETANILIDE AS AN ANALYTICAL REAGENT

In a continuation of earlier work on the reactivity of various isonitrosoacetarylides, the simplest of the series, isonitrosoacetanilide was examined. In acidic medium, this reagent gives a specific reaction with palladium (dilution limit 1 : 400,000), and in ammoniacal medium a very sensitive reaction with cobalt (dilution limit 1 : 1,000,000). The composition of the complexes involved was established as R_2Pd and R_3Co_2 . The effect of substitution on the reactivity is discussed.

F. BUSCARÓNS AND F. BUSCARÓNS, JR.,
Anal. Chim. Acta, 32 (1965) 568-574

A SEPARATION SCHEME FOR GALLIUM, INDIUM,
THALLIUM, GERMANIUM, TIN AND LEAD BY SOLVENT
EXTRACTION WITH N-BENZOYL-N-PHENYLHYDROXYL-
AMINE

Gallium, indium, thallium, germanium, tin and lead in mixtures containing up to 1 mg/ml of each element are extracted separately with N-benzoyl-N-phenylhydroxylamine (BPFA) and chloroform under suitable conditions. Germanium is extracted into chloroform alone from 8 M hydrochloric acid and tin(IV) from 0.8 M hydrochloric or 4 M perchloric acid into BPFA in chloroform. The remaining elements are extracted from 0.05 M acetic acid-acetate buffered solutions. Gallium is extracted at pH 3.1, indium at 5.3, and lead at 7.8. Good separations of all these elements from each other are thus quickly obtained. Optimum conditions for partition of each metal ion between the two liquid phases are given.

S. J. LYLE AND A. D. SHENDRIKAR,
Anal. Chim. Acta, 32 (1965) 575-582

COPRECIPITATION OF SUBSTITUTED ANILINES WITH
ZINC FERROCYANIDE: ANALYSIS OF *p*-AMINOBENZOIC
ACID-PROCAINE MIXTURES

(Short Communication)

A. G. FOGG AND G. F. REYNOLDS,
Anal. Chim. Acta, 32 (1965) 582-586

A NEW SOLVATOCHROMIC CHELATING AGENT

(Short Communication)

J. W. FALLER AND J. P. PHILLIPS,
Anal. Chim. Acta, 32 (1965) 586-589

ULTRAPURITY ANALYSIS OF ZONE-MELTED ORGANIC
COMPOUNDS

(Short Communication)

R. FRIEDENBERG AND P. J. JANNKE,
Anal. Chim. Acta, 32 (1965) 589-592

TITRIMETRIC DETERMINATION OF SULFATE IN
SEA-WATER

(Short Communication)

J. O. PAGE AND W. W. SPURLOCK,
Anal. Chim. Acta, 32 (1965) 593-595

FLUORESCENT GALLIUM COMPLEXES EXTRACTABLE BY
BENZENE FROM 6 N HYDROCHLORIC ACID

(Short Communication)

R. J. ARGAUER AND C. E. WHITE,
Anal. Chim. Acta, 32 (1965) 596-599

A SIMPLE SEMIMICRO CELL FOR THE MEASUREMENT OF SPECTRAL REFLECTANCE

ROLAND W. FREI AND MICHAEL M. FRODYMA

Department of Chemistry, University of Hawaii, Honolulu, Hawaii (U.S.A.)

(Received August 24th, 1964)

During a recent investigation dealing with the application of spectral reflectance to thin-layer chromatography the need for a cell capable of accommodating 40–100-mg samples became apparent. After such a cell had been devised, the components of dye mixtures resolved on thin-layer plates could be determined by carrying out reflectance measurements on spots removed from the plates and packed in the cell¹. The present study represents an attempt to correlate the performance of the cell with current theories of reflectance spectroscopy.

For the purpose at hand probably the most appropriate theory treating diffuse reflection and the transmission of light-scattering layers also happens to be the most general theory developed by KUBELKA AND MUNK^{2,3}. When applied to an infinitely thick, opaque layer, the KUBELKA–MUNK equation may be written as

$$\frac{(1 - R_{\infty}')^2}{2R_{\infty}'} = \frac{k}{s}$$

where R_{∞}' is the absolute reflectance of the layer, k is its molar absorption coefficient, and s is the scattering coefficient. Instead of determining R_{∞}' , however, it is customary in practice to work with the more convenient relative diffuse reflectance, R_{∞} , which is measured against a standard such as magnesium oxide or barium sulfate. In these cases it is assumed that the k values for the standards are zero and that their absolute reflectance is one. Since the absolute reflectance of the standards exhibiting the highest R_{∞}' values never exceeds 0.98 to 0.99, however, one is actually dealing in such instances with the relationship

$$\frac{R_{\infty}' \text{ sample}}{R_{\infty}' \text{ standard}} \equiv R_{\infty}$$

and it is essential that the standard employed be specified. If this expression is introduced into the initial equation, it will assume the form

$$F(R_{\infty}) \equiv \frac{(1 - R_{\infty})^2}{2R_{\infty}} = \frac{k}{s}$$

which indicates that a linear relationship should be observed between $F(R_{\infty})$ and the absorption coefficient, k , provided s remains constant. s is rendered independent of wavelength by employing scattering particles whose size is large relative to the wave-

length being used. During the research described herein, the constancy of s was ensured by making use of powders consisting of particles having an approximate diameter of 5μ .

A straight-line relationship between $F(R_\infty)$ and k is observed, however, only when dealing with weakly absorbing substances and only when the grain size of the powders employed is less than 1μ in diameter. Furthermore, any significant departure from the state of infinite thickness of the adsorbent layer assumed in the derivation of the KUBELKA-MUNK equation results in background interference which, in turn, is responsible for nonideal diffuse reflectance. When adsorbents having a large grain size or when large concentrations of the absorbing species are used, plots of $F(R_\infty)$ vs. k or concentration deviate from straight lines in that there is a decrease in slope at higher concentrations.

In his explanation of this phenomenon, KORTUM⁴⁻⁷ postulates that the reflected radiation is the result of both regular and diffuse reflectance. The first can be described as a mirror reflection whereas the second occurs when impinging radiation is partly absorbed and partly scattered by a system so that it is reflected in a diffuse manner, *i.e.* with no defined angle of emergence. Regular reflectance for cases involving normal incidence is described by the FRESNEL equation

$$R_{\text{reg}} \equiv \frac{I_{\text{REFL}}}{I_0} = \frac{(n - 1)^2 + n^2 k^2}{(n + 1)^2 + n^2 k^2}$$

where k is the absorption coefficient and n is the refractive index. Diffuse reflectance is described by the KUBELKA-MUNK function given earlier. Since regular reflectance is superimposed on diffuse reflectance, a distortion of the diffuse reflectance spectrum results which is responsible for the anomalous relationship observed between $F(R_\infty)$ and k at high concentrations of the absorbing species. It is essential, therefore, to eliminate as far as possible the interference caused by regular reflectance, R_{reg} . This can be accomplished by selecting appropriate experimental conditions. Especially effective are the use of powders having a small grain size and the dilution of the light absorbing species with suitable diluents.

EXPERIMENTAL

The cell employed consisted of white paperboard to which a $3.7 \times 2.5 \times 0.1$ cm microscope cover glass had been affixed with two pieces of masking tape. The white backing paper was cut to a size ($4.0 \times 3.0 \times 0.1$ cm) which permitted its introduction into the sample holder of the reflectance attachment of the Beckman Model DU Spectrophotometer. These data are presented schematically in Fig. 1, as is a sketch of the assembled cell. The 40-mg analytical sample, consisting of silica gel plus varying amounts of adsorbed dye, was carefully compressed between the cover glass and the paper until a thin layer having an approximate thickness of 0.4 mm and an approximate diameter of 1.8 cm was obtained.

Merck silica gel G and McCormick blue, a food dye marketed by McCormick and Co., Inc., Baltimore, Md., constituted the system used to study the performance of the cell. The dilution series employed to study the relationship between concentration of the dye and reflectance was prepared from a stock solution containing 1500 mg of the dye in 100 ml of distilled water. Solutions were applied to chromatoplates as

spots by means of a 10- μ l Hamilton microsyringe in 5- μ l increments. After the plates had been dried for 15 min at 110°, each spot was removed from its plate and diluted with silica gel from the same plate until the aggregate totaled 40.0 ± 0.2 mg. This constituted the analytical sample which was then ground in a small agate mortar for 2 periods of 15 sec each to ensure homogeneity and uniform particle size.

Cells employing white, gray and black backing paper were used to investigate background reflectance and interference. A Beckman Model DU Spectrophotometer fitted with a standard reflectance attachment was employed to determine the dye concentration-reflectance relationship. All other spectral data presented were obtained with the use of a similarly outfitted Beckman Model DK-2 Spectrophotometer.

RESULTS AND DISCUSSION

The reflectance of 3 empty cells employing white, gray and black backing paper, respectively, was measured relative to magnesium oxide to determine the extent of background interference that might be anticipated with the use of the cell. As expected and as may be seen from a consideration of Fig. 2, which presents the spectra obtained, the values observed differed considerably. At 640 $m\mu$, for example, the reflectance ranged from 90% R to 12% R . Based on magnesium oxide having an absolute reflectance of 98%, the absolute reflectance values, R_a , found at this wave-

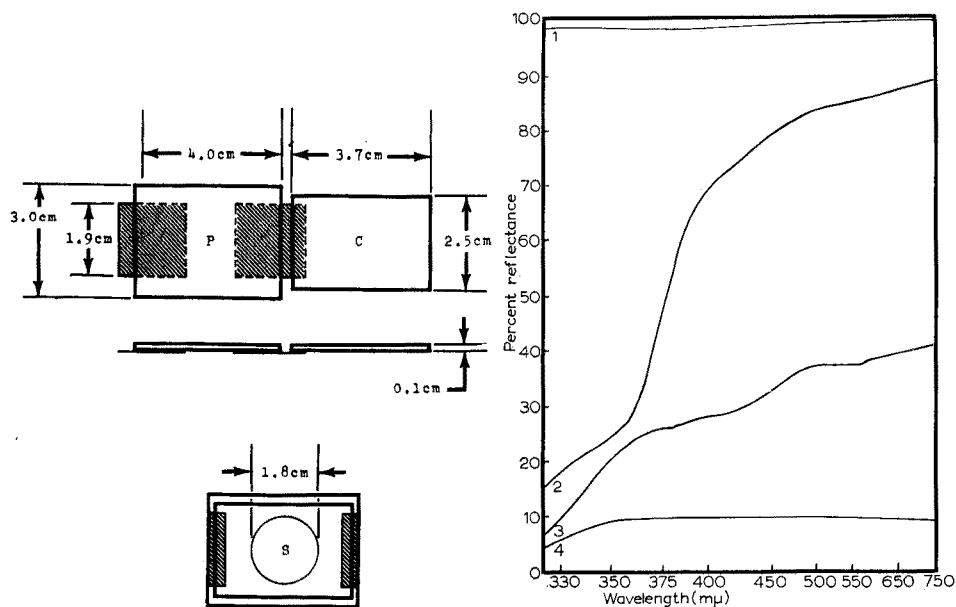


Fig. 1. Dimensions of cell elements and sketch of assembled cell. P, backing paper; c, microscope cover glass; s, sample.

Fig. 2. Reflectance spectra of various background materials relative to MgO. (1) MgO. (2) White backing paper. (3) Gray backing paper. (4) Black backing paper.

length for the white, gray and black cells were 88%, 40% and 10% respectively. At 400 $m\mu$, the other end of the visible spectrum, the corresponding R_a values were 68%, 28% and 10%. When 40 mg of silica gel were introduced into each of the 3 cells and their reflectance was measured relative to silica gel of the same quality, however, the 3 spectra were almost identical, differing by no more than one reflectance unit between 350 and 700 $m\mu$. In all respects the 3 closely resembled the magnesium oxide curve shown in Fig. 2. Since the 1% difference in reflectance observed among the spectra is coincident with the degree of precision inherent in the reflectance technique¹, one can conclude that when the cell is used with finely powdered samples compressed to an approximate thickness of 0.4 mm the background interference encountered is too small to be of practical significance and the sample layer may be assumed to have an infinite thickness.

To check the suitability of the cell for paper chromatography, the reflectance of the cell employing the black backing paper was measured relative to Whatman No. 1 filter paper. As indicated in Fig. 3, which shows cell reflectance as a function of the number of thicknesses of filter paper introduced into the cell, 5 layers of paper were required to eliminate background interference. These results are in agreement with data obtained by INGLE AND MINSHALL⁸.

Varying concentrations of McCormick blue adsorbed on silica gel were employed to verify the relationship between dye concentration and reflectance. In that

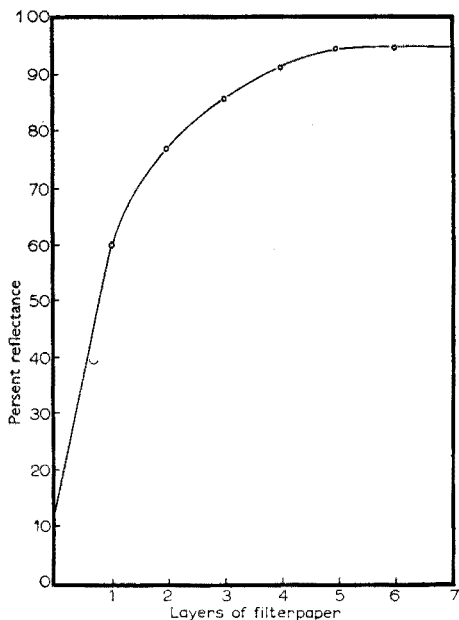


Fig. 3. Reflectance as a function of the number of thicknesses of filter paper introduced into the cell.

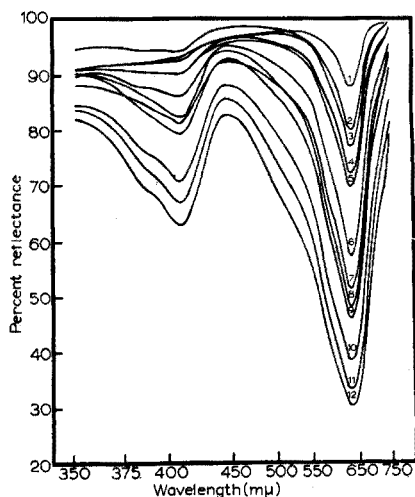


Fig. 4. Reflectance spectra of various concentrations of McCormick blue adsorbed on silica gel. Concentrations in mg/100 ml: (1) 10; (2) 20; (3) 40; (4) 60; (5) 120; (6) 180; (7) 240; (8) 300; (9) 600; (10) 900; (11) 1200; (12) 1500.

it absorbs in the visible portion of the spectrum and is stable in the absence of moisture and light, the system proved to be most convenient for this purpose. The spectra obtained for different concentrations of adsorbed dye are presented in Fig. 4. As may be seen, variation of the dye concentration had no significant effect upon the positions of the absorption maxima when the measurements were carried out under controlled experimental conditions. When the reflectance at $630\text{ m}\mu$ is plotted against the concentration of adsorbed dye, as shown in Fig. 5, the result is the typical smooth curve

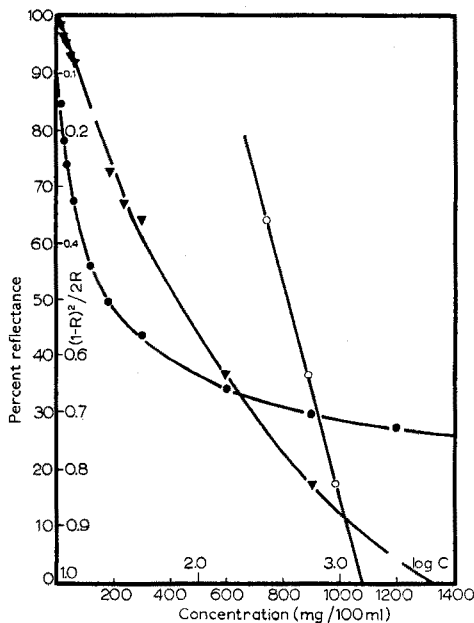


Fig. 5. Reflectance data obtained at $630\text{ m}\mu$ for McCormick blue adsorbed on silica gel. ●—● % reflectance as a function of concentration. ▼—▼ KUBELKA-MUNK values as a function of concentration. ○—○ KUBELKA-MUNK values as a function of the logarithm of concentration.

that is capable of being employed for calibration purposes. Alternatively these data may be graphed as concentration *vs.* $(1 - R)^2/2R$, the form of the KUBELKA-MUNK expression that is most often used⁹. A consideration of this curve, which is also presented in Fig. 5, supports the validity of applying the KUBELKA-MUNK law to the system being investigated when concentrations less than 300 mg of dye/100 ml of solvent are involved, or, in other words, when conditions of low absorbance and ideal diffuse reflectance obtain. In this region the dye has been so diluted with silica gel, which acts as a neutral diluent, that the contribution to the reflected radiation of regular reflectance has become negligible and one is dealing principally with diffuse reflectance. Accordingly within this concentration range it is appropriate to employ the relationship $F(R_{\text{diffuse}}) = kc d_{\infty}$, which is valid for reflectance from layers having an infinite thickness, d_{∞} , that precludes background interference. At higher concentrations increased absorptivity is associated with increased deviation from

ideal behavior as manifested by the gradual increase in slope which eventually results in the curve becoming asymptotic to the horizontal axis. This last was ascribed by KORTÜM *et al.*¹⁰ to a saturation effect in the first adsorption monolayer marking the shift from chemical to physical adsorption.

Some of the interference encountered was no doubt due to FRESNEL reflectance resulting from the use of thin-layer chromatographic grade silica gel which has an approximate grain size of 5 μ . Although it is possible to eliminate this effect by milling the particles down to a 1- μ grain size as recommended by KORTÜM⁴, the employment of such a step in an analytical procedure would not only result in an inordinate expenditure of time and effort but would also introduce more problems than it would solve. If it is desired to work with higher concentrations of an absorbing species, one can make use of the relationship

$$(1 - R)^2/2R = k \log C,$$

which was found to be applicable to more highly concentrated dye systems¹. When the data obtained during the present study were plotted in the form $(1 - R)^2/2R$ vs. the logarithm of concentration, as is done in Fig. 5, the result was a straight line which extended from a concentration of 300 mg/100 ml of solvent to one of 1400 mg/100 ml of solvent.

Two difficulties associated with the use of the microscope cover glass were circumvented by employing matched cells for the sample and the reference standard. In this way it was possible to cancel out the effects due to radiation being absorbed by the glass, which can amount to a decrease in reflectance as large as 6.0 reflectance units¹, and to radiation being reflected from its surface. When reflectance measurements for a dilution series were carried out employing cells with and without cover glasses, identical slopes were obtained for KUBELKA-MUNK function-concentration plots of the 2 sets of data. The packing of the sample in the cell presented no problems. Because the background interference was negligible, the sample layer thickness was not overly critical and a packing reproducibility corresponding to 0.7 reflectance units for 3 replicate packings of the same sample was achieved without any difficulty¹.

CONCLUSION

The cell described herein has proved to be most useful for the measurement of the spectral reflectance of semimicro samples such as those which are obtained from thin-layer chromatographic plates. Indeed, since there is no significant background interference with sample layers having an approximate thickness of 0.4 mm, it is capable of being employed with any finely powdered samples. The cell is inexpensive and simple to construct and can, therefore, be produced in large numbers to expedite serial analyses. Its size can be varied according to the requirements of the reflectance attachment and it can be mounted vertically as well as horizontally if proper care is exercised. For measurement in the near UV and IR regions, the cell may be employed with a quartz cover or without any cover glass at all provided that the surface of the sample is smooth.

The situation that would exist if the cell were employed with sample layers that were thinner and more transparent would be analogous to one that would result from the use in reflectance photometry of a flat, highly reflecting backing paper in

conjunction with a more or less transparent sample distant from the light, as suggested by LUGG¹¹. Such a procedure might provide advantages over transmission methods when dealing with paper chromatograms characterized by low transmission. In these instances, however, the thickness of the sample layer becomes more critical and it would be necessary to employ a high quality grade of chromatographic paper. Furthermore the amount of radiation reflected from the backing sheet would reach such proportions that the KUBELKA-MUNK relationship would no longer apply¹².

SUMMARY

The construction and method of employment of a simple cell suitable for the measurement of the spectral reflectance of semimicro samples, such as those removed from chromatoplates, are described. An attempt is also made to correlate the performance of the cell with current theories of reflectance spectroscopy using data obtained with a system consisting of Merck silica gel G and McCormick blue, a food dye.

RÉSUMÉ

Les auteurs donnent la description d'une cellule simple pour mesure du pouvoir de réflexion spectrale et son mode d'emploi. Les essais ont été effectués sur des échantillons de poudre, en quantité semimicro, échantillons prélevés par exemple sur des couches chromatographiques. Ils ont examiné les relations entre les résultats obtenus et les théories courantes de spectroscopie de "réflectance", en utilisant un système gel de silice G Merck et "McCormick blue".

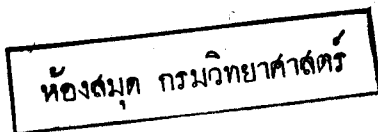
ZUSAMMENFASSUNG

Ein Probenhalter für die Messung von semimikro Quantitäten in der Reflexionsspektroskopie sowie seine Anwendung auf dem Gebiete der Dünnschichtchromatographie wird beschrieben. Merck Silikagel G und McCormick Blau Lebensmittelfarbe wurden angewandt um die Zusammenhänge zwischen den Messungen und den neuesten Theorien der Reflexionsspektroskopie zu studieren.

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PHOTOMETRIC DETERMINATION OF BORON WITH OXAZINE DERIVATIVES

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In 1957 DUCRET¹ introduced methylene blue as a reagent in photometric determination of boron. Boric acid was reacted with fluoride to form borofluoride ions which form an extractable complex with methylene blue. PÁSZTOR AND BODE² examined other thionine derivatives which also gave extractable complexes with borofluoride. The complexes must be separated from the deeply coloured reaction solution by extraction. PÁSZTOR AND BODE found 1,2-dichloroethane, *cis*-dichloroethylene and dichloromethane to be good extraction agents for the thionine derivatives. The first of these solvents was used by DUCRET and was also used in the present investigation. Eight commercially available oxazine derivatives (shown in Fig. 1) were examined, four of which form extractable complexes with borofluoride and can therefore be used in the photometric determination of boron.

EXPERIMENTAL

Equipment

The spectrophotometric measurements were made with a Beckman DB ultraviolet spectrophotometer with ratio recording and 1-cm glass cells. The sample solutions were prepared in 20-ml polyethylene bottles with stoppers equipped with a tapered plastic tube.

Reagents

All chemicals except the dyes were of reagent-grade quality. Ordinary distilled water from an all-metal still was used. 1,2-Dichloroethane ("purum" from Fluka AG) was used.

Standard solutions

Standard boron solution, $2.5 \cdot 10^{-5}$ M boric acid. 0.6184 g of boric acid was dissolved in water and diluted to 1 l (10^{-2} M); 50 ml were diluted to 1 l ($0.5 \cdot 10^{-3}$ M) and then 50 ml of this solution were diluted again to 1 l ($2.5 \cdot 10^{-5}$ M).

Standard borofluoride solution, 10^{-5} M boric acid and 0.5 M hydrofluoric acid. 20.45 ml of $0.5 \cdot 10^{-3}$ M boric acid solution was diluted to 1 l with water. This solution and 22.5 ml of a 40% hydrofluoric acid solution were mixed in a polyethylene bottle

and kept for 4 h at room temperature to ensure complete formation of BF_4^- and later below 5° . A ten times stronger borofluoride solution, $10^{-4} M$, was prepared in the same way taking 204.5 ml of the boric acid solution.

Hydrofluoric acid, 10 M. 44 ml of a 40% acid solution was diluted with water to 100 ml and kept in a polyethylene bottle.

Hydrofluoric acid, 0.5 M. 22.5 ml of a 40% acid solution was diluted to 1 l with water and kept in a polyethylene bottle.

Aqueous dye solutions, $5 \cdot 10^{-3}$, $5 \cdot 10^{-4}$ and $10^{-4} M$. The solutions were prepared from commercially available (G.T. Gurr Ltd.) dyes. The dyes were first dried in a desiccator over concentrated sulphuric acid to constant weight. Some hydrochloric acid solution was added to celestin blue, gallamine blue and gallocyanine to dissolve the dye. The last two compounds gave in a 0.1 M hydrochloric acid solution only a concentration of respectively $4.2 \cdot 10^{-5} M$ and $28 \cdot 10^{-5} M$ (estimated by weighing the amount not dissolved). The solutions were all kept in a dark place. Some of them were purified by a preliminary extraction with 1,2-dichloroethane as noted later in the text.

Procedure for preliminary tests (Procedure A)

Pipet 5 ml of standard borofluoride solution (containing $0.54 \mu\text{g B}$), 5 ml of dye solution and 5 ml of 1,2-dichloroethane into the above-mentioned 20-ml polyethylene bottle. A calibrated polyethylene pipet is used for the borofluoride solution. Cap the bottle, shake well for 3 min and centrifuge. Invert the bottle, and squeeze the organic phase into another 20-ml polyethylene bottle. Before this operation, force some air out of the bottle; when the bottle is inverted, release the pressure so that air and dichloroethane solution remove any residual drops of water from the tube. After this, nearly all the dichloroethane can be separated from the aqueous phase. Add 5 ml of water and shake the bottle for 3 min and centrifuge. Squeeze the dichloroethane phase (as just described) into a 1-cm glass cell.

In the blank solutions add 5 ml of water instead of 5 ml of standard borofluoride solution.

Procedure for determination (Procedure B)

This procedure is similar to that used in some earlier investigations^{3,4}. Pipet 2 ml of water, 1 ml of standard boron solution (containing $0.27 \mu\text{g B}$), 0.5 ml of 10 M hydrofluoric acid and 0.5 ml of 30% hydrogen peroxide into the 20-ml polyethylene bottle. Use a calibrated polyethylene pipet for the hydrofluoric acid solution. Mix the solutions and leave for 3 h at room temperature. Add 1 ml of dye solution and 5 ml of 1,2-dichloroethane, shake the mixture and then complete the determination as in Procedure A. In the blank solutions add 1 ml of water instead of 1 ml of standard boron solution.

RESULTS AND DISCUSSION

The structural formulae (corresponding to the Colour Index number given by G. T. Gurr Ltd.) of the eight oxazine derivatives used in this investigation can be seen in Fig. 1. The dyes are all salts except gallamine blue, and the organic ions are cations except for lacmoid. They have, as have the thionine derivatives (*e.g.* methylene blue),

a tertiary nitrogen atom in a six-membered ring. Except for lacmoid the dyes have also at least one amine group.

The procedure for preliminary testing was first used on the eight dyes to investigate their properties of forming extractable complexes with boron fluoride. For comparison similar tests were carried out with methylene blue. The results are given in Table I. Different concentrations of the dye solutions were used as shown in column 2 of the Table. The distribution of the colour in the two phases was observed visually; the ratios between their measured intensities are given in columns 3 and 4. The extinctions were taken from the recording paper at the wavelength of the absorption maximum.

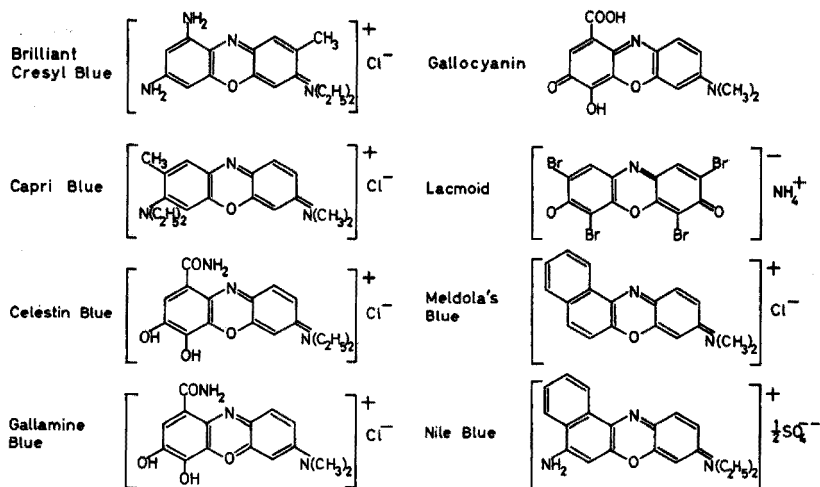


Fig. 1. Oxazine derivatives tested.

TABLE I
RESULTS OBTAINED BY PRELIMINARY PROCEDURE

Dye	Dye solution (M)	Relative colour distribution ^a		Wave-length (m μ)	Extinction (1000 · E)		pS ^b
		After extraction	After washing		Blank	Test + blank	
Brilliant cresyl blue	0.0001	50 : 50		653	200	410	3.58
				510	90	—15	
	0.0005	70 : 3	60 : 40r, f	653	250	770	3.85
				510	710	—40	
	0.0005 ^c	80 : 20	50 : 50r, f	653	230	720	3.82
				510	410	—20	
	0.005 ^c	80 : 20	50 : 50f	653	720 ^d	740 ^d	3.84
				510	1250 ^d	40 ^d	
Capri blue	0.0001	10 : 90		652	450	850	3.89
	0.0005	50 : 50	85 : 15	652	320	> 1100	> 4.00
	0.0005 ^c	50 : 50	80 : 20	652	480	> 1000	> 3.97
	0.005 ^c	70 : 30	90 : 10	652	1490 ^d	1440 ^d	4.12

TABLE I (Continued)

Dye	Dye solution (M)	Relative colour distribution ^a		Wave-length (m μ)	Extinction (1000·E)		pS ^b
		After extraction	After washing		Blank	Test + blank	
Celestin blue	0.00005 ^e in 5 · 10 ⁻⁴ N HCl	50r : 50	0 : 100	625	650	20	
	0.001 in 10 ⁻² N HCl	50r : 50	0 : 100	650 625	560 > 4000 ^d	30	
	Gallamine blue	0.000042 ^e in 0.1 N HCl	95r : 5	10 : 90	652	130	—35
Gallocyanin	0.00014 ^e in 0.05 N HCl	50r : 50	5r : 95	630	1160	0	
	0.00028 in 0.1 N HCl	50r : 50	0 : 100	630	1580	ca. 0	
Lacmoid	0.001 ^e	98br ^f : 2	0 : 100	651	295	0	
Meldola's blue	0.0001	90 : 10		580 525	35 35	40 20	2.57
	0.0005	90 : 10	70 : 30	580 525	105 190	95 50	2.94
	0.0005 ^o	90 : 10	80 : 20	580 525	40 30	110 50	3.01
	0.005 ^o	95 : 5	80v : 20 or	580 525	130 ^b 170 ^b	160 ^b 70 ^b	3.17
	Nile blue	0.0001	10 : 90		650 500	540 490	750 440
Methylene blue	0.0005	15 : 85	85 : 15v	650 500	495 1380	825 100	3.88
			15 : 85v ^g	650 500	270 1300	640 0	3.77
	0.0005 ^o	50 : 50	80 : 20r	650 500	525 1200	810 —70	3.88
	0.005 ^o	80 : 20	60 : 40v	650 500	1140 ^b 1450 ^b	780 ^b 50 ^b	3.86
		0.0001	80 : 20	60 : 40	660	300	600
	0.005	95 : 5	70 : 30	660	620 ^b	880 ^b	3.91

^a *i.e.* Percentage distribution of colour intensity between the aqueous phase and the organic phase. Colours other than blue are indicated as: r = red, v = violet, r, v = red-violet, or = orange, br = brown.

^b See text.

^c The dye solution was first purified by extracting 20 ml of the solution with 5 ml of 1,2-dichloroethane.

^d The extinction was measured in 0.5-cm glass cells and twice the extinction value is given in the Table.

^e The test contained ten times more boron as the strong standard borofluoride solution (10⁻⁵M) was used.

^f Brown precipitate was seen in the aqueous phase.

^g The dichloroethane phase was washed for a second time with 5 ml of water.

All the dyes gave an absorption maximum at a wavelength which was the same for test and blank (between 630 and 660 $m\mu$) except for Meldola's blue. For Meldola's blue 580 $m\mu$ was chosen because this wavelength gave the greatest extinction difference between test and blank. The absorption curves for brilliant cresyl blue, Meldola's blue and Nile blue had also a maximum about 500 $m\mu$. This red coloured component was probably due to contaminations in the dyes. Nile blue was divided into a blue and a red component by extracting an aqueous solution of Nile blue with 1,2-dichloroethane. The red component from the dichloroethane phase gave in acid and in alkaline solution absorption curves somewhat different from those of the blue component in the two media. The red component changed colour from acid to alkaline solution at a lower pH value than the blue component. An infra-red spectrum of the two components showed much the same absorption, hence the red component appears to be closely related to Nile blue. For the other dyes the red component could also entirely or partly be another form of the dye. To control the concentration of this component the extinction was also read at its maximum.

In the last column in Table I the negative logarithm of the spectrophotometric sensitivity is introduced, denoted as pS; the author proposes to call it the spectrophotometric sensitivity index. S is the spectrophotometric sensitivity as defined by SANDELL⁵. From the Table it can be seen that pS was, in general, increased with increasing dye concentration, but the blank in most cases increased at a higher rate.

TABLE II

RESULTS OBTAINED BY THE PROCEDURE FOR DETERMINATION

Dye	Dye solution (M)	Relative colour distribution		Wave-length (m μ)	Extinction (1000 · E)		pS
		After extraction	After washing		Blank	Test + blank	
Brilliant cresyl blue	0.0005	70 : 30	95 : 5v	655	170	130	3.38
	0.005	75 : 25	60 : 40r,v	520	125	— 5	3.74
				655	570	300	
0.005 ^a	80 : 20	95 : 5v	655	280 ^b	320 ^b	3.77	
Capri blue	0.0005	0 : 100	95 : 5	655	245	215	3.60
	0.005	40 : 60	90 : 10	655	890	500	3.97
				655	510	410	3.88
	0.005 ^a	40 : 60	95 : 5	655	720 ^b	560 ^b	4.01
Nile blue	0.0005	5 : 95	80 : 20r	650	375	215	3.60
				505	420	0	
	0.005	10 : 90	60 : 40r,v	650	940	370	3.84
				505	1400	ca. 0	
0.005 ^a	20 : 80	90 : 10v	650	710 ^b	380 ^b	3.84	
Methylene blue	0.0005	80 : 20	95 : 5	660	160	290	3.73
	0.005	90 : 10	95 : 5	660	420	380	3.84
	0.005 ^a	90 : 10	95 : 5	660	280 ^b	370 ^b	3.84

^a The dye solution was first purified by extracting 5 ml of the solution with two 5-ml portions of 1,2-dichloroethane. All the other abbreviations and notes are the same as in Table I.

With Nile blue a second washing of the dichloroethane phase lowered the blank about 40% while pS was lowered about 20%. The red coloured component at 500 m μ was not appreciably removed by this extra washing. The purification of the dye solution by a preliminary extraction with dichloroethane seemed to have no advantage, except in the case of Meldola's blue.

The 5 ml of 1,2-dichloroethane used in the purification of the dye solution was washed with 10 ml of water. The relative distributions of colour intensities between the aqueous and organic phase after the purification and after the washing were as follows: for brilliant cresyl blue, 30b (b = blue): 70r (r = red) and 5b: 95v (v = violet); for Meldola's blue, 60r: 40r (orange precipitate) and 5v: 95(orange); and for Nile blue, 30b: 70v and 0: 100r. The quite different distribution after the two extractions indicates, as discussed above, that these three dyes are contaminated. If so, the real dye concentrations will be somewhat less than those given in the Tables.

Brilliant cresyl blue, Capri blue and Nile blue were compared with methylene blue in a full boron determination. The results can be seen in Table II. The procedure used was a modification^{3,4} of DUCRET's method¹ and involved an addition of hydrogen peroxide.

For a particular dye concentration, the values of blank and pS were somewhat higher by the preliminary test procedure (Table I) than by the quantitative procedure but the mutual distribution of the values among the dyes was much the same. For quantitative purposes Capri blue appeared to be more sensitive than methylene blue, and it is of interest to note that pS increased at a higher rate for Capri blue with increasing dye concentration than for methylene blue. With Capri blue, a preliminary purification by two extractions with 1,2-dichloroethane gave a drop in the blank and no decrease in pS. The relative distributions of colour intensities between the aqueous and organic phase after the first and second extractions were as follows: for brilliant cresyl blue, 80b: 20v and 90b: 10v; for Capri blue, 95b: 5b and 95b: 5b; for Nile blue, 70b: 30v and 80b: 20v; and for methylene blue, 98b: 2b and 98b: 2b.

The author thanks Prof. HAAKON HARALDSEN for the opportunity of carrying out this investigation.

SUMMARY

Eight oxazine derivatives were examined for their ability to form extractable complexes with boron fluoride. Brilliant cresyl blue, Capri blue and Nile blue form such complexes and can be used as sensitive photometric reagents for boron. Capri blue can even be more sensitive to boron than methylene blue.

RÉSUMÉ

L'auteur a examiné huit dérivés oxazine, du point de vue de leur propriété à former des complexes extractibles au moyen de fluorure de bore. Quatre d'entre eux forment des complexes et peuvent être utilisés comme réactifs pour le dosage photométrique du bore. Le bleu de Capri peut même être plus sensible que le bleu de méthylène.

ZUSAMMENFASSUNG

8 Oxazin-Derivate wurden auf ihre Fähigkeit extrahierbare Komplexe mit Borfluorid zu bilden untersucht. Brilliantkresylblau, Capriblau und Nilblau bilden solche Komplexe und können als empfindliches photometrisches Reagenz für Bor dienen. Capriblau ist sogar empfindlicher für Bor als Methylenblau.

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THE PHOTOMETRIC TITRATION OF MERCURY WITH TRIEN

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The complexing properties of polyamines towards metal ions are well recognized¹⁻³; since polyamines form complexes with a restricted set of metal ions, they are useful as selective titrants. For example, trien (triethylenetetramine) as a titrant was described by REILLEY AND SHELDON², who detected end-points by metallochromic indicators or potentiometrically with a mercury electrode. WILKINS AND HIBBS⁴ used trien to titrate copper in brass and bronze. End-points in metal ion titrations with trien have been detected photometrically. FLASCHKA AND SOLIMAN⁵ used this technique to determine copper in the presence of several metal ions; the formation of the colored copper-trien complex was followed in the spectrophotometer.

The selectivity offered by photometric titration was illustrated by FRITZ AND PIETRZYK⁶, who titrated scandium in presence of rare earths, uranium(IV), aluminium, and most transition metals with EDTA. In some cases up to 70:1 mass ratios of metal ion to scandium caused no interference. UNDERWOOD devised methods for the photometric EDTA titration of copper and iron(III) mixtures⁷ and bismuth⁸. MALMSTADT AND GOHRBRANDT⁹ determined thorium. In all of these methods the end-point was detected by the formation of the copper-EDTA complex. Other methods illustrating selectivity are reviewed by HEADRIDGE¹⁰.

REILLEY AND SHELDON² determined the stability constants of several metal-trien complexes. The log K values for mercury(II) and copper(II) are 25.0 and 20.1 respectively. Since the mercury complex is colorless at 580 m μ and the copper complex absorbs at 580 m μ , the difference in complex strength should be sufficient for the copper ion to be used as an indicator for the photometric titration of mercury with trien. However, REILLEY AND SHELDON² and RINGBOM¹ point out that comparisons according to log K values can be misleading. One should compare effective formation constants, which take into account competitive equilibria such as metal ion hydrolysis, complexing action of buffers, and the effect of pH. If one computes the effective constants for mercury and copper, a reversed order is found, *i.e.* $\log K_{E\text{Hg}} > \log K_{E\text{Cu}}$. This reversal problem was corrected by adding another complexing agent, iminodiacetic acid, which formed complexes with both mercury and copper, the copper complex being the stronger. The stability constants of these complexes were weaker than the corresponding trien complexes. Thus, with the selective chelating agent present, the effective constants were reversed again to the order $\log K_{E\text{Hg}} > \log K_{E\text{Cu}}$.

EXPERIMENTAL

Apparatus

Measurements were made in a modified Beckman Model B spectrophotometer as described by FRITZ AND PIETRZYK⁶. The titration cells used were 180-ml tall-form beakers with a path length of approximately 4.5 cm.

Reagents

Trien (triethylenetetramine). Trien (Eastman Kodak) was purified by crystallization as the bisulfate². To prepare a 0.05 *M* solution, ca. 17 g were dissolved in 1 l of distilled water containing 2 moles of sodium hydroxide. The solution was standardized by photometric titration of a standard mercury solution as described below.

IDA (iminodiacetic acid) solution, 0.1 M. 13.3 g of IDA (Dow Chemical Company) were dissolved in 1 l of distilled water.

Mercury(II) nitrate solution, 0.05 M. 16.2 g of mercury(II) nitrate (Mallinckrodt Analytical Reagent) was dissolved in 20 ml of concentrated nitric acid and a small volume of distilled water; the solution was diluted to 1 l. The solution was standardized against standard EDTA with methyl thymol blue indicator¹¹ or potentiometrically with the mercury electrode¹².

Buffer. A 0.1 *M* sodium acetate–0.1 *M* acetic acid solution was prepared.

Metal ions. Copper nitrate used as indicator and metal ion salts (nitrate or sulfate) used in the interference study were of the best grade available.

Procedure

The concentrations suggested in this procedure are adapted for a path length of 4.5 cm and an initial volume of 100 ml.

Dissolve a sample containing 0.15–0.45 mmoles of mercury in nitric acid in the titration cell. Add 1 ml of 0.06 *M* cupric nitrate and 10 ml of buffer and adjust to pH 4.7–5.0 with solid sodium acetate if needed. Add 0.15–0.45 mmoles of IDA (adjust to the concentration of mercury) and dilute to 100 ml. Place the cell in the cell compartment and insert a 10-ml buret containing 0.05 *M* trien through the lid until the tip is just under the surface of the liquid. Turn the stirrer on and set the absorbance at an arbitrary point, for example, zero and wavelength at 580 $m\mu$. Add titrant in small increments and record the absorbance reading. Special attention should be given to points during the first half of the mercury titration and last half of the copper titration. Correct the absorbance readings for dilution if large volumes of titrant are used and determine the end-point graphically. Best accuracy is obtained if the trien is standardized against standard mercury by this procedure.

RESULTS AND DISCUSSION

The selection of the optimum pH of 4.7–5.0 was influenced by two factors. Firstly, the color formation of the copper–trien complex limited the pH range. Absorption curves of the complex at various pH values showed a broad absorbance maximum at about 580 $m\mu$ which remained stable over the pH range 4.5–9.5. (See FLASCHKA AND SOLIMAN⁵ for a detailed discussion of the absorbance properties of the copper–trien complex.) On the other hand, the titration of mercury with trien is also influ-

enced by pH. The optimum pH for the titration on the basis of effective formation constants² is about 7.

At the chosen pH of 4.7–5.0, a simple acetate buffer was suitable, and the possibilities of precipitation of metals were reduced. At a higher pH a nitrogen type buffer would be necessary which would result in considerable color formation as well as an additional competitive equilibrium.

At pH 5.0 the calculated effective formation constants for mercury–trien and copper–trien are 7.0 and 8.8, respectively, which is a reversal of the log K values². A pH-controlled differential titration is therefore not possible, nor under ordinary conditions could copper be used as an indicator for the photometric titration of mercury. One would expect on the basis of the effective constants and mass action that the initial additions of trien would react predominantly with the copper. In terms of a photometric titration in which the formation of the purplish-blue copper–trien complex is followed, a titration curve such as A (no IDA) in Fig. 1, would be measured; the absorbance rises immediately indicating the formation of the copper–trien complex and as more trien is added, the curvature indicates titration of copper and mercury, until finally all the copper is complexed and the absorbance levels off. The amount of trien added to this point is equivalent to the sum of mercury and copper present, and mercury could be determined if a measured amount of standard copper solution were added.

It would be better if the copper–trien complex had a lower effective constant than the mercury–trien complex, so that mercury would be titrated first and then

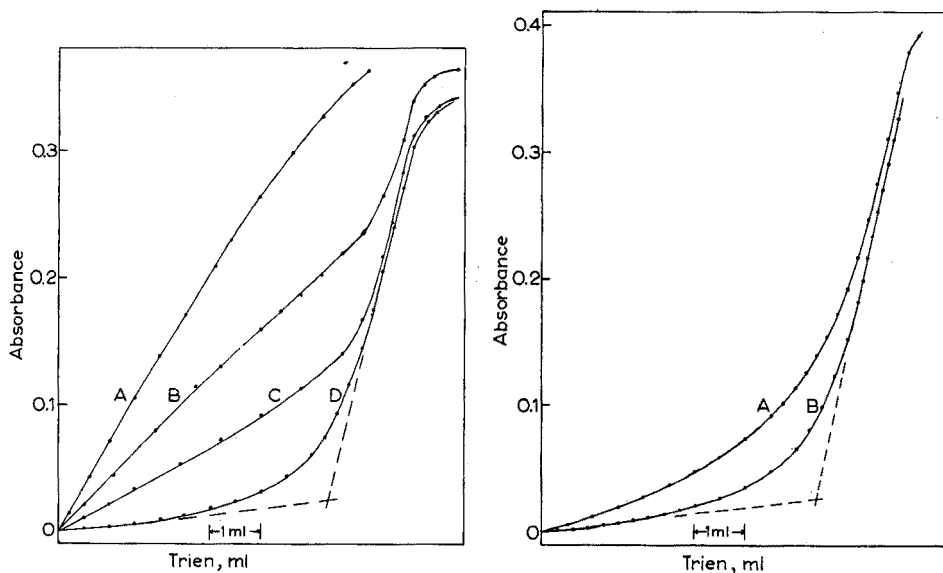


Fig. 1. The effect of IDA concentration on the photometric titration of mercury. (A) No IDA; (B) 0.03 mmole IDA; (C) 0.05 mmole IDA; (D) 0.15 mmole IDA.

Fig. 2. Photometric titration of mercury in the presence of cobalt. (A) 0.1 mmole IDA; (B) 0.3 mmole IDA.

the absorbance would increase as the copper was titrated. This would be possible with a reagent which would form a stronger complex with copper than with mercury, both complexes being weaker than the trien complexes; the effective constant of the copper–trien complex would thus be reduced more than the constant of the mercury–trien complex. BJERRUM *et al.*¹³ list stability constant data for the copper and mercury complexes of methyliminodiacetic acid as $\log \beta_2 = 18$ and 9, respectively. A readily available reagent of similar structure is iminodiacetic acid (IDA), for which $\log \beta_2$ for copper is 16 and no data are given for mercury¹³; however, one would expect a corresponding lower value for mercury. The effect of IDA on the photometric titration of mercury is illustrated in Fig. 1; as more IDA is added, the curve approaches the dashed line, which illustrates the usual extrapolation for the end-point.

The optimum concentration of IDA was found to be about equivalent to the total concentration of mercury and copper present, although the permissible range was large. For example, in the outlined procedure if the sample contained 0.31 mmole of mercury and copper (0.25 and 0.06 mmoles, respectively), 0.15–5 mmoles of IDA could be used. If the concentration of IDA was too low, the titration curve had a considerable curvature in the vicinity of the end-point.

Since the copper served only as an indicator, the amount necessary was small. Further, when too much copper was present, the mercury was not titrated first in the presence of IDA. (In the absence of IDA even with mass ratios of 10:1 mercury to copper, copper was still titrated first or at least along with the mercury.) The concentration in the procedure, about 10:1 mercury to copper, is suggested for a path length of 4.5 cm and an initial volume of 100 ml. Increased path length and decreased volume would allow titration of smaller amounts of mercury.

Interference study

Data for the titration of individual synthetic mercury samples and mercury–metal mixtures are presented in Table I. The accuracy with which mercury could be determined by the method was limited somewhat by the necessity of graphical location of the end-point; it also depended on the quantity and type of foreign cation present. The average error for all titrations was about 1% relative.

The concentration of IDA was important when possible interferences were present. IDA forms complexes with many metals, which is helpful in that precipitation is prevented, but copper is thus freed, causing considerable curvature in the titration curve and therefore poor accuracy. Figure 2 illustrates the effect of IDA concentration on the titration of mercury in the presence of cobalt; 0.3 mmole IDA was necessary to obtain accurate end-point extrapolation. In the case of all the other metals listed as noninterfering in Table I, 0.3 mmole of IDA was sufficient. With higher concentrations of lanthanum or calcium (10:1), and silver (30:1), poor results were obtained. In the first two cases low results were found while in the latter case high results were found; moreover, silver acetate began to precipitate at higher silver concentrations if excessive buffer was used. Larger concentrations of most of the other metals in Table I, although not tested, could probably be tolerated.

Of the metals tested, interferences were caused by nickel (absorbance varied with time), iron and bismuth (precipitation at this pH), and lead (lead sulfate formed during the titration). If the trien were purified by the nitrate method², lead would not interfere. The principal interfering anion was chloride, which had to be absent.

TABLE I

TITRATION OF MERCURY IN THE PRESENCE OF OTHER METALS

<i>Metal present</i>	<i>Mole ratio metal:Hg</i>	<i>mg Hg taken</i>	<i>mg Hg found</i>
—	—	37.7	37.8
—	—	50.2	50.3
—	—	62.8	62.1
—	—	75.4	75.4
—	—	87.9	88.5
Co	5:1	50.2	50.5
Cd	5:1	50.2	50.0
Cd	10:1	48.9	48.8
Cd	20:1	48.9	48.2
Zn	5:1	50.2	50.1
Zn	10:1	50.2	50.7
Zn	20:1	48.9	48.9
UO ₂ (II)	5:1	48.9	50.2
Ag	5:1	50.2	50.1
Ag	10:1	48.9	49.0
Ag	20:1	48.9	50.5
Mn	5:1	50.2	50.0
Mn	10:1	48.9	49.4
Mg	5:1	48.9	48.6
Mg	10:1	48.9	48.9
Mg	25:1	50.2	49.7
Ca	5:1	50.2	50.2
Al	5:1	48.9	49.5
Al	10:1	48.9	48.8
Al	20:1	48.9	48.5
La	5:1	48.9	48.3

SUMMARY

A mercury(II) solution containing copper ion can be titrated photometrically at pH 4.7 with triethylenetetramine solution (trien) after the addition of iminodiacetic acid (IDA); IDA causes a reversal of the effective formation constants of Hg-trien and Cu-trien and permits the titration. Copper-trien which absorbs at 580 $m\mu$ serves as the indicator for the titration. Mercury can be determined in presence of many other metals with an accuracy of about 1%; the main interferences are iron(III), nickel, bismuth and chloride ion.

RÉSUMÉ

On décrit une méthode de titrage photométrique, à pH 4.7, du mercure(II), en présence de cuivre, au moyen de triéthylènetétramine (trien), après addition d'acide iminodiacétique. Le cuivre-trien sert d'indicateur. Le mercure peut ainsi être dosé en présence de nombreux autres métaux, avec une précision d'environ 1%. Les principaux ions gênants sont: Fe(III), Ni, Bi et chlorure.

ZUSAMMENFASSUNG

Eine Quecksilber(II)-Lösung, die Kupferionen enthält, kann photometrisch beim pH-Wert 4.7 mit Triäthyltetraamin-Lösung (Trien) nach Zugabe von Imino-diessigsäure (IDA) titriert werden. IDA verursacht eine Umkehrung der effektiven Bildungskonstanten des Hg-Triens und Cu-Triens und erlaubt somit die Titration. Kupfertrien, das bei 580 μ absorbiert, dient als Indikator für die Titration. Quecksilber kann in Gegenwart von vielen anderen Metallen mit einer Genauigkeit von etwa 1% bestimmt werden. Störungen treten durch Eisen(III), Nickel, Wismut und Chloridionen auf.

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ANALYSIS FOR AROMATIC COMPOUNDS ON PAPER AND THIN-LAYER
CHROMATOGRAMS BY SPECTROPHOTOPHOSPHORIMETRY
APPLICATION TO AIR POLLUTION

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The direct spectrophosphorimetric analysis for polycyclic aromatic and heterocyclic hydrocarbons and their polar derivatives on paper or thin-layer chromatograms would simplify the identification of these derivatives in polluted air and other complicated mixtures. Such a procedure would save time and allow the use of a wide variety of solvents and reagents, whereas the usual spectrophosphorimetric procedure is limited to neutral solvents and to extracted solutions of the spots. Thus, spectra could be determined in neutral, alkaline, acid, reducing, or oxidizing media. Organic synthetic reactions can be performed on the unknown spot, and use of this wide variety of reactions would greatly increase the amount of data available for the characterization of unknowns.

The acquirement of phosphorimetric spectra from glass-fiber and other types of paper is described in this paper. The method is applied to the phosphorimetric study of fractions obtained from complex airborne particulate and air pollution source mixtures after column and paper chromatographic separations.

EXPERIMENTAL

Reagents and equipment

The chemicals were obtained from commercial sources in their purest form. Any chemicals that were found to contain impurities were purified by crystallization. All solvents were distilled before use.

The solvent systems used in the paper chromatographic work were formamide-water (35:65, v/v) and dimethylformamide-water (35:65, v/v). The solvent used to obtain solution spectra in a cell was EPA, a mixture of diethyl ether, isopentane and ethanol in volume ratio of 5:5:2.

Circular paper chromatography was performed with a Kaweran Circular Chromatography Apparatus with specially cut circles of filter paper, all supplied by Consolidated Laboratories, Inc., Chicago Heights, Illinois. With a dish of 26 cm diameter, a run required 2-3 h; with a dish of 14 cm diameter, 1-2 h. A Petri dish pair with a glass-fiber wick and Whatman No. 1 paper could also be used in the chromatography.

Phosphorimetric work was done with an Aminco-Keirs spectrophosphorimeter Slit arrangement No. 3, as described in the Aminco manual, was used throughout.

Phosphorimetric procedure

The first step after chromatography was to cut out the separated spot, which could be on paper, glass-fiber paper, or a thin-layer chromatogram. The thin-layer plates used in the TLC work were sheets of a 0.015-in. thick vinyl plastic, VSA-3310 clear 31 Matte 06, obtained from the Union Carbide Corp. of Cincinnati, Ohio. The plastic sheet was coated with a 500- μ layer of cellulose before use. A 5 \times 8 mm slice of the chromatogram was placed in the open end of a quartz sample tube (I.D. = 5 mm). This tube was positioned upside down in the cell compartment so that the spot to be examined was in the light beam and perpendicular to it. The tube could be turned to other positions with the spot in the light beam so that maximum intensity could be obtained at the wavelength maximum; when this was done, however, the blank usually gave greater interference. The perpendicular position was selected because it gave good sensitivity, the blank interference was smaller, the position was reproducible, and the bubbles from the open end of the tube did not pass through the light beam.

For the determination of the phosphorescence spectra of known compounds on glass-fiber paper, the diameter of the spot was kept at about the slit length of the light beam (about 6 mm). For standard substances 0.01 ml of solution was used.

RESULTS

Paper chromatography

With the aqueous formamide system unsubstituted aza heterocyclic hydrocarbons are separated in the following order of decreasing adsorbability: dicyclic, tricyclic, tetracyclic pericondensed, tetracyclic linear or angular, pentacyclic pericondensed, pentacyclic linear or angular, and hexacyclic compounds (Table I). The latter two types of compounds are best separated by aqueous dimethylformamide. The parent compounds are separated readily from their monoalkyl and dialkyl derivatives, *e.g.*, R_F values of benz(c)acridine and its 7-methyl and 7,10-dimethylbenz(c)acridine are 0.44, 0.34, and 0.22 respectively. Polynuclear aromatic hydrocarbons such as benzo(e)pyrene and perylene remain at the origin in the aqueous formamide system.

Spectrophosphorimetry on an adsorbent

Examination of the data in Table II indicates that certain definite classes of compounds give phosphorescence spectra that are much more intense and fine-structured than the adsorption and fluorescence spectral curves of the same compounds. The compounds that give the most intense phosphorescent spectra are aromatic molecules absorbing below 370 m μ and polar compounds such as ring carbonyl, aromatic carbonyl, and quinonic and nitro derivatives. These are the types of compounds for which methods of separation from complex mixtures and of characterization have not yet been developed.

Most of the compounds examined show little or no phosphorescence when they are present on glass-fiber paper as dry spots. Two exceptions are 4-hydroxyacetophe-

TABLE I

PAPER CHROMATOGRAPHIC R_F VALUES OF AZA HETEROCYCLIC HYDROCARBONS

Compound	Formamide-water (35 : 65, v/v)	Dimethylformamide-water (35 : 65, v/v)
Acridine	0.78	0.85
Benzo(f)quinoline	0.78	0.87
Benzo(h)quinoline	0.78	0.87
Phenanthridine	0.75	0.85
3-Methylbenzo(f)quinoline	0.72	0.85
3-Methylacridine	0.67	0.84
Acenaphtho(1,2-b)pyridine	0.62	0.84
Indeno(1,2,3-ij)isoquinoline	0.62	0.84
Benzo(lmn)phenanthridine	0.60	0.81
Benz(a)acridine	0.44	0.78
Benz(c)acridine	0.44	0.78
7-Methylbenz(c)acridine	0.34	0.73
7,10-Dimethylbenz(c)acridine	0.29	0.66
Pyrenoline	0.28	0.67
7,9-Dimethylbenz(c)acridine	0.22	0.64
Dibenz(a,j)acridine	0.00	0.58
Dibenz(a,h)acridine	0.00	0.44
14-Phenyldibenz(a,j)acridine	0.00	0.44 ^a
7-Phenyldibenz(c,h)acridine	0.00	0.20

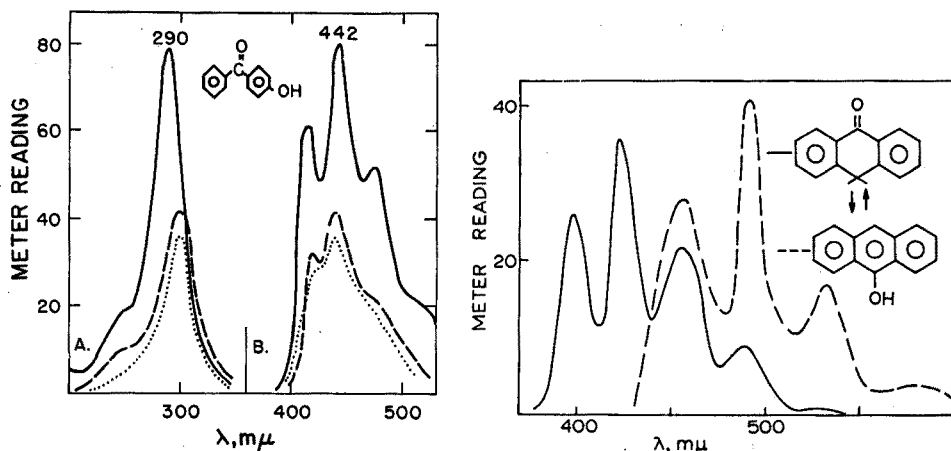
^a Tails.

Fig. 1. Phosphorescence spectra of 4-hydroxybenzophenone. $10^{-6}M$ in EPA solution at MM 0.01. (—) (A) Excitation spectrum at emission wavelength 442 $m\mu$. (B) Emission spectrum at excitation wavelength 290 $m\mu$. In EPA solution on glass-fiber paper at MM = 0.01. (A) Excitation spectra at emission wavelength 440 $m\mu$. (B) Emission spectra at excitation wavelength 300 $m\mu$. 10 ng wet with chloroform (----); 100 ng dry (.....).

Fig. 2. Phosphorescence emission spectra of anthrone (194 ng) on glass-fiber paper at MM 0.1. Wet with EPA (—); dry (----).

TABLE II
PHOSPHORESCENCE EXCITATION AND EMISSION SPECTRA OF AROMATIC COMPOUNDS IN EPA SOLUTION AND ON GLASS-FIBER PAPER

Compound	EPA			CHCl ₃ on paper				
	Det. limit (ng/0.1 ml)	Molarity	Spectra		Quantity (μg)	Spectra		
			Ex λ (MT)	Em λ (MT)		Ex λ (MT)	Em λ (MT)	
4-Hydroxyacetophenone	1.0	10 ⁻⁶	220(0.02)	4108 ^a (0.1)	0.5	0.001 ^c	288(0.1)	415 ^a (0.1)
			280 ^b (0.12)	430(0.12)			435(0.1)	
				4508(0.06)				
4-Nitroaniline	1.0	10 ⁻⁶	380(0.3)	510(0.3)	6.0	0.014	375(0.04)	530(0.04)
				530(0.2)				
				402(1.1)				
Benzophenone	0.9	10 ⁻⁶	257(1.7)	433(1.6)	10.0	180	260(0.2)	410(0.2)
				465(1.1)			435(0.22)	
				505(0.4)			4608(0.15)	
				415(0.8)			5108(0.05)	
				443(1.1)				
4-Hydroxybenzophenone	1.0	10 ⁻⁵	2508(0.2)	475(0.6)	1.0	0.01 ^d	2508(0.1)	420(0.3)
			290(1.1)	5158(0.07)			300(0.4)	440(0.4)
				485(0.16)				4728(0.2)
				510(0.18)				
				5408(0.09)				
2-Naphthol	70	10 ⁻⁴	230(0.18)	405(1.9)	70	0.14	230(0.07)	480(0.16)
			275(0.12)	430(2.5)			278(0.12)	516(0.16)
			328(0.19)	4758(1.6)			324(0.15)	550(0.07)
				4508(2.0)			2658(0.05)	4108(0.12)
				2678(1.4)			290(0.20)	430(0.20)
Anthracene	200	5·10 ⁻⁴	295(2.4)	485(0.09)	900	18.0	290(0.20)	460(0.20)
				530(0.045)			320(0.06)	485(0.10)
				578(0.006)				460(0.75)
				395(0.7)				492(1.4)
				425(1.0)				535(0.63)
Anthraquinone	1	10 ⁻⁶	248(0.1)	485(0.04)	2	0.21	249(1.0)	402(0.6)
			2708(0.05)	578(0.006)			270(1.1)	430(0.7)
			320(0.04)	395(0.7)			330(1.4)	460(0.4)
				425(1.0)				495(0.15)
				305(0.4)				5408(0.03)
Anthrone	0.1	10 ⁻⁵	265(0.9)	455(0.6)	2	0.02 ^e	275(0.7)	459(0.07)
			295(0.4)	490(0.2)			310(0.5)	490(0.06)
			305(0.4)	530(0.05)				528(0.04)
Benzo(f)quinoline	9	10 ⁻⁵	2458(0.60)	455(0.78)	20	0.018	270(0.10)	459(0.07)
			270(1.0)	488(0.87)			2908(0.09)	490(0.06)
			2908(0.65)	525(0.4)			320(0.06)	528(0.04)
			330(0.36)				340(0.06)	
			340(0.45)					

Compound	EPA			CHCl ₃ on paper				
	Det. limit (ng/0.1 ml)	Molarity	Spectra		Det. limit (ng)	Quantity (μg)	Spectra	
			Ex λ (MT)	Em λ (MT)			Ex λ (MT)	Em λ (MT)
Benzo(h)quinoline	20	10 ⁻⁵	275(0.69)	460(0.38)	200	1.8	270(0.09)	460(0.04)
			330(0.17)	490(0.65)			325(0.03)	490(0.04)
			340(0.20)	530(0.25)			340(0.03)	530(0.02)
			565S(0.05)				550S(0.003)	
10,11-Dihydro-5H-dibenzo(a,d)- cyclohepten-5-one	2	10 ⁻⁶	268(0.11)	430(0.08)	1.0	0.2 ^e	270(0.8)	432(0.6)
			290S(0.05)	460(0.11)			290S(0.6)	460(0.7)
				495(0.08)			340(0.1)	490S(0.5)
				535S(0.03)				525S(0.2)
2-Nitrofluorene	10	10 ⁻⁵	240(0.05)	485(0.56)	1.0	0.02	250(0.015)	495(0.11)
			340(0.6)	517(0.59)			340(0.12)	522(0.12)
				550(0.24)				555S(0.07)
Phenanthrene	1	10 ⁻⁵	255(0.2)	460(0.18)	18	0.18	255(0.2)	460(0.2)
			270S(0.15)	497(0.18)			278(0.19)	497(0.19)
			290(0.13)	532(0.09)			285(0.2)	532(0.08)
				570S(0.02)				570S(0.02)
Phenanthridine	20	10 ⁻⁵	250(0.54)	455(0.41)	20.0	0.09	255(0.06)	455(0.06)
			290(0.22)	485(0.53)			295(0.06)	485(0.06)
			328(0.08)	520(0.32)			326(0.03)	520S(0.04)
			340(0.09)	550S(0.09)			340(0.03)	555S(0.01)
6-Aminochrysene	200	10 ⁻⁴	280(0.11)	545(0.13)	2000.0	12.0 ^f	280(0.02)	548(0.05)
			355(0.13)	585S(0.05)			348(0.05)	585S(0.02)
			398S(0.04)				375S(0.03)	
Benz(a)acridine	1000	10 ⁻⁴	250S(0.02)	562(0.04)	200.0	0.58	250S(0.016)	570(0.05)
			285(0.05)	610(0.006)			290(0.05)	610S(0.006)
			338S(0.025)				335S(0.03)	
			340(0.03)				350S(0.04)	
			362(0.03)				360(0.05)	
		380(0.033)		385(0.05)				
Benz(c)acridine	1000	10 ⁻⁴	285(0.16)	565(0.16)	300.0	2.3	285(0.2)	569(0.2)
			335S(0.08)	610(0.02)			335S(0.08)	615(0.02)
			345(0.09)				345(0.09)	

TABLE II (continued)

Compound	EPA		CHCl ₃ on paper			
	Det. limit (ng/0.1 ml)	Molarity	Spectra		Quantity (μg)	Spectra
			Ex λ (MT)	Em λ (MT)		
Benzo(b)fluoranthene	100	5·10 ⁻⁴	360(0.09)		3000.0	360(0.09)
			380(0.10)			380(0.09)
Triphenylene	2	10 ⁻⁶	300(2.5)	525(4.0)	2	300(0.05)
			350(3.5)	570(2.1)		350(0.065)
			255(0.17)	435s(0.04)		255(0.13)
			280s(0.08)	460(0.17)		280(0.09)
				489(0.06)		
	515s(0.01)	515s(0.02)				
Benzo(e)pyrene	100	10 ⁻⁴	290(0.64)	532(0.66)	10	290(0.15)
			320s(0.61)	580(0.23)		320s(0.16)
			330(0.7)			330(0.18)
5,12-Dihydro-5-naphthacene	100	10 ⁻⁵	250s(0.05)	516(0.1)	80	250s(0.07)
			285s(0.1)	555(0.07)		285s(0.2)
			290(0.1)			292(0.23)
			310(0.06)			310(0.17)
			370s(0.024)			370s(0.12)
			387(0.030)			390(0.2)
	405(0.030)	405(0.2)				
Indole	59	10 ⁻⁴	220(0.27)	405(0.66)	6	256s(0.12)
			280(0.90)	430(1.10)		282(0.14)
				450(0.75)		300s(0.08)
		480s(0.36)				
Tryptophan ^g	2000.0	10 ⁻⁴	225(0.10)	410(0.08)	20	228(0.15)
			280(0.12)	435(0.12)		289(0.34)
				455s(0.08)		455s(0.18)

^a s = Shoulder.

^b Values in italics are excitation (or emission) wavelengths used to obtain emission (or excitation) spectra.

^c Dry spectra same as wet but 1/10 intensity.

^d Dry spectra are 1/10 intensity of wet, and emission spectrum shows only one band at 440 mμ.

^e Dry spectra changed in that the emission spectral bands at 402 and 430 mμ disappear.

^f Dry spectra same as wet.

^g Trace of hydrochloric acid necessary to dissolve the tryptophan.

none and 4-hydroxybenzophenone, which are therefore more readily characterized. The compounds that do show phosphorescence in the dry state give less intense spectra in that state than in solution or in the wet state on paper. An example of this phenomenon is shown in Fig. 1 for 4-hydroxybenzophenone. The drastic changes that can occur in the phosphorescence spectra of a compound in solution as compared to the compound in the dry state on glass-fiber paper are shown in Fig. 2. In EPA or alcohol on paper or in EPA in a cell, anthrone shows 5 bands ranging from 400 to 530 $m\mu$. This is probably the spectrum of the anthrone tautomer, for MEYER has shown that in alcoholic solution 89% of the anthrone tautomer is present¹. The spectrum of the same spot in the dry state shows 4 prominent bands ranging from 455 to 580 $m\mu$. This is probably the spectrum of the anthrol tautomer. Since the latter spectrum is closely similar to that of wet anthraquinone, the hypothesis needs further study.

Tautomers could not be found for the analogous 5,12-dihydro-5-naphthacene. This compound gave no phosphorescence spectra in the dry state on glass-fiber paper or even in the presence of sulfuric acid. Enolization has not been detected for this compound².

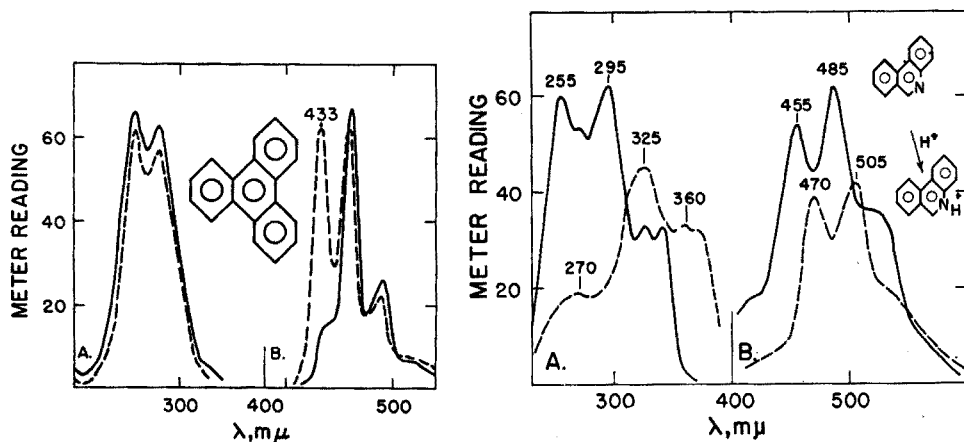


Fig. 3. Phosphorescence spectra of triphenylene (0.2 μg) on glass-fiber paper. MM = 0.03. (A) Excitation spectra at emission wavelength 460 $m\mu$. (B) Emission spectra at excitation wavelength 258 $m\mu$. Wet with EPA (—); wet with CHCl_3 (---).

Fig. 4. Phosphorescence spectra of phenanthridine on glass-fiber paper. 0.09 μg wet with chloroform at MM 0.001. (—) (A) Excitation spectra at emission wavelength 485 $m\mu$. (B) Emission spectra at excitation wavelength 295 $m\mu$. 0.9 μg wet with trifluoroacetic acid at MM 0.003. (---) (A) Excitation spectra at emission wavelength 505 $m\mu$. (B) Emission spectra at excitation wavelength 325 $m\mu$.

An example of a solvent effect is shown in Fig. 3. The emission spectrum of triphenylene on glass-fiber paper shows a band at 433 $m\mu$ when wet with chloroform but when the spot is moistened with EPA, the band disappears. This band is also missing in the spectrum of triphenylene obtained from its EPA solution in a cell. The band is present on glass-fiber paper when the spot is wet with solvents like isobutylamine, tetrachloroethane, carbon tetrachloride, dimethylsulfoxide, and

TABLE III

PHOSPHORESCENCE EXCITATION AND EMISSION SPECTRA OF AROMATIC COMPOUNDS IN ACID AND ALKALINE SOLUTION ON GLASS-FIBER PAPER

Compound	Solvent	Det. limit (ng)	Quantity (μ g)	Spectra ^a			
				Ex λ	(MT)	Em λ	(MT)
4-Hydroxyacetophenone	H ₂ SO ₄	1	0.02	330	(0.33)	470	(0.35)
4-Hydroxyacetophenone	TEA ^b	7	0.02	320	(3.7)	440 460s	(3.7) (3.5)
Benzophenone	H ₂ SO ₄	9	0.02	340	(0.11)	455 476	(0.11) (0.11)
4-Hydroxybenzophenone	H ₂ SO ₄	2	0.1	298s 360	(0.25) (0.8)	482 495s	(0.8) (0.8)
4-Hydroxybenzophenone	TEA	10	0.1	335	(0.6)	475	(0.6)
Azulene	TFA ^c or H ₂ SO ₄	100	1.3	260 350	(0.08) (0.3)	482 512	(0.3) (0.3)
Benzo(f)quinoline	TFA or H ₂ SO ₄	200	0.18	280 355s 370	(0.08) (0.12) (0.13)	480 512 550s	(0.08) (0.07) (0.02)
Anthrone	H ₂ SO ₄ or TFA	4	0.20	275 350	(0.18) (1.5)	500	(1.5)
10,11-Dihydro-5H-dibenzo- (a,d)cyclohepten-5-one	H ₂ SO ₄	10	0.21	292 350	(0.09) (0.4)	520	(0.4)
10,11-Dihydro-5H-dibenzo- (a,d)cyclohepten-5-one	TFA	20	0.21	283s 312	(0.3) (0.44)	450s 482	(0.3) (0.44)
Phenanthridine	TFA	20	0.90	270 325 360 370s	(0.05) (0.12) (0.09) (0.09)	470 505 540s	(0.1) (0.1) (0.05)
6-Aminochrysene	H ₂ SO ₄ or TFA	100	1.2	272 310	(0.37) (0.36)	510 542	(0.39) (0.28)

^a Values in italics are excitation (or emission) wavelengths used to obtain emission (or excitation) spectra. s = Shoulder.

^b TEA = 29% methanolic tetraethylammonium hydroxide.

^c TFA = trifluoroacetic acid.

ethylene bromide; it is absent when the spot is wet with cyclohexane, dimethylformamide, ethanol, and triethylamine. The 430-m μ band shows up when the adsorbent is alumina from a thin-layer chromatogram treated with Neatan, even when the spot is wet with EPA.

The similarity of the phosphorescence spectra in EPA solution to the spectra on glass-fiber paper holds even for a compound as polar as 6-aminochrysene. The phosphorescence emission spectrum of this amine on glass-fiber paper treated with trifluoroacetic acid fumes is closely similar to the emission spectrum of chrysene either in solution or on paper.

The phosphorescence spectra of the smaller aza heterocyclic compounds and their cationic salts can be also obtained on paper (Fig. 4). The neutral spectra are closely similar to those obtained in EPA solution (Table II). The azulene cationic salt was also found to be phosphorescent (Fig. 5). The solvent on the glass-fiber paper can be either sulfuric or trifluoroacetic acid.

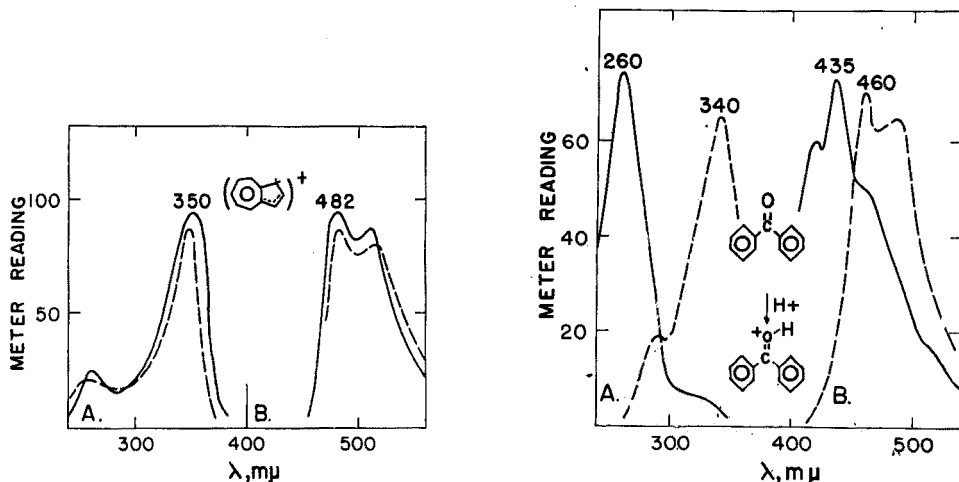


Fig. 5. Phosphorescence spectra of 1.28 μg azulene on glass-fiber paper at MM 0.003 in sulfuric acid (—) and trifluoroacetic acid (---). (A) Excitation spectra at emission wavelength 482 $\text{m}\mu$. (B) Emission spectra at excitation wavelength 350 $\text{m}\mu$.

Fig. 6. Phosphorescence spectra of 0.18 μg benzophenone on glass-fiber paper. Wet with chloroform (—). (A) Excitation spectrum at emission wavelength 440 $\text{m}\mu$. (B) Emission spectrum at excitation wavelength 260 $\text{m}\mu$. Wet with sulfuric acid (---). (A) Excitation spectrum at emission wavelength 480 $\text{m}\mu$. (B) Emission spectrum at excitation wavelength 342 $\text{m}\mu$.

With aromatic carbonyl compounds the spectra of the neutral compound and the cationic salt can be obtained. For example, with benzophenone the change in spectra obtained by adding a drop of sulfuric acid is very striking (Fig. 6).

With hydroxycarbonyl compounds phosphorescence spectra of the neutral, cationic, and anionic salts can be obtained, as shown for 4-hydroxybenzophenone (Fig. 7). These types of spectra should be of help in characterizing some of the unknown carbonyl compounds present in auto exhaust particulates.

Phosphorescence emission spectra are less sensitive than the excitation spectra to impurities and concentration effects. In the more concentrated solutions the shortest wavelength band in some excitation spectra is reduced in intensity relative to the other bands as the concentration of the examined compound increases.

Of all the various adsorbents tried as a supporting "cell" for the determination of phosphorescence spectra, glass-fiber paper was most useful since it gave the least phosphorescent blank.

It must be emphasized that phosphorescence spectra of anionic and cationic

salts are much more readily obtained on paper or on thin-layer chromatograms than in solution. When spectra are obtained on an adsorbent a wide variety of solvents can be used. The usual cell method requires the use of solvent mixtures that form transparent non-cracking glasses; on an adsorbent, however, any solvent can be used

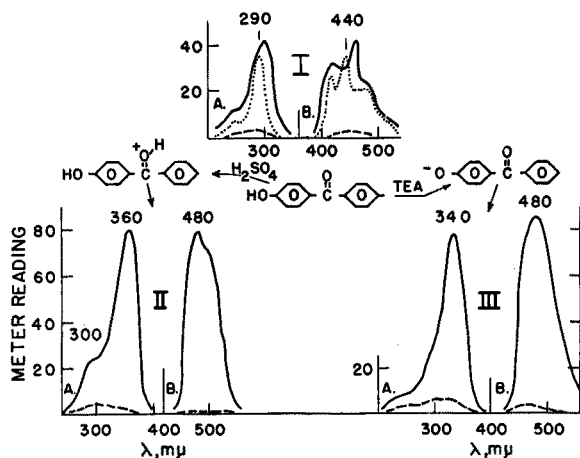


Fig. 7. Phosphorescence spectra of 4-hydroxybenzophenone. (A) Excitation spectra at most intense emission wavelength maximum. (B) Emission spectra at most intense excitation wavelength maximum. (I) 0.01 μ g on glass-fiber paper wet with chloroform. MM = 0.01 (—); $10^{-5}M$ in EPA solution. MM = 0.03 (·····); blank (---). (II) 0.1 μ g on glass-fiber paper wet with sulfuric acid. MM = 0.01 (—); blank (---). (III) 0.001 μ g on glass-fiber paper wet with 29% methanolic tetraethylammonium hydroxide (—); blank (---).

as long as the phosphorescence due to the solvent is negligible. In addition an unknown compound on a paper or thin-layer chromatogram can be reacted with some reagent to form a new derivative with a more characteristic and intense phosphorescence spectrum. These techniques should be extremely useful in the analysis of fractions after chromatographic separation of complex mixtures.

APPLICATION

Phosphorimetric analysis following column chromatography

Fractions obtained from alumina column chromatography of an urban airborne particulate sample³ were analyzed spectrophosphorimetrically in EPA solution and on paper. One fraction contained aliphatic hydrocarbons and monocyclic, dicyclic, tricyclic, and tetracyclic aromatic hydrocarbons. The excitation and emission spectra of phenanthrene were readily obtained from this fraction. The excitation spectrum of the fraction was identical to the excitation spectrum of a partially quenched phenanthrene spectrum, *e.g.*, a band at 288 $m\mu$ with the 2 shorter wavelength bands quenched to a shoulder at 255 $m\mu$.

Benzo(e)pyrene was readily characterized in the benzpyrene fraction of urban airborne particulates (Fig. 8). The spectra of benzo(e)pyrene and the benzpyrene fraction were identical whether the spectra were obtained on glass-fiber paper moistened with chloroform or in a cell in EPA solution.

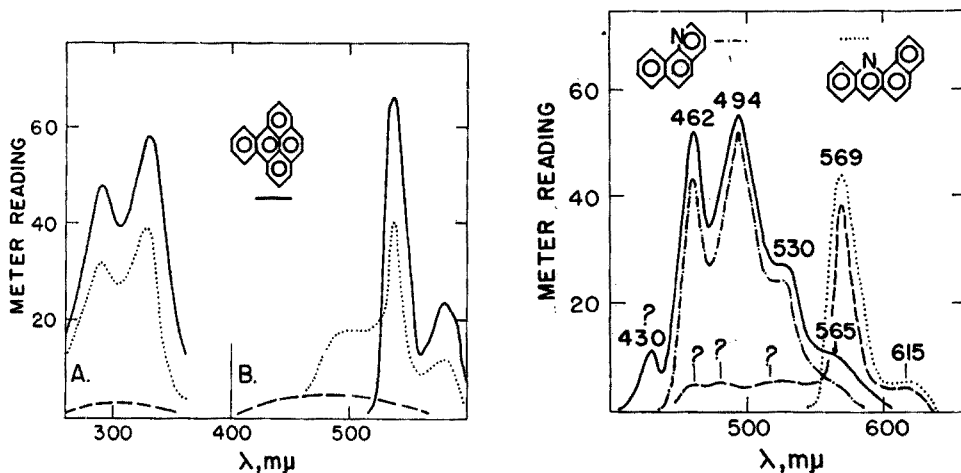


Fig. 8. Phosphorescence spectra on glass-fiber paper. Spots wet with chloroform. MM 0.003. Benzo(e)pyrene (0.25 μg) (—); benzpyrene fraction ($\cdots\cdots$); blank (---). (A) Excitation and (B) emission spectra obtained at most intense emission and excitation wavelength maxima, respectively.

Fig. 9. Phosphorescence emission spectra in chloroform on glass-fiber paper. Benzo(h)quinoline, 1.8 μg (---) MM 0.01, excitation wavelength 340 $\text{m}\mu$. Benz(c)acridine, 12.5 μg ($\cdots\cdots$) MM 0.003, excitation wavelength 383 $\text{m}\mu$. Column chromatographic subfraction of the basic fraction of coal tar pitch. At MM 0.01 and excitation wavelength 340 $\text{m}\mu$ (—). At MM 0.001 and excitation wavelength 383 $\text{m}\mu$ (----). Spectra in EPA solution were similar.

Basic fractions were also separated on the column and examined spectro-phosphorimetrically. For example, an early fraction containing sterically hindered aza heterocyclic hydrocarbons was obtained through chromatography of a basic fraction of a coal tar pitch sample by the alumina column chromatographic procedure³ but with greater percentages of ether in the developer. This fraction was examined on paper and in solution. The emission spectra of benzo(h)quinoline and benz(c)-acridine were obtained readily (Fig. 9). Clearcut excitation spectra for these compounds could not be obtained from this mixture without additional separation.

A later fraction obtained through column chromatography apparently contained benzo(f)quinoline as shown by the similarity of the phosphorescence emission spectrum to that of pure benzo(f)quinoline.

Phosphorimetric analysis following column and paper chromatography

A circular paper chromatogram of benzo(h)quinoline, benz(c)acridine, and a column chromatographic subfraction of the basic fraction of a coal tar pitch sample is

shown in Fig. 10. All of these spots in the Figs. were found in the same fraction in alumina column chromatography with pentane-ether solutions. With the cellulose system, pure benzo(h)quinoline and benz(c)acridine were readily separated while the subfraction was separated into at least 6 spots, 2 of which gave the R_F values and

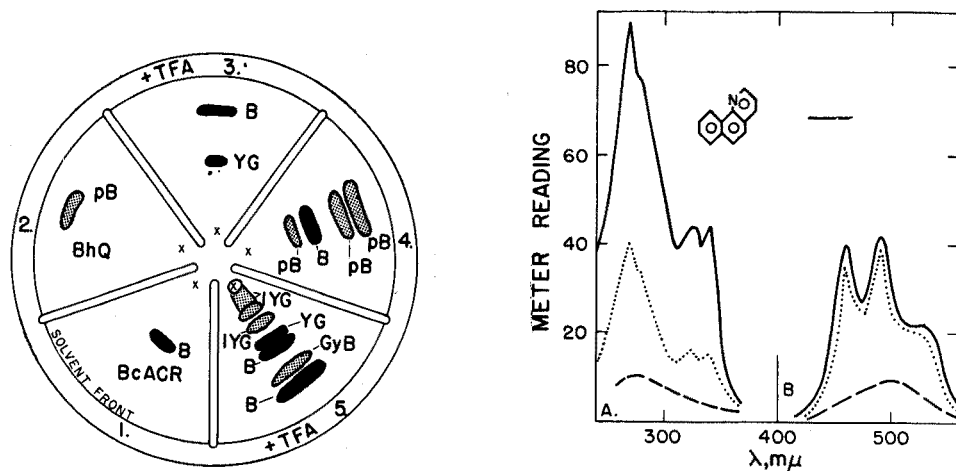


Fig. 10. Circular paper chromatograms of benz(c)acridine, $R_F = 0.44$ in runs 1 and 3, of benzo(h)quinoline in runs 2 and 3, and of a fraction (from the column chromatography of the basic fraction of a coal tar pitch sample) in runs 4 and 5. The fluorescence colors in runs 1, 2, and 4 are reported as seen in the ultraviolet light on the wet paper; in runs 3 and 5 fluorescence colors after treatment with trifluoroacetic acid fumes.

Fig. 11. Phosphorescence spectra on paper of $0.18 \mu\text{g}$ of benzo(h)quinoline wet with chloroform. $\text{MM} = 0.001$ (—). Paper chromatogram spot $R_F = 0.78$ wet with aqueous formamide. $\text{MM} = 0.003$ (· · · · ·). Blank paper with aqueous formamide. $\text{MM} = 0.003$ (- - - -).

fluorescence colors of benzo(h)quinoline and benz(c)acridine. The top spot was cut out and its phosphorescence spectra determined directly on the paper. The excitation and emission spectra were identical to that of pure benzo(h)quinoline (Fig. 11). It must be emphasized that the spot under benzo(h)quinoline and the 2 or 3 spots under benz(c)acridine are probably alkyl derivatives of these aza compounds. This is especially important in the latter case for the carcinogenic activity of 7-methylbenz(c)acridine is 3+ on the skin of an animal, while the activity of 7,9- and 7,10-dimethylbenz(c)acridine is 4+ on the skin and 3+ in subcutaneous tissue⁴. These dialkyl derivatives are about as potent carcinogenically as benzo(a)pyrene.

A circular paper chromatogram of benzo(f)quinoline, benz(a)acridine, and a column chromatographic subfraction of a basic fraction was run just as for the benzo(c)quinoline fraction. The separation of the benzo(f)quinoline subfraction gave 7 spots. The top spot, $R_F = 0.78$, was cut out and its phosphorescence spectra determined directly on the paper. The excitation and emission spectra were identical to the analogous spectra of pure benzo(f)quinoline. The R_F value of the spot believed to

contain benz(a)acridine was the same as for benz(a)acridine; the spot was nicely separated from all the other components of the mixture. The phosphorescence emission spectrum of this spot was very closely similar to the analogous spectrum of pure benz(a)acridine on paper.

The data in this paper show the potentialities of this quick simple method of analysis.

SUMMARY

A technique is introduced in spectrophosphorimetric analysis by means of which spectra can be obtained directly on an adsorbent after chromatography. Spectra of the phosphorescent compound, its salts, its reduced or oxidized forms, or its derivatives can be obtained in all types of solvents. Examples of this simple technique are given; detection limits range from 0.1 ng to μg amounts. A new system for the circular paper chromatographic separation of aza heterocyclic hydrocarbons using aqueous formamide is described. Many of these heterocyclic compounds can be separated from each other as can the parent compounds from their alkyl derivatives.

Air pollution mixtures separated by column and paper chromatography are analyzed with the phosphorimetric technique. Spots obtained on the paper chromatograms are analyzed directly in the phosphorimeter. With these techniques benzo(f)quinoline, benzo(h)quinoline, benz(a)acridine, benz(c)acridine, and hydrocarbons such as phenanthrene and benzo(e)pyrene are readily characterized.

RÉSUMÉ

Une technique par analyse spectrophosphorimétrique est présentée, à l'aide de laquelle des spectres peuvent être obtenus directement sur un adsorbant après chromatographie. Des exemples sont donnés. Limite de détection: de 0.1 ng à des teneurs de l'ordre du μg . On décrit un nouveau système pour la séparation chromatographique sur papier, circulaire, d'hydrocarbures aza-hétérocycliques, utilisant la formamide. En ce qui concerne la pollution de l'air, des mélanges ont été séparés par chromatographie sur colonne et sur papier et analysés par phosphorimétrie. Grâce à ces techniques, benzoquinoléines, benzacridines et hydrocarbures tels que phénanthrène et benzopyrène peuvent être rapidement caractérisés.

ZUSAMMENFASSUNG

Es wird eine Technik für die spektralphosphorimetrische Analyse eingeführt, mit der Spektren unmittelbar vom Adsorbens nach der Chromatographie erhalten werden können. Spektren der phosphoreszierenden Verbindung, seiner Salze, seiner reduzierten oder oxydierten Form oder seiner Derivate können bei Anwendung verschiedenster Lösungsmittel erhalten werden. Die Nachweisgrenzen liegen zwischen 0.1 ng bis zu Mikrogrammen. Ein neues System für die ringpapierchromatographische Trennung von azaheterocyclischen Kohlenwasserstoffen unter Anwendung wässrigen Formamids wird beschrieben. Viele dieser heterocyclischen Verbindungen können voneinander getrennt werden, ebenso die Stammverbindungen ihrer Alkylderivate. Durch Kolonnen- und Papierchromatographie getrennte Luftverunreinigungen

werden mit der phosphorimetrischen Technik analysiert. Flecken von Papierchromatogrammen werden direkt im Phosphorimeter analysiert. Mit dieser Technik werden folgende Verbindungen schnell charakterisiert: Benzo(f)chinolin, Benzo(h)chinolin, Benz(a)acridin, Benz(c)acridin und Kohlenwasserstoffe wie Phenanthren, Benzopyren.

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COMPLEX FORMATION OF IRON(III) WITH ERIOCHROME CYANINE R

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Some analytically important derivatives of fuchson (*e.g.* xylenol orange, chrome azurol S and eriochrome cyanine R) are characterized by containing 4 bond-forming groups equally apportioned between two benzene rings. As demonstrated^{1,2} for complexes with xylenol orange and independently³ for the system iron(III)–chrome azurol S, an essential feature of this group of ligands is that they react with metal ions to form (in addition to other species) ring complexes of the general composition A_2B_2 .

It was considered of interest to try to detect the presence of dimeric compounds in other systems than the two mentioned above, and in the present paper the interaction of iron(III) ions with eriochrome cyanine R is described.

Eriochrome cyanine R is commercially available as the di- or trisodium salt of 5- $[\alpha$ -(3-carboxy-5-methyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2-sulfobenzyl]-3-methylsalicylic acid*. In the present study the trisodium salt (chemical composition $C_{23}H_{15}O_9SN_3$ — in formulas designated Na_3HER) was employed as the starting material. From this impure compound, the tetrabasic acid (H_4ER) was prepared in a pure state. A possible structure of H_4ER in acid solution is shown in Fig. 1**. The dissociation constants of the acid have been determined by SUK AND MIKEŤUKOVÁ⁴, and their data were employed in the present investigation. (It should be noted that SUK AND MIKEŤUKOVÁ made their measurements on solutions having an ionic strength of 0.2 *M*, while in the present investigation measurements were made on solutions 0.1 *M* with regard to inert salt.)

Very few metal complexes with eriochrome cyanine R have been investigated

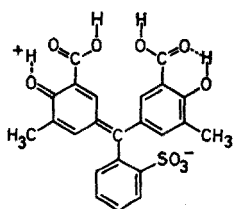


Fig. 1. Probable structure of the ligand in acid solution.

* Other designations: Mordant Blue 3, Colour Index (2nd edition) number 43820; Schultz-Lehmann: Farbstofftabellen (7th edition) number 722.

** In the present investigation it was assumed that H_4ER participated in the reactions as the zwitterion shown in Fig. 1.

with regard to composition and stability. SAKELLARIDIS AND ROUFOGALIS⁵ studied the complexes of gallium and indium using the method of continuous variation and found the mole ratio of both complexes to be 1 : 1. The colour lake with aluminium was suggested by MILLNER⁶ to have the composition $\text{Al}(\text{ER})_3$.

EXPERIMENTAL

Instruments and equipment

Extinction measurements were made with a Zeiss spectrophotometer PMQ II and a Beckman DB recording spectrophotometer. For measurements below 340 m μ 1-cm silica cells were employed; other measurements were made in 4-cm glass cells. These measurements were made at room temperature ($20 \pm 3^\circ$).

For the potentiometric titrations and for the measurement and adjustment of pH a Beckman Zeromatic pH meter (glass (pH range 0-11) and calomel electrodes) was used. The pH meter was standardized with 0.05 M potassium hydrogen phthalate (pH 4.00 at 20°). The titrations were done in a specially made double-walled titrating vessel, water from a thermostat being circulated through the jacket. Titrations were made at $20 \pm 0.1^\circ$.

Reagents

The eriochrome cyanine R used in the present study was specified by the producer (E. Merck) to be the trisodium salt. From this impure salt the pure tetrabasic acid was prepared. The spectrographically standardized iron sponge (Johnson, Matthey and Co., Ltd.) contained the following metallic impurities (given in p.p.m.): manganese-3; nickel-2; sodium-2; copper, magnesium, silicon and silver—each element < 1. As the product contained appreciable amounts of non-metals (probably oxygen), standard solutions could not be prepared by direct weighing. All other chemicals were of reagent-grade quality. Ordinary distilled water from an all-metal still was used.

Ionic strength

During the photometric measurements the ionic strength was kept approximately constant by maintaining a concentration of 0.1 M potassium chloride and low concentrations of ligand and metal ion.

Analysis of eriochrome cyanine R

A weighed sample of eriochrome cyanine R was transferred to a porcelain crucible previously ignited to constant weight at 850° , evaporated to dryness in the presence of concentrated sulfuric acid and ignited in the presence of ammonium carbonate. The crucible was finally ignited to constant weight at 850° . From the weight of the residue (assumed to consist of disodium sulphate) the content of sodium was calculated to 16.2%, against a theoretical value (calculated from the composition $\text{C}_{23}\text{H}_{15}\text{O}_9\text{SNa}_3$) of 12.86%.

Preparation of the tetrabasic acid

The tetrabasic acid was prepared from the impure trisodium salt as follows: 4.0 g of trisodium salt were dissolved in 60 ml of water and the solution was cooled

in ice water. Under vigorous stirring 40 ml of concentrated hydrochloric acid were added and the red-violet tetrabasic acid precipitated. After 1 h, the acid was collected on a glass filter crucible (porosity 20–30 μm), washed with hydrochloric acid (1 : 1) and dried in a vacuum over potassium hydroxide. This procedure was repeated twice, the final product being dried in a vacuum, first over potassium hydroxide, and then to constant weight over phosphorus pentoxide.

Investigations of the tetrabasic acid

A redetermination of sodium by the procedure used above showed a content of less than 0.1%.

The purity of the preparation was also tested by potentiometric titration with standard alkali: 0.1176 g of the acid was dissolved in freshly boiled water, transferred to a 250-ml volumetric flask and diluted to volume with boiled water; 25 ml were pipetted into the titrating vessel, and 25 ml of boiled water and 5.55 ml of 1.0 *M* potassium chloride solution were added. After thermal equilibrium was reached, 0.05656 *N* sodium hydroxide solution was added in small increments from a 5-ml buret under continuous stirring. After each addition the pH was recorded as soon as constant values were obtained. The resulting titration curve exhibited an abrupt change after titration of three equivalents of acid. From the inversion point the equivalent weight was calculated to be 157.0, against a theoretical value of 156.81 (molecular weight of $\text{H}_4\text{ER} = 470.43$).

Absorption curves at pH 4.20 of $6.25 \cdot 10^{-5}$ *M* solutions of the tetrabasic acid and of eriochrome cyanine R were recorded. The form of the curves was identical.

In all subsequent experiments the tetrabasic acid was used.

Standard solutions

A $1.000 \cdot 10^{-3}$ *M* solution of the tetrabasic acid was prepared by weighing out 0.1176 g, transferring the reagent to a 250-ml volumetric flask and diluting to volume with water. From this stock solution $1.000 \cdot 10^{-4}$ *M* solutions were prepared by dilution.

A solution of iron(III) (about 10^{-2} *M*) was prepared by dissolving 0.5585 g of metal in about 30 ml of hydrochloric acid (1 : 1). Complete oxidation was obtained by adding 2 ml of concentrated nitric acid and boiling. The excess of nitric acid was removed by boiling. Complete oxidation was controlled by the reaction with a freshly prepared solution of potassium ferricyanide. The iron solution was transferred to a 1-l volumetric flask and diluted to volume with diluted hydrochloric acid (about 0.05 *N*). The iron concentration was determined gravimetrically and was found to be $0.9774 \cdot 10^{-2}$ *M*. From this solution a $1.000 \cdot 10^{-3}$ *M* solution was prepared by transferring 51.16 ml to a 500-ml volumetric flask and diluting to volume with water. The pH of this solution was 1.7. From this stock solution $1.000 \cdot 10^{-4}$ *M* iron(III) solutions were prepared by dilution immediately before use.

Investigations of the complex formation

Absorption curves. Absorption curves were recorded for 4 series of solutions containing the reactants in varying mole ratios. Within each series (consisting of 6 solutions) the mole ratio was maintained constant, while the pH was varied. All solutions were prepared by pipetting into 100-ml volumetric flasks 10 ml of 1.0 *M*

potassium chloride solution and the proper volumes of 10^{-4} M solutions of iron(III) and the tetrabasic acid. The order of addition is given in Table I. After dilution with water to *ca.* 98 ml, the pH was adjusted by addition of either diluted hydrochloric acid or sodium hydroxide solution and the solution was finally made up to volume with water. All measurements were made in 4-cm cells against blanks containing the same amounts of inert salt and ligand and adjusted to the same pH.

The composition of the solutions prepared is given in Table I, and the resulting absorption curves in Fig. 2. The absorption curves indicated the presence of three different species. At the higher pH values (3.90 and 4.20) a complex with an absorption

TABLE I
SURVEY OF SOLUTIONS PREPARED FOR MEASUREMENT OF ABSORPTION CURVES^a

Ml added of			Mole ratio of iron(III) to H ₄ ER	Absorption curves re- produced in Fig. 2
1.0 M KCl solution	10 ⁻⁴ M iron(III) solution	10 ⁻⁴ M H ₄ ER solution		
10	20	5	4 : 1	(a)
10	10	10	1 : 1	(b)
10	5	20	1 : 4	(c)
10	4	20	1 : 5	(d)

^a In the first three series the order of addition was: inert salt solution, iron(III) solution and ligand solution. In the fourth series the ligand solution was added before the iron(III) solution.

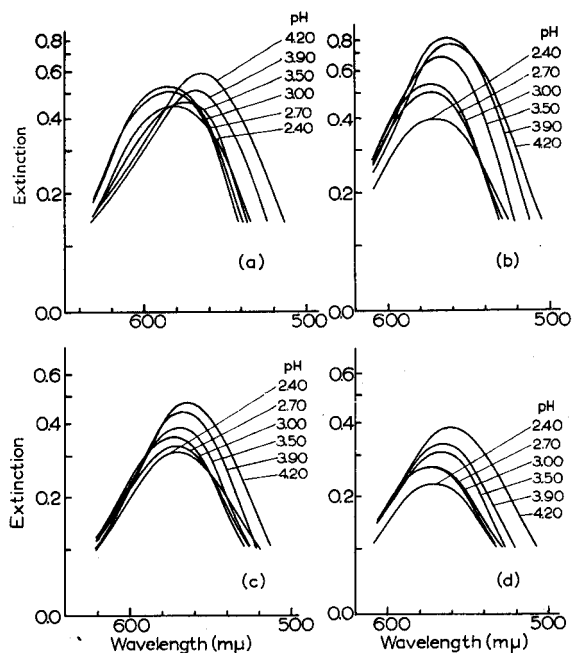


Fig. 2a-d. Absorption curves at different pH values of series of solutions containing the reactants in different mole ratios. For details see Table I and accompanying text.

maximum about $560\text{ m}\mu$ predominated in all series. This complex—which must be comparatively stable—predominated irrespective of the mole ratio of the reactants and of the order of addition. In the lower pH range two other complexes were detected, one predominating in the presence of an excess of iron(III) (absorption maximum about $586\text{ m}\mu$) and another in the presence of an excess of ligand (absorption maximum about $573\text{ m}\mu$). Below pH 1.0 and above pH 5.0 very little complex formation seemed to take place.

The method of continuous variations

On the basis of the above preliminary conclusions, it was decided to plot a curve of continuous variations at pH 4.20. At lower pH values the absorption curves indicated the presence of mixtures of at least two complexes, and under these conditions curves of continuous variations were assumed to be of little value.

For a plot of the curve at pH 4.20 mixtures of the reactants with a constant total concentration of 10^{-5} M were prepared. The proper volumes of the 10^{-4} M standard solutions were pipetted into 100-ml volumetric flasks, the order of addition being inert salt, iron(III) and ligand solution. After dilution to about 98 ml, adjustment of pH and dilution to the mark, the extinctions were measured in 4-cm cells at $560\text{ m}\mu$ against a blank of water. For correction purposes a standard curve of solutions of the ligand was recorded at the same pH and wavelength. The absorption of iron(III) ions in the mixtures was considered to be negligible.

In Fig. 3 the resulting curve is reproduced. The maximum at the mole fraction 0.5 showed the presence of a complex A_mB_n for which $m = n$. In addition both curve branches exhibited an inversion point and approached the limits parabolically. This

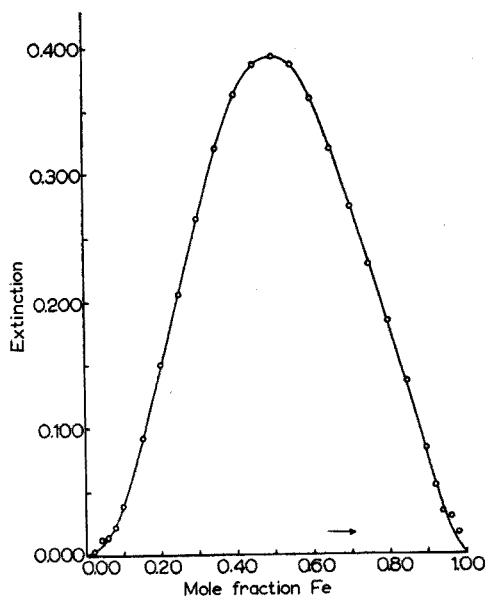
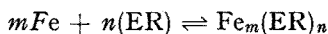


Fig. 3. Curve of continuous variations plotted at the wavelength $560\text{ m}\mu$ of solutions maintained at pH 4.20. Constant concentration of reactants 10^{-5} M . The curve is corrected for the absorption of the amount of ligand added.

type of curve, which has been discussed by KLAUSEN AND LANGMYHR⁷, clearly demonstrated the presence of a complex for which $m = n > 1$.

The straight-line method. This method was introduced by ASMUS⁸ and was extended by KLAUSEN AND LANGMYHR⁹.

The straight-line method was applied to 6 series of solutions maintained at either pH 2.70 or 4.20. Each series consisted of 8 solutions. The solutions were prepared in the same way as for the method of continuous variations from 10^{-4} M standard solutions. The extinction data were corrected by subtracting the contribution from the amount of ligand added. The absorption of iron(III) ions in the mixtures was considered as negligible. Table II surveys the series of solutions prepared, their pH and the wavelength of measurement. Assuming the equilibrium



and omitting ionic charges and the possible presence of hydroxo or proton complexes, Table II also gives the value of m or n for which a straight line was obtained.

TABLE II
SURVEY OF SOLUTIONS PREPARED FOR THE USE OF THE STRAIGHT-LINE METHOD

Concentration of the reactant maintained constant	Concentration range of the reactant varied	pH	Measurement made at ($m\mu$)	Straight line obtained for
10^{-5} M Fe	$(1.0-7.0)10^{-6}$ M ER	2.70	586	$n = 1$
10^{-6} M Fe	$(1.0-7.0)10^{-6}$ M ER*	2.70	586	$n = 1$
10^{-5} M ER	$(1.0-7.0)10^{-6}$ M Fe	2.70	586	$m = 1$
10^{-6} M ER	$(4.0-28.0)10^{-6}$ M Fe*	2.70	586	$m = 2$
10^{-5} M Fe	$(1.0-7.0)10^{-6}$ M ER	4.20	560	$n = 2$
10^{-5} M ER	$(1.0-7.0)10^{-6}$ M Fe	4.20	560	$m = 2$

* In these series a variation of the straight-line method was employed, *viz.* varying the reactant present in excess.

THE COMPOSITION OF THE COMPLEXES

From the investigations described above the following conclusions were drawn as to the composition of the three complexes detected.

In the pH range 3.90-4.20 a complex with absorption maximum near 560 $m\mu$ predominated in all mixtures. While the curve of continuous variations showed a complex $\text{Fe}_m(\text{ER})_n$ for which $m = n > 1$, the straight-line method established the value of both m and n to be two. These results clearly pointed to a complex with the composition $\text{Fe}_2(\text{ER})_2$.

In the lower pH range, around pH 2.70, two species were formed depending on the mole ratio between the reactants.

In the presence of an excess of iron(III), the straight-line method gave the coefficients $m = 2$ and $n = 1$, corresponding to the composition $\text{Fe}_2(\text{ER})$. This complex exhibited an absorption maximum about 586 $m\mu$.

Mixtures containing an excess of the ligand favoured the formation of another complex for which the straight-line method gave the coefficients $m = 1$ and $n = 1$

and the composition $\text{Fe}(\text{ER})$. The absorption maximum of this complex was found near $573 \text{ m}\mu$,

Unfortunately, the methods employed in the present investigation did not give any information on the presence of protons or hydroxyl groups in the complexes. However, it can be assumed that—depending on the pH of the solutions—one or more protons or hydroxyl groups are incorporated in the complexes detected.

The structure of the complexes

In Fig. 4 a structure is proposed for the dimer $[(\text{Fe}(\text{H}_2\text{O})_2(\text{ER}))_2]^{2-}$. In this compound all the bond-forming groups of the ligand and 4 of the 6 sites around each iron(III) ion are engaged in complex formation. It is assumed that the remaining sites around the metal ions are occupied by water molecules.

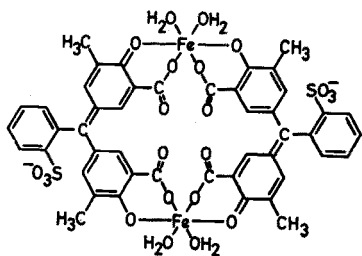


Fig. 4. Suggested structure of the dimer $[(\text{Fe}(\text{H}_2\text{O})_2(\text{ER}))_2]^{2-}$.

In the complex $\text{Fe}_2(\text{ER})$ one metal ion can be expected to be attached to each of the two bidentate groups. If it is assumed that the remaining 4 sites around the metal ions are occupied by water molecules, the formula $[(\text{Fe}(\text{H}_2\text{O})_4)_2(\text{ER})]^{2+}$ is obtained. The corresponding structure can easily be derived from Fig. 4.

In the monomer $\text{Fe}(\text{ER})$ the metal ion may be attached to either of the two bidentate groups, and consequently two formulas and structures are possible.

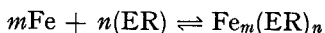
STABILITY CONSTANTS

The experimental data from the methods employed to establish the composition of the three complexes were used to calculate the conditional and absolute stability constants.

The stability constant of the $\text{Fe}_2(\text{ER})_2$ complex

Calculated from the straight-line method. The calculations were carried out as directed by ASMUS⁸ and by KLAUSEN AND LANGMYHR⁹.

Assuming as before the equilibrium



it followed that the conditional constant $k_{(2,2)\text{H}}$ could be calculated from the expression

$$k_{(2,2)\text{H}} = \frac{G}{m^2} \left(\frac{V}{a_0 v_0} \right)^{m-1} \left(\frac{V}{b_0} \right)^n$$

The straight line on the two figures relating to the present complex gave two values for G (0.23 ml^{-2} and 0.13 ml^{-2}), and by introducing $m = n = 2$ and the experimental data: $\text{pH} = 4.20$, $V = 100 \text{ ml}$, $a_0 = b_0 = 10^{-4} M$ and $v_0 = 10 \text{ ml}$, the two values obtained for the conditional constant were: $\log k_{(2,2)\text{pH } 4.20} = 15.8$ and 15.5 , respectively.

Taking into consideration the formation of proton complexes of the ligand (the dissociation constants published by SUK AND MIKEŤUKOVÁ⁴ were applied for this correction) and the equilibria between the ions Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}_2(\text{OH}_2)^{4+}$ (the constants of HEDSTRÖM¹⁰ were used) the absolute stability constants $k_{2,2}$ of the dimer, as defined by

$$k_{2,2} = k_{(2,2)\text{H}} \cdot \alpha_{\text{H}}^2 \cdot \alpha'^2$$

(the values of α_{H} and α' being calculated as in a previous paper³; at $\text{pH } 4.20$ α_{H} and α' were $10^{9.19}$ and $10^{1.79}$, respectively) were found to be: $\log k_{2,2} = 37.7$ and 37.5 , mean value $\log k_{2,2} = 37.6$.

Calculated from the method of continuous variations. Following the directions given by FOLEY AND ANDERSON¹¹ and assuming the equilibrium mentioned above, the conditional constant of the dimer was found from a plot of two curves of continuous variations. The curve shown in Fig. 3 was used in combination with a new curve recorded at the same pH and wavelength, but at a different total concentration of reactants ($0.8 \cdot 10^{-5} M$). This method gave the conditional constant $\log k_{(2,2)\text{pH } 4.20} = 16.22$. The absolute constant was calculated as described above and was found to be $\log k_{2,2} = 38.2$.

The stability constant of the $\text{Fe}_2(\text{ER})$ complex

This constant was found by means of the straight-line method, the equilibrium given above being assumed. From the straight line on the two figures relating to the present complex two values of the conditional constant

$$k_{(2,1)\text{H}} = \frac{GV^2}{4a_0v_0b_0}$$

were calculated. With $G = 0.13 \text{ ml}^{-1}$, $\text{pH} = 2.70$, $a_0 = b_0 = 10^{-4} M$, $V = 100 \text{ ml}$ and $v_0 = 10 \text{ ml}$; $\log k_{(2,1)\text{pH } 2.70} = 9.5$. Similarly, with $G = 0.33 \text{ ml}^{-1}$, $\text{pH} = 2.70$, $a_0 = b_0 = 4 \cdot 10^{-4} M$, $V = 100 \text{ ml}$ and $v_0 = 10 \text{ ml}$; $\log k_{(2,1)\text{pH } 2.70} = 10.3$.

From the equation

$$k_{2,1} = k_{(2,1)\text{H}} \cdot \alpha_{\text{H}} \cdot \alpha'^2$$

(at $\text{pH } 2.70$ α_{H} and α' were $10^{12.23}$ and $10^{0.20}$, respectively) the absolute stability constants were calculated to be $\log k_{2,1} = 22.1$ and $\log k_{2,1} = 22.9$, respectively. Mean value $\log k_{2,1} = 22.5$.

The stability constant of the $\text{Fe}(\text{ER})$ complex

This constant was also calculated from the straight-line method again assuming the equilibrium given above. From the straight line on one of the figures relating to the present complex the conditional constant

$$k_{(1,1)\text{H}} = GV/b_0$$

was calculated, the experimental data being $G = 0.33 \text{ ml}^{-1}$, $\text{pH} = 2.70$, $V = 100 \text{ ml}$ and $b_0 = 10^{-4} \text{ M}$. The conditional constant was found to be $\log k_{(1,1)\text{pH } 2.70} = 5.5$ and the absolute stability constant, defined by

$$k_{1,1} = k_{(1,1)\text{H}} \cdot \alpha_{\text{H}} \cdot \alpha'$$

(α_{H} and α' having the same values as in the preceding section) was $\log k_{1,1} = 17.9$.

All stability constants are valid at an ionic strength of 0.1 M and at room temperature ($20 \pm 3^\circ$).

SUMMARY

The complex formation of iron(III) with the trisodium salt of 5-[α -(3-carboxy-5-methyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2-sulfobenzyl]-3-methylsalicylic acid (eriochrome cyanine R) was studied by spectrophotometry. The pure tetrabasic acid of the ligand (H_4ER) was prepared and used in the investigation. In the pH range 2.7–4.2 three complexes were detected: a ring-formed dimer $\text{Fe}_2(\text{ER})_2$, $\text{Fe}_2(\text{ER})$ and $\text{Fe}(\text{ER})$; the absolute stability constants (at an ionic strength of 0.1 M and at room temperature ($20 \pm 3^\circ$)) were $\log k = 37.9$, $\log k = 22.5$ and $\log k = 17.9$, respectively.

RÉSUMÉ

Les auteurs ont effectué une étude spectrophotométrique sur la formation du complexe fer(III)–Eriochrome cyanine R (ER). On a pu détecter ainsi trois complexes entre les pH 2.7 et 4.2: $\text{Fe}_2(\text{ER})_2$, $\text{Fe}_2(\text{ER})$ et $\text{Fe}(\text{ER})$. Leurs constantes de stabilité ($\log k$) sont respectivement 37.9, 22.5 et 17.9 (à température ordinaire et force ionique de 0.1 M).

ZUSAMMENFASSUNG

Die Komplexbildung des Eisen(III) mit dem Trinatriumsalz des Eriochromcyanin R wurde spektralphotometrisch untersucht. Die reine tetrabasische Säure des Liganden (H_4ER) wurde dargestellt und für die Untersuchung benutzt. Im pH-Bereich von 2.7–4.2 wurden 3 Komplexe nachgewiesen: Ein ringförmiges dimeres $\text{Fe}_2(\text{ER})_2$, $\text{Fe}_2(\text{ER})$ und $\text{Fe}(\text{ER})$. Die absoluten Stabilitätskonstanten betragen $\log k = 37.9$, $\log k = 22.5$ bzw. $\log k = 17.9$ (bei einer Ionenstärke von 0.1 M und bei einer Raumtemperatur von $20 \pm 3^\circ$).

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SOME METALLOFLUORESCENT DERIVATIVES OF 2,2'-DIAMINO-DIPHENYL-N,N,N',N'-TETRAACETIC ACID

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Recently the use of the N,N,N',N'-tetracarboxymethyl derivatives of several 3,3'-disubstituted benzidines as metallofluorescent indicators has been described^{1,2}. The fluorescence of these compounds, excited by ultraviolet light, is quenched completely by a number of cations and is restored by the addition of an excess of EDTA. The compounds can thus be used for the visual detection of the end-points in the titration of cations with EDTA; the end-point is denoted by the appearance (or disappearance in a back-titration) of fluorescence when the titration solution is exposed to a source of ultraviolet radiation.

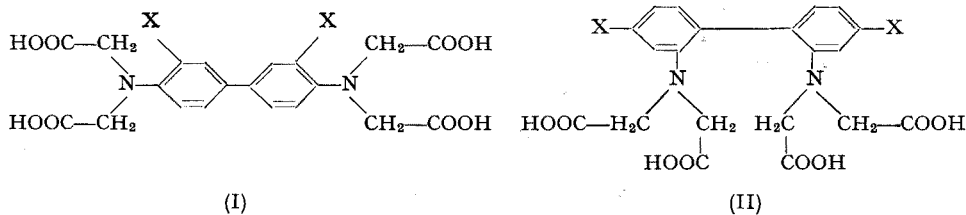
From considerations of the structure of these compounds it was thought that extension of the conjugation of the molecule might result in the corresponding N,N,N',N'-tetracarboxymethyl derivatives having superior properties as metallofluorescent indicators. The N,N,N',N'-tetracarboxymethyl derivatives of 4,4'-diaminostilbene and its 2,2'-disulphonic acid were therefore prepared. As reported earlier³ these compounds proved to be approximately 50 and 25 times more effective fluorescers than the *o*-dianisidine derivative, which itself was the most effective of several benzidine derivatives examined. The two compounds were suitable for the titration of dilute solutions of copper(II) with EDTA and for the titrations of Bi, Co, Fe, Ni, Pb, In and V by back-titration of an excess of EDTA with copper(II).

These metallofluorescent complexans (I) have each an iminodiacetic acid group in the 4-position in each aromatic ring, that is, at the extremities of the molecule where no possible interaction of the groups can occur. As a result, each iminodiacetic acid group reacts as a tridentate ligand, and each molecule of the complexan reacts with two metal ions. The fact that these compounds are weak chelating agents is related to the position of the ligand groups in the molecule. If the iminodiacetic acid groups were to be brought much nearer to one another, the resulting compounds would be expected to form appreciably stronger chelates with metal ions. A hexadentate ligand could be obtained by having the iminodiacetic acid groups in the positions adjacent to the 1,1'-bond between the aryl groups in the diphenyl molecule, that is, the 2,2'-positions (II).

However, the introduction of bulky substituents in these positions would cause the diphenyl nucleus to become non-planar, and this would have a detrimental effect on the fluorescence emission of the compound because of the effective decrease in the electronic conjugation of the system. Substitution of suitable groups in the 4,4'-positions of the molecule might counteract this effect by providing an extension of

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the π -electron system of each aryl nucleus, but the fluorescence might still not approach the intensity of the benzidine-type complexans.



A series of 5 compounds based on formula (II) has now been synthesised in which the 4,4'-substituents are $X = -H, -CH_3, -OH, -OCH_3, -COOH$. The new compounds all exhibit blue or blue-green fluorescence in aqueous solution above pH 4 which is quenched by metal ions, thus enabling them to be studied as metallo-fluorescent indicators. The fluorescence of these compounds is, as expected, less intense than that of the corresponding benzidine types, but the new compounds have an important advantage in providing more stable fluorescent systems. This has led to their examination as fluorimetric reagents for the determination of metals, and a quantitative study of the quenching of their fluorescence has now been made.

The preparation of the new complexans involved first the syntheses of the appropriate 4,4'-substituted 2,2'-diaminodiphenyls. These were made by Ullmann synthesis from the corresponding 1-chloro-2-nitro-4-substituted benzenes followed by reduction of the dinitrodiphenyl with iron powder and hydrochloric acid. 4,4'-Dihydroxy-2,2'-diaminodiphenyl was made by demethylation of 4,4'-dimethoxy-2,2'-diaminodiphenyl and 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid by oxidation of 4,4'-dimethyl-2,2'-dinitrodiphenyl followed by reduction of the nitro groups with tin and hydrochloric acid. Full details of these syntheses are given elsewhere⁴. The preparation of the actual complexans from these diamines is described below.

EXPERIMENTAL

Preparation of complexans

*2,2'-Diaminodiphenyl-*N,N,N',N'*-tetraacetic acid (tetrasodium salt).* 2,2'-Diaminodiphenyl (7.5 g) was dissolved in ethanol (50 ml), and water (50 ml) containing a small amount of phenolphthalein was added. The mixture was refluxed with stirring on a steam-bath. A solution of sodium chloroacetate (36 g) in water (100 ml) was added dropwise over a period of 10 h. The reaction mixture was maintained at *ca.* pH 8 by the dropwise addition of 2 *N* sodium hydroxide solution as required. The alkaline reaction mixture was cooled and filtered, the ethanol was distilled off on the steam-bath, and the volume of the mixture was reduced to *ca.* 50 ml by distillation under reduced pressure. The inorganic material which precipitated was filtered off. The filtrate was then carefully acidified by the dropwise addition of concentrated hydrochloric acid. The tarry brown deposit of the free tetraacetic acid was collected and dried in a vacuum over P_2O_5 . The crude acid was purified by dissolving it in warm dry ethanol, and filtering the solution to remove inorganic material. A solution of sodium metal (2.5 g) in ethanol (100 ml) was added to the pale brown solution of the acid, and the mixture was stirred and kept warm for several minutes on a hot water-bath. The

white precipitate of the sodium salt so obtained was filtered off and dried in a vacuum over P_2O_5 . Yield 11 g. The equivalent weight of the sodium salt, determined by non-aqueous titration, was 120.6 (theoretical equivalent weight, 126).

4,4'-Dimethyl-2,2'-diaminodiphenyl-N,N,N',N'-tetraacetic acid (tetrasodium salt). The procedure adopted for the conversion of the diamine to its N,N,N',N'-tetraacetic acid by condensation with chloroacetate was similar to that used for the preparation of 2,2'-diaminodiphenyl-N,N,N',N'-tetraacetic acid. The yield of the white tetrasodium salt of 4,4'-dimethyl-2,2'-diaminodiphenyl-N,N,N',N'-tetraacetic acid was 7 g from 10 g of 4,4'-dimethyl-2,2'-diaminodiphenyl.

4,4'-Dimethoxy-2,2'-diaminodiphenyl-N,N,N',N'-tetraacetic acid (tetrasodium salt). A solution of sodium chloroacetate (36 g) in water (120 ml) was added slowly to a refluxing stirred solution of 4,4'-dimethoxy-2,2'-diaminodiphenyl (9.5 g) in aqueous ethanol (50%, 60 ml). The reaction was allowed to proceed for 8 h. The tarry product was isolated and converted to the sodium salt by the procedure used for 2,2'-diaminodiphenyl-N,N,N',N'-tetraacetic acid. The yield of hygroscopic white sodium salt was 7 g.

4,4'-Dihydroxy-2,2'-diaminodiphenyl-N,N,N',N'-tetraacetic acid (sodium salt). 4,4'-Dihydroxy-2,2'-diaminodiphenyl (5 g) was suspended in water (100 ml) containing a little phenolphthalein, and the suspension was heated with stirring on a water-bath. A solution of sodium chloroacetate (20 g) in water (75 ml) was added slowly to the mixture over 3 h. The reaction mixture was maintained at *ca.* pH 8 by the addition of 2 N sodium hydroxide solution when required. The reaction mixture was cooled, filtered, and a strong solution of barium chloride, followed by a small volume of ethanol (20 ml), was added. The precipitated barium salt was filtered off, washed with a small volume of water and dried. The finely powdered barium salt was suspended in dry ethanol (100 ml), and dry gaseous hydrogen chloride was passed into the ice-cold suspension until conversion to the free acid was considered to be complete. The solution was filtered to remove the inorganic material, and the filtrate was added to a fresh solution of sodium ethoxide. The sodium salt was filtered off, washed with ethanol and dried in a vacuum over P_2O_5 . Yield, 2 g.

The sodium salt was further purified by suspending it in dry ethanol and again converting it to the free acid in a current of dry hydrogen chloride. The sodium chloride was filtered off, and the filtrate concentrated by distillation under reduced pressure. The solution was then filtered again and added to a fresh solution of sodium ethoxide. The sodium salt was filtered off, washed with ethanol and dried. Yield of grey powder, 1.7 g.

2,2'-Diaminodiphenyl-4,4'-dicarboxylic acid-N,N,N',N'-tetraacetic acid. 2,2'-Diaminodiphenyl-4,4'-dicarboxylic acid (7 g) was dissolved in ethanol (50 ml) and water (35 ml) containing a little phenolphthalein. The solution was refluxed and stirred on a boiling water-bath, and a solution of sodium chloroacetate (25 g) in water (100 ml) was added in small portions over 10 h. The reaction mixture was maintained at *ca.* pH 8 by the addition of 2 N sodium hydroxide solution when required. The white sodium salt of 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid-N,N,N',N'-tetraacetic acid was isolated as described above for 2,2'-diaminodiphenyl-N,N,N',N'-tetraacetic acid. Yield, 4 g. The sodium content by the sulphated ash method was 20.4% (theoretical 21.7%). The pure free acid of this compound was obtained by dissolving the sodium salt in water, making the solution strongly acid with hydrochloric acid, and

extracting the solution with diethyl ether in a liquid-liquid extraction apparatus for several days. The white flakes of the free acid which deposited in the ether phase were filtered off and dried. Yield, 1.5 g. (Calculated for $C_{22}H_{20}N_2O_{12}$: C, 52.4%; H, 3.96%; N, 5.55%; found: C, 52.2%; H, 4.14%; N, 5.53%.)

Electrophoresis

The apparatus and procedure previously described⁵ were used.

Titration of metal ions with EDTA

The apparatus used is described by BELCHER AND NUTTEN⁶. The ultraviolet source was a Mazda mercury vapour electric discharge lamp of type MBW/U, 230-240 V, 125 W.

Action of cations on fluorescence of compounds

Procedure. 3-4 drops of buffer solution (pH 2-13) and 1 drop of 0.01 M complexan solution were added to a semi-micro test-tube. The solution was diluted to ca. 1 ml, 1-2 drops of a 0.1 M solution of the metal ion were added, and the solution was shaken and viewed. A few drops of 0.1 M EDTA solution were added and the solution was again shaken and viewed. A similar procedure was adopted when 0.1 M CDTA was used in place of EDTA.

Fluorimetry. An E.I.L. direct reading fluorimeter (Model 27A) fitted with a 125-W high-pressure mercury vapour lamp, and similar to that described by BREALEY AND ROSS⁷, was used in the studies of the stability of the fluorescence and its variation with pH. Excitation and emission spectra were recorded using a double monochromator spectrofluorimeter (Farrand Optical Co., Cat. No. 104244) fitted with a 150-W xenon arc lamp (Hanovia Division, Cat. No. 901 C-1).

RESULTS AND DISCUSSION

The new compounds gave single blue or blue-green fluorescent spots on paper when subjected to electrophoresis at pH 10 in a borate buffer. When sprayed with ceric sulphate solution, the chromatograms indicated the presence of a second minor component in the samples of the 4,4'-dimethyl and 4,4'-dimethoxy derivatives. The rate of migration observed on the chromatograms was in each instance proportional to the charge expected on the molecules of the compounds at this pH.

Fluorescence characteristics

The new compounds exhibit a blue or blue-green fluorescence in aqueous solution above pH 4. A comparison of the intensity of fluorescence at different pH values for this series of complexans is shown in Fig. 1. It is evident that although the intensity of the fluorescence of the complexans in aqueous solution depends greatly on the 4,4'-substituents, the variation of the intensity of fluorescence of each complexan with pH is very similar. The intensity of the fluorescence of each complexan rises to a maximum at approximately pH 7 and then remains unchanged with further increase of pH. 2,2'-Diaminodiphenyl-4,4'-dicarboxylic acid complexan possesses the most intense fluorescence in aqueous solution. The other complexans, with the possible exception of 2,2'-diaminodiphenyl complexan, are very weakly fluorescent and are un-

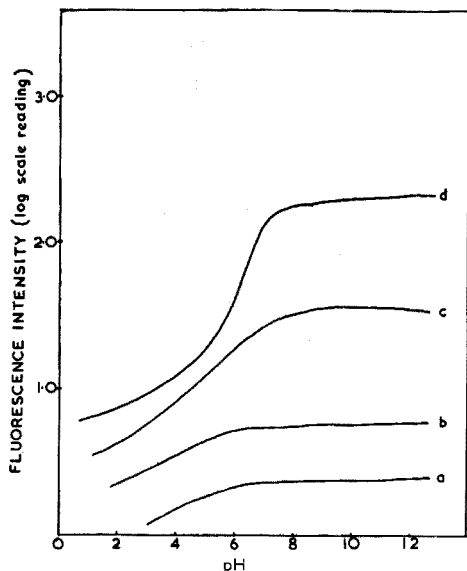


Fig. 1. Effect of pH on fluorescence of 10^{-5} M solutions of the sodium salts of the N,N,N',N'-tetraacetic acid derivatives of: (a) 4,4'-dimethoxy-2,2'-diaminodiphenyl; (b) 4,4'-dimethyl-2,2'-diaminodiphenyl; (c) 2,2'-diaminodiphenyl; (d) 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid.

likely to be of use as metallofluorescent chelating agents. Consequently, only the properties of the 4,4'-dicarboxylic acid derivative were studied further.

The excitation and emission spectrum of the sodium salt of 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid-N,N,N',N'-tetraacetic acid in alkaline solution is shown in Fig. 2. This compound exhibits single excitation and emission maxima at $360\text{ m}\mu$ and $460\text{ m}\mu$ respectively. The positions of these maxima are unaffected by change of pH, although the intensity of the fluorescence emission varies as shown in Fig. 1. The stability of the fluorescence to continuous ultraviolet radiation from the mercury vapour lamp was examined in the fluorimeter and was found to be dependent upon the pH of the solution. As the pH is raised the fluorescence becomes less stable, until at pH 13 the fluorescence decays quite rapidly (20% in 15 min for a $5 \cdot 10^{-5}$ M solution). In daylight or artificial light, however, a 10^{-3} M solution can be left for several hours without significant decay of its fluorescence when measured in the fluorimeter.

Effect of metal ions on fluorescence

The effect of 32 metal ions on the fluorescence of an aqueous solution of 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid-N,N,N',N'-tetraacetic acid was investigated. The addition of solutions of certain metal ions, notably Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Mn^{2+} , Pb^{2+} and Zn^{2+} , to the fluorescent complexan solution between pH 5 and 10 produced a non-fluorescent chelate. The copper(II), cobalt(II) and nickel(II) chelates were not easily destroyed by the addition of EDTA to the solution. The addition of CDTA (*trans*-1,2-diaminocyclohexanetetraacetic acid) solution, however, destroyed the non-fluorescent chelates in every instance, and restored the fluorescence of the solution. It thus appears that the non-fluorescent metal chelates of copper(II), cobalt(II) and nickel(II) are very stable.

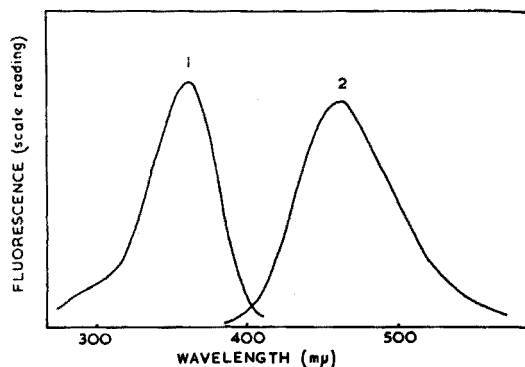


Fig. 2. Excitation (1) and emission (2) spectra of fluorescence of 10^{-4} M solution of sodium salt of 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid complexan at pH 11.

Nature of the complexes

It was expected that 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid complexan would form strong 1 : 1 complexes with the transition metal ions. A study of the nature of the copper(II) and nickel(II) complexes was made by the mole ratio method and the method of continuous variations. In these methods, the concentration of the complex formed was taken to be proportional to the decrease in the fluorescence produced. Consequently, it was first established that the fluorescence of the complexan was proportional to its concentration over the concentration ranges employed.

The results shown in Fig. 3 for the mole ratio method indicate the formation of strong 1 : 1 chelates between the complexan and Cu^{2+} or Ni^{2+} at pH 7.5. The similar results obtained at pH 7.5 in the method of continuous variations are shown in Fig. 4.

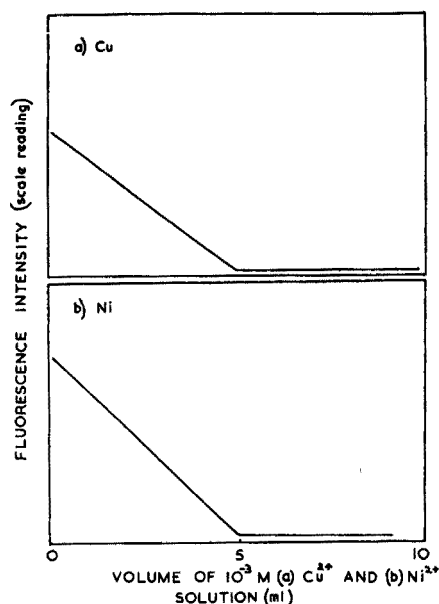


Fig. 3. Mole ratio study for complex formation between 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid complexan and (a) Cu^{2+} and (b) Ni^{2+} at pH 7.5. 5 ml of 10^{-3} M complexan solution in both. Excitation at 360 m μ , emission measured at 460 m μ .

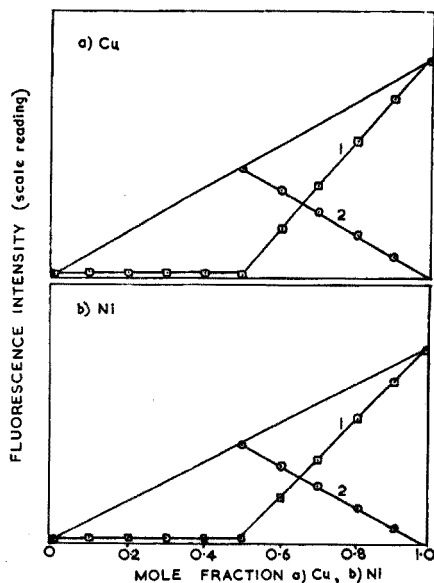


Fig. 4. Continuous variations curves for complex formation between 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid complexan and (a) Cu or (b) Ni at pH 7.5. 50 ml of solution containing 10 ml pH 7.5 buffer. Excitation at $360\text{ m}\mu$, emission measured at $460\text{ m}\mu$. (a) Cu: curve 1 = total concentration Cu + complexan solution = $5\text{ ml } 10^{-3}\text{ M}/50\text{ ml}$; curve 2 = after correction of curve 1 for reagent fluorescence. (b) Ni: curve 1 = total concentration Ni + complexan solutions = $5\text{ ml } 10^{-3}\text{ M}/50\text{ ml}$; curve 2 = after correction of curve 1 for reagent fluorescence.

Fluorimetric determination of metal ions

Although the fluorescence of 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid complexan is quenched by a number of metal ions, the quenching reactions can be made more selective by the application of suitable masking agents. At pH 7.5, $1\text{--}8\text{ }\mu\text{g}$ of nickel(II) may be determined fluorimetrically in 50 ml of solution ($0.02\text{--}0.16\text{ p.p.m. Ni}^{2+}$) in the presence of a ten-fold excess of copper(II) or a ten-fold excess of mercury(II) after the addition of an excess of potassium cyanide to the complexan solution. The formation of the stable copper(II) and mercury(II) cyanide complexes prevents the reaction of these metal ions with the complexan at this pH. The quenching action of cadmium and zinc ions, however, is not masked by cyanide at this pH.

Use of the complexan as a titrant

The titration of dilute copper(II) solutions with 2,2'-diaminodiphenyl-4,4'-dicarboxylic acid complexan solution as a self-indicating titrant was attempted. The titration of a 10^{-3} M solution of copper(II) with a 10^{-3} M solution of the complexan at pH 6 gave an end-point which was marked by the appearance of fluorescence in the solution. However, at this dilution, the end-points obtained were not sharp and the procedure necessarily involved over-titration.

In the reverse titration, the end-point, denoted by the quenching of the fluorescence in the titrated complexan solution, was also not sufficiently sharp, a gradual quenching of the fluorescence occurring during the titration.

The use of the complexan as a metallofluorescent indicator for the titration of metal ions with EDTA was hampered because of the formation of strong complexes with metal ions. The end-points of the titrations (which should have been marked by the appearance of fluorescence) were too ill-defined for practical purposes; the fluorescence either appeared very slowly on over-titration, or in certain cases did not appear at all. The replacement of EDTA by CDTA as titrant gave better results, but

in general the quality of both the fluorescence and the end-points was inferior to that obtained with the metallofluorescent complexans derived from the 3,3'-disubstituted benzidines^{1,2} or 4,4'-diaminostilbene³. The main significance of this type of metallofluorescent compound lies in the enhanced stability, not only of the non-fluorescent metal chelates, but also of the fluorescence of the uncombined reagent. The development of more strongly fluorescent complexans based on the structure of the present compound should be possible. This could provide extremely sensitive reagents for the fluorimetric determination of a number of metal ions.

SUMMARY

The N,N,N',N'-tetraacetic acid derivatives of five 4,4'-disubstituted 2,2'-diaminodiphenyls have been prepared and their fluorescent properties examined. 2,2'-Diaminodiphenyl-4,4'-dicarboxylic acid-N,N,N',N'-tetraacetic acid exhibits intense fluorescence in aqueous solution above pH 4, and forms stable non-fluorescent 1 : 1 complexes with copper(II) and nickel(II) ions at pH 7.5. The quenching of the fluorescence of the compound by nickel(II) may be used in the fluorimetric determination of nickel.

RÉSUMÉ

Les auteurs ont préparé et examiné les dérivés de l'acide N,N,N',N'-tétraacétique de cinq 2,2'-diaminodiphényl-4,4'-disubstitués. L'acide 2,2'-diaminodiphényl-4,4'-dicarboxylique-N,N,N',N'-tétraacétique donne une fluorescence intense en solution aqueuse à un pH > 4, et forme des complexes stables non-fluorescents avec le cuivre et le nickel, au pH 7.5. Le nickel peut ainsi être dosé par fluorimétrie, en mesurant l'affaiblissement de la fluorescence du réactif.

ZUSAMMENFASSUNG

Die Derivate der N,N,N',N'-Tetraessigsäure von fünf 4,4'-disubstituierten 2,2'-Diaminodiphenylen wurden hergestellt und ihre Fluoreszenzeigenschaften geprüft. 2,2'-Diaminodiphenyl-4,4'-dicarboxyl-N,N,N',N'-tetraessigsäure zeigt in wässriger Lösung oberhalb vom pH-Wert 4 eine intensive Fluoreszenz und bildet stabile nichtfluoreszierende 1 : 1 Komplexe mit Kupfer(II) und Nickel(II)-Ionen beim pH-Wert 7.5. Das Ausbleiben der Fluoreszenz bei der Ni(II)-Verbindung kann für die fluorometrische Bestimmung von Nickel benutzt werden.

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THE ANALYSIS OF ANHYDROUS TITANIUM TRICHLORIDE

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In the course of an investigation of the stoichiometry of various forms of titanium trichloride, determinations of titanium and of chloride were required at a high level of accuracy. Preliminary determinations under conditions simulating typical samples of the trichloride showed that the Jones Reductor procedure for titanium and the Volhard procedure for chloride were subject to certain interferences. For example, during the preparation of samples of trichloride for analysis, dry-box operations were minimised by using gelatin capsules to transfer weighed samples; this introduction of gelatin created an interference both in titanium and chloride determinations. Even without gelatin however, summations involving accurately known amounts of each ion were frequently in the vicinity of only 99% and this paper reports procedures developed to avoid the various interferences.

EXPERIMENTAL AND RESULTS

Titanium determination

Reduction technique. The Jones Reductor technique¹ was studied in some detail with aliquots of a standard titanium solution prepared from high purity (99.9%) titanium metal. The sample containing 100.0 mg of titanium(IV) in 2 N sulphuric acid, was passed through the column, the reduced titanium being received into excess ferric alum under carbon dioxide; the iron(II) was titrated with 0.1 N permanganate. Recoveries corrected for blank ranged from 99.3% to 99.9% with a mean of 99.5%. Chloride ion was absent in these tests, thus permanganate was a satisfactory titrant to evaluate column reproducibility, but with typical trichloride samples the small amount of chloride present was sufficient to give erroneous titres at the high precision level demanded. For this reason, as well as the desirability of eliminating titration of the iron impurity blank, ferric alum titrant with thiocyanate indicator was adopted in subsequent work. While this procedure allowed chloride to be present, the relatively high solution volumes arising from the column technique led to reduced sharpness in the end-point.

Disadvantages of the column appeared to be avoidable with the alternative reduction technique introduced by RAHM², in which a titanium solution in sulphuric and hydrochloric acids is reduced to titanium(III) with aluminium metal and titrated with ferric alum. Further data were required on such variables as the amount of aluminium, its form and purity, solution volume, acidity, and sensitivity of the

reduced titanium solution to reoxidation after complete dissolution of the aluminium metal. According to RAHM, up to 150 mg Ti is reduced in a volume of 150 ml of 3 *N* sulphuric acid including 20 ml of 12 *N* hydrochloric acid, with 1 g of aluminium foil. In our experience, sheet aluminium (0.023'') was superior to both wire (0.028'') and foil (0.002'') in giving highest recoveries, a steady rate of dissolution and, with our particular samples, a lower blank than foil. Although 1 g of aluminium was adequate if the rate of dissolution was controlled, a 3-g quantity was chosen in our work to ensure complete titanium reduction.

Reduction vessel. A 500-ml long-necked, round-bottom flask fitted with a side-arm angled upwards at 45° to permit nitrogen blanketing during cooling and titration, was used. This type of flask was more suitable than an Erlenmeyer of similar capacity, as spray from the vigorous hydrogen evolution tended to be either confined to the bottom section or more rapidly returned to the reaction, minimising losses due to unreduced solution.

For critical examination of absolute recoveries in the RAHM procedure, a standard solution of 99.9% titanium metal was prepared by dissolving weighed turnings in concentrated sulphuric acid–ammonium sulphate³ to produce on dilution a titanium concentration of 5.000 g/l in 3.6 *N* sulphuric acid. Ferric alum titrant after oxidation of any iron(II) with permanganate was standardised against dried N.B.S. potassium dichromate.

The RAHM procedure was followed using 100.0 mg of titanium added to 20 ml of 20 *N* sulphuric acid and 20 ml of 11 *N* hydrochloric acid in the reduction flask. At a final volume of 145 ml, reduction was effected in 20 min using 3 g of aluminium sheet, after which a sodium bicarbonate trap was fitted (Contat–Gockel type)⁴ to prevent introduction of air during cooling. During titration oxygen-free nitrogen was passed through the side-arm.

Under these conditions recoveries of not higher than 99.4% were consistently obtained.

Deaeration of titrant. Although procedures for direct titration of titanium(III) usually specify titration in an inert atmosphere, little consideration appears to have been given to the presence of dissolved oxygen in the ferric alum titrant and possibly the sodium bicarbonate solution used in the air-exclusion trap.

Oxygen sensitivity was tested firstly by adding 50-ml volumes of air-saturated water to reduced titanium solutions immediately before titration, simulating the addition of 50 ml of air-saturated ferric alum titrant. In this test recovery was reduced from 99.2% to 98.8%. In further tests oxygen contamination was eliminated by using deaerated ferric alum titrant delivered in a simple transfer system (Fig. 1). This allowed a two-way buret to be filled and discharged only under nitrogen, giving the results shown in Table I.

Use of sodium bicarbonate. Although deaeration of the titrant gave improved recoveries it was noted that a further source of interference occurred when the bicarbonate solution was drawn into the reduction flask during cooling. This frequently caused local hydrolysis of titanium and its use was therefore abandoned. The Contat–Gockel trap was retained with deaerated, 2 *N* sulphuric acid as a seal liquid to maintain a positive pressure and provide a visual indication of gas flow. The deaerated 2 *N* sulphuric acid delivered under nitrogen was also used as a wash liquid rather than water. Under these conditions results were consistently satisfactory (Table I).

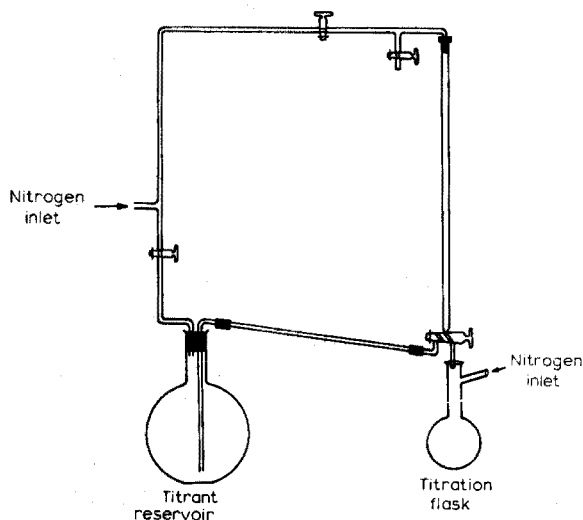


Fig. 1.

TABLE I

TITANIUM RECOVERY

(Ti taken: 100.0 mg. Titrant: ferric alum standardised against $K_2Cr_2O_7$. Titres \approx 50 ml)

Titrant solution in trap	Non-deaerated $NaHCO_3$	Deaerated	
		$NaHCO_3$	2 N H_2SO_4
Recovery (%) ^a	99.3	99.5	99.9
	99.4	99.6	99.9
	99.4	99.7	99.9

^a Corrected for blank (0.13 ml 0.04 N titrant) 3 g Al.

Gelatin effect. Gelatin caused excessive frothing, diminishing the efficiency of the aluminium reduction to less than 90%. An evaporation with sulphuric acid to the fuming point was adequate to avoid this difficulty.

Chloride determination

Effect of titanium and sulphuric acid. A preliminary test of the gravimetric silver chloride procedure showed that contamination with titanium could lead to high results. Tests on the Volhard titration also showed that in the presence of amounts of sulphuric acid required to prevent titanium hydrolysis, flocculation of silver chloride was retarded. Recoveries which were slightly lower than theoretical in the nitrobenzene procedure were obtained, especially when titanium was also present. Heating after precipitation of silver chloride improved flocculation and eliminated the error. Results expressing a mean of several determinations are shown in Table II.

Effect of gelatin. With the addition of a freshly prepared gelatin solution in 3.6 N sulphuric acid (in an amount represented by the fraction of a capsule normally expected) it was found impossible to coagulate the silver chloride precipitate even

TABLE II

EFFECT OF TITANIUM AND SULPHURIC ACID ON CHLORIDE RECOVERIES

(Volhard titration, nitrobenzene procedure, Cl taken: 30.77 mg. AgNO_3 : 0.06 N)

H_2SO_4 present (meq.)	Ti present (mg)	Temp. of AgCl coagulation	Cl recovery (%)
Nil	Nil	20	99.9
10	30	20	99.8
20	30	20	99.7
30	30	20	99.5
50	15	20	99.6
50	15	60	99.9

with heating, to permit filtration or nitrobenzene treatment. Titanium in this instance was without influence.

Of several flocculants tried, tannic acid was found to be effective, producing an easy filtration of the mixed precipitate of silver chloride and titanium-tannin complex. Slight coloration of the filtrate was avoided by addition of decolorising carbon before filtration.

A simpler procedure which was almost as effective was to add potassium nitrate after silver chloride precipitation and heat. In either case, filtration gave quantitative recovery of the excess silver ion, although addition of a little nitrobenzene before titration proved desirable. The use of nitrobenzene as a substitute for filtration was, however, not successful with either procedure.

Results are shown in Table III. The tannin flocculation procedure was preferred as it gave a rather more rapid filtration rate than the use of potassium nitrate.

TABLE III

CHLORIDE RECOVERIES BY VOLHARD TITRATION

(Cl taken: 30.77 mg. Ti present: 30 mg. Gelatin: 10 mg)

Flocculation agent	Cl recovery (%)
Tannin 4 ml 0.5%	99.9, 100.0
Potassium nitrate	99.9, 100.0

RECOMMENDED PROCEDURES

Reagents

Ferric alum solution 0.04 N. Weigh 19.3 g of ferric alum (analytical reagent) and dissolve in 300 ml of distilled water containing 20 ml of 36 N sulphuric acid with warming to 80°. Add 0.1 N potassium permanganate solution to a pink coloration, cool, and dilute to 1 l. Transfer to a storage flask, boil for 20 min while passing nitrogen through a glass sinter, and cool with continuous nitrogen flow.

Aluminium metal sheet. Laboratory grade material. Approximately 0.023" thickness.

Nitrogen. Oxygen-free grade.

Other reagents were of analytical reagent quality.

Sample preparation

Transfer the weighed gelatin capsule containing about 0.5 g of sample to a 100-ml volumetric flask and dissolve in 50 ml of 2 *N* sulphuric acid. Dilute to volume with water.

Titanium determination

Transfer a 50-ml aliquot to a small conical beaker, add 10 ml of 20 *N* sulphuric acid and 3.5 g of ammonium sulphate. Evaporate, fume for 5 min, then cover the beaker and raise the temperature to allow sulphuric acid to reflux and dissolve any titanium hydrolysis products on the beaker wall. Continue heating until a clear yellow colour indicates complete destruction of the gelatin.

Transfer the solution to a 500-ml long-necked, round-bottom flask fitted with side-arm 2.5" from the top, sloping upwards at 45°. Add 20 ml of 20 *N* sulphuric acid followed by 20 ml of 11 *N* hydrochloric acid and dilute to approximately 145 ml. Cut 3 g of sheet aluminium into 6 pieces and add to the flask, and fit a Contat-Gockel trap⁴ containing deaerated 2 *N* sulphuric acid.

Heat the flask with the side-arm unrestricted. When the reaction has diminished in vigour, connect the side-arm to a nitrogen supply and allow gas to escape through the trap. Continue heating for several minutes after complete dissolution of metal (usually less than 20 min total time), and cool in a water bath. Remove the trap and wash down with oxygen-free 2 *N* sulphuric acid from a nitrogen-pressurised storage vessel. Add 3 ml of 45% potassium thiocyanate and titrate with ferric alum solution using the apparatus as shown in Fig. 1. Minimise agitation until about 90% of the expected volume of titrant has been added.

Standardise the ferric alum titrant using the purest available grade of titanium metal dissolved as described earlier, or against standard 0.04 *N* potassium dichromate solution.

Chloride determination

Transfer an aliquot containing about 60 mg of chloride ion to a 200-ml beaker, add 4 ml of 7 *N* nitric acid and 4 ml of 0.5% tannic acid solution. Dilute to 60 ml. Stir to coagulate the precipitate, and add 0.025 g of decolorising carbon followed by an excess of 0.05 *N* silver nitrate solution (40 ml). Heat to 60° to complete coagulation of the precipitate, and then cool, filter and wash on 11-cm Whatman No. 40 paper. Add 1 ml of nitrobenzene to the filtrate to collect any trace of colloidal silver chloride and titrate with 0.05 *N* ammonium thiocyanate using ferric alum indicator as usual.

Standardise using oven-dried A.R. sodium chloride.

DISCUSSION

Standardisation of ferric alum titrant for routine titanium determinations is frequently obtained empirically using weight standard solutions of the purest available grade of titanium metal. While this approach was considered in the present work, results were based rather on the ultimate standardisation with potassium dichromate to make possible a study of all the variables affecting the accuracy of titanium determination.

With the Jones Reductor it was noted that during continued use, the reduction efficiency of the column tended to decline. After a period of standing more nearly correct answers were obtained. Although the inference is that the Jones Reductor procedure is somewhat less satisfactory than aluminium metal reduction, it is true that results of acceptable accuracy are obtained if standards are run to determine column condition and establish the titanium value of the iron titrant. The aluminium metal procedure, by using fresh reductant for each test, is inherently more reproducible provided that the time of metal dissolution is not extensively varied. End-point precision is improved also through a smaller liquid volume being required than with the column reduction.

With all variables at optimum levels, results remained slightly short of quantitative (about 0.6% low) until deaerated titrant was used and the use of bicarbonate in the air-exclusion trap was abandoned. The deaerated titrant appears to be essential for high accuracy work in view of the likely variability in dissolved oxygen content of prepared ferric alum solutions.

In the chloride determinations the flocculation problem arose mainly through the use of gelatin. In situations where gelatin was not used, a slight interference due to the retarding of silver chloride flocculation by titanium still remained, producing results approximately 0.5% low in the nitrobenzene procedure. If flocculation was promoted by warming with potassium nitrate and the silver chloride removed by filtration, no error could be detected using 50-mg samples of trichloride.

SUMMARY

Titrimetric determinations of titanium and chloride were examined for their suitability in establishing the stoichiometry of titanium trichloride. Aluminium metal reduction of titanium(IV) to titanium(III) in aqueous sulphuric acid solution gave higher precision than the Jones Reductor procedure; in both cases exceptional care was necessary before titration in order to prevent some reoxidation of reduced titanium by dissolved oxygen in the titrant. Deaerating the ferric alum titrant and delivering it under nitrogen made it possible to obtain a virtually complete titanium recovery. A convenient apparatus is described. A procedure is also described for the elimination of interference in the Volhard chloride determination due to the presence of high concentrations of titanium sulphate and of gelatin used for sample encapsulation.

RÉSUMÉ

On a examiné les dosages titrimétriques de titane et chlorure, en vue d'établir la formule du trichlorure de titane. La réduction du titane(IV) en titane(III) par l'aluminium, en solution sulfurique, permet d'obtenir une précision meilleure que le procédé au réducteur Jones. Il est cependant indispensable dans les deux cas d'éviter une réoxydation du titane réduit par l'oxygène dissous dans le réactif de titration (un appareil approprié est décrit). On propose également un procédé pour le dosage du chlorure selon Volhard (évitant que le sulfate de titane, en fortes proportions, et la gélatine gênent).

ZUSAMMENFASSUNG

Die massanalytischen Bestimmungen des Titans und Chlorids wurden auf ihre Eignung bei der Ermittlung der Stöchiometrie des Titantrichlorids geprüft. Die Reduktion des Titan(IV) zum Titan(III) in wässriger, schwefelsaurer Lösung mit Aluminiummetall, ergab eine höhere Genauigkeit als mit dem Reduktionsverfahren nach Jones. In beiden Fällen war eine aussergewöhnliche Sorgfalt vor der Titration notwendig, um eine teilweise Reoxydation des reduzierten Titans durch gelösten Sauerstoff zu verhindern. Die Eliminierung der Störungen bei der Chloridbestimmung nach Volhard bei Gegenwart hoher Konzentrationen an Titansulfat unter Anwendung von Gelatine wird beschrieben.

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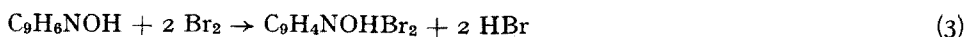
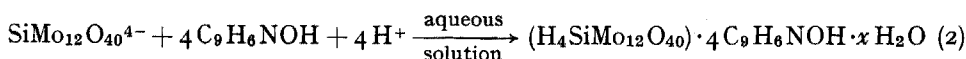
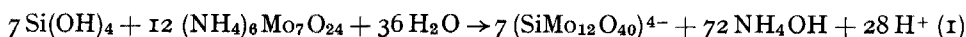
DETERMINATION OF SILICA IN GLASSES, CERAMICS AND REFRACTORIES

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Gravimetric¹⁻³ and titrimetric^{2,4} methods based on the precipitation of the silico-12-molybdate complex with 8-quinolinol, according to eqns. (1) and (2), have often been employed for the determination of silica.



In the titrimetric procedure, the amount of silica is found by adding excess of 8-quinolinol and determining the excess by an extended series of reactions involving bromination of the 8-quinolinol with bromate-bromide solution and subsequent iodometric determination of the excess bromine^{2,4}. This procedure may be greatly improved in accuracy and simplicity by employing a direct coulometric titration of the excess of 8-quinolinol with bromine according to eqn. (3). The coulometric titration of 8-quinolinol with bromine was first described by CARSON⁵ and has been applied to the determination of cobalt⁶ and aluminum⁷. The direct coulometric titration should be carried out in 0.03 *N* or weaker hydrochloric acid^{5,8}, but for this technique to be applicable to the determination of silica, the titration of 8-quinolinol must be carried out in 1-2 *N* acidic medium.

For any titrimetric procedure for silica based on the above reactions, the solubility of the 8-quinolinol precipitate of the silico-12-molybdate complex (Si-Mo-Ox) becomes a controlling factor, and the acidity during precipitation is important. Other workers^{2,4} using the iodometric procedure, precipitated the Si-Mo-Ox complex from about 1 *N* hydrochloric acid, but found that an empirical factor was necessary. In the present work on the development of an accurate, versatile method for the determination of silica in glasses and glass ceramics, the effect of different strengths of sulfuric, hydrochloric and perchloric acids on the precipitation of the Si-Mo-Ox complex was studied.

EXPERIMENTAL

Apparatus

A Cahn Electrobalance (Model M-10) was used to weigh samples, and a Leeds and Northrup pH meter (Model 7660) was employed for pH measurements.

A Leeds and Northrup coulometric analyzer (Cat. 7960) equipped with the

titration cell kit (Cat. 7961) and American Time Products frequency standard (Type 2005A) was employed for the constant current coulometric titration. The container part of the cell kit was a double-walled beaker with a capacity of 100 ml. This cell was kept at constant temperature during the titration by circulating constant temperature water from a water bath through the jacket. A Sargent Thermonitor (Cat. S-82050) was used to control the temperature of the water bath. The end-points were detected amperometrically using a Leeds and Northrup Electro-Chemograph Type E (Cat. 62200) equipped with platinum electrodes (straight wire, 1.5×0.09 cm diameter). Magnetic stirring was employed during the titration.

Reagents

Unless otherwise specified reagent-grade chemicals were used.

Silica calibration standards. Silica standard materials used in this study were two Corning Code 7940 samples and an ultrapure silica obtained from Atomergic Chemical Company.

Flux. In most cases the flux consisted of 5 parts by weight of potassium carbonate and 1 part of anhydrous sodium tetraborate. For some glasses high in ZrO_2 or TiO_2 and all glass ceramics and refractories, the amount of sodium tetraborate was increased.

Ammonium molybdate solution. A 0.1 M solution was prepared by dissolving 62.0 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 ml of distilled water and stored in a plastic bottle.

8-Quinolinol solution. A 0.1 M (0.4 N) solution was prepared by dissolving 29.0 g of HOC_9H_6N in 20 ml of 9 M sulfuric acid and 200 ml of water, and diluting to 2 l. The solution was filtered before dilution and stored in a plastic bottle. No appreciable concentration change was observed over a period of about one month.

Cell supporting electrolyte. The supporting electrolyte for coulometric generation of bromine consisted of a solution 0.2 M in NaBr, 1 M in H_2SO_4 , and 0.16 M in oxalic acid.

Cathode compartment electrolyte. The solution in the isolated cathode compartment was a 1.4 M Na_2SO_4 solution.

Development of the method using pure silica

About 10–25 mg of pure silica was weighed, fused, dissolved in water, and acidified. Then, 16 ml of ammonium molybdate solution was added and the pH of the solution adjusted to 1.3 to 1.4. After the formation of silico-12-molybdate, the acidity of the solution was adjusted to a predetermined normality. The solution was then diluted to 150 ml, and 25.00 ml of 8-quinolinol solution was added. The solution was diluted to 250.0 ml and a 10.00-ml aliquot of the filtered supernatant solution was taken for coulometric titration.

Since the excesses of ammonium molybdate and 8-quinolinol were expected to influence the precipitation, the amounts added were held constant, as specified above. The acidity for the precipitation of silico-12-molybdate with 8-quinolinol, however, was varied from 1 to 2 N in sulfuric, hydrochloric, and perchloric acids. Some representative results obtained from 1.5 N sulfuric acid are given in Table I. The equivalents of 8-quinolinol consumed were obtained by subtracting 25 times the equivalents of 8-quinolinol coulometrically titrated, according to eqn. (3), from the equivalents of

8-quinolinol added. The amount of silica present was then calculated, the theoretical stoichiometry of eqns. (1) and (2) being assumed. According to eqns. (1), (2) and (3), one equivalent of Br₂ is equivalent to 3.756 g of SiO₂.

The completeness of precipitation seemed to depend not only on the strength of the acid employed but also on the kind of acid and on the amount of silica. The completeness of precipitation in different acids of the same normality decreased in the order, sulfuric acid, hydrochloric acid and perchloric acid. For a given acid, the recovery of silica was more complete, the more dilute the acid. For a given concentration of any acid, the percentage recovery increased as the amount of silica increased; this effect was not due to the greater volumes of precipitate which were formed at higher silica concentrations (the precipitate was not separated before the dilution to 250 ml), for over the range 10–25 mg of silica the volumes of the precipitates were only 0.2–0.5 ml, *i.e.* the difference was negligible. Hence it was concluded that this increase in recovery with the amount of silica was mainly due to a variation in the solubility of the precipitate which is a function of the excess of reagents present; the less silica, the larger the excess of reagents and hence the more complete the precipitation.

With the concentrations of ammonium molybdate and 8-quinolinol chosen, the data indicated that for quantitative results, sulfuric acid was the preferred medium. The choice of acid concentration during the precipitation must be a compromise; the recovery of silica increases as the acidity decreases, whereas the selectivity of 8-quinolinol for silico-12-molybdate is greater the higher the acidity. The acid concentration chosen was 1.5 *N* just before the addition of 8-quinolinol.

In order to determine silica at major constituent levels by the proposed method it was necessary to correct for the incomplete recovery of silica. This was readily accomplished since it was found that the data for silica recovery in Table I fitted the

TABLE I

STUDY WITH PURE SILICA IN SULFURIC ACID MEDIUM

(Sulfuric acid added: 12.5 ml of 18.0 *N* H₂SO₄; acidity before addition of 8-quinolinol: 1.5 *N*; acidity after dilution to 250 ml: 0.9 *N*)

SiO ₂ taken (mg)	8-Quinolinol consumed (meq.)	SiO ₂ found (mg)	SiO ₂ taken : SiO ₂ found
12.83	3.425	12.86	0.997
13.83	3.683	13.83	1.000
16.51	4.393	16.50	1.001
18.79	4.983	18.72	1.004
19.29	5.113	19.20	1.005
21.83	5.770	21.67	1.007
24.66	6.495	24.40	1.011

linear function $f^* = a + bx$, where $f^* = \text{SiO}_2 \text{ taken} : \text{SiO}_2 \text{ found}$, and $x = \text{mg SiO}_2 \text{ found}$.

Fitting 33 data points similar to and including the data in Table I by least squares to this function, yielded values for the constants, $a = 0.9832$, and $b = 0.001123$. When this function was used analytically or graphically, f^* could be determined at any level (between 14–24 mg) of silica and applied to the experimental data to yield the true silica value. It was found convenient in view of the pre-selected reagent concentrations to limit the range of the method to 14–24 mg SiO₂.

Recommended procedure for glasses and glass ceramics

Weigh the ground sample, sufficient to give 14–24 mg SiO₂, to ± 0.01 mg and transfer to a 30-ml platinum crucible; for samples of over 100 mg weigh to the nearest 0.1 mg. Cover the sample with 10–15 times its weight of flux and then fuse. Disintegrate the melt and transfer to a 250-ml beaker with about 100 ml of distilled water. To ensure complete transference of the melt, rinse the crucible with about 1.5 ml of 3 *M* sulfuric acid followed with a little water. The amount of acid used is varied according to the amount of flux employed; the pH should not be lower than 1.3.

Some changes in the above procedure are required for samples containing greater than 5% of titanium dioxide, refractories, or certain low silica–high lead glasses (see under RESULTS AND DISCUSSION).

After complete dissolution of the sample, add 16 ml of ammonium molybdate solution and adjust the pH of the solution to 1.3–1.4 with 9 *M* sulfuric acid and/or dilute ammonium hydroxide. Leave the solution for about 30 min to allow complete development of the yellow silico-12-molybdate complex. Transfer the solution to a 250-ml volumetric flask. Add 12.5 ml of 9 *M* sulfuric acid and dilute to an 150-ml mark made on the flask. Then pipet in slowly 25.00 ml of 8-quinolinol solution with constant agitation. Rinse down any 8-quinolinol solution on the neck of the flask with a little water. Place the flask in a water bath at 60–70° for 15 min and occasionally agitate it. Remove the flask from the bath, cool to room temperature and finally dilute to the mark. After the precipitate settles, filter on a dry double thickness of No. 42 Whatman paper. Cover the funnel with a watch glass and collect the filtrate in a 100-ml volumetric flask to minimize evaporation. Use the first 10 ml of the filtrate to rinse the receiving flask and discard this. Collect 20–30 ml more filtrate for coulometric titration of the excess 8-quinolinol in the filtrate.

Pour 60 ml of the cell supporting electrolyte into the thermostatted cell and bring the cell contents to 30°. Insert the generator and indicator electrodes, turn on the magnetic stirrer and titrate with the Coulometric Analyzer set at a constant current of 64.3 mA. Set the current range of the Electro-Chemograph at 50 μ A and the damping at position 1. Impress a polarizing potential of 0.3 V across the indicator electrodes.

Generate *ca.* 4 μ eq. of bromine in the supporting electrolyte and take the current reading. This pre-titration current reading, corrected for the effect of diluting the supporting electrolyte volume by 10.00 ml (the anticipated sample volume to be added) is recorded as the pre-titration end-point current. Add a 10.00-ml aliquot of the filtrate to the titration cell and then titrate. Establish the number of equivalents of bromine required to reach the end-point by reading the indicator current before and after the pre-titration end-point current has been reached and interpolating to the pre-titration end-point. The amount of 8-quinolinol back-titrated is 0.25–0.14 meq. for 14–25 mg of silica.

Standardize the 8-quinolinol solution by the procedure described above, using the same pipets to eliminate the necessity for pipet calibrations.

The silica is calculated as follows:

$$\% \text{ SiO}_2 = \left(\begin{array}{cc} \text{Equiv.} & 25 \cdot \text{Equiv.} \\ \text{8-quinolinol} & \text{8-quinolinol} \\ \text{added} & \text{titrated} \end{array} \right) \cdot 3.756 \cdot f^* \cdot 100 / \text{wt. of sample (g)}$$

The electrodes must be cleaned between titrations by rinsing them first with 6 *M*

hydrochloric acid and then with water. Otherwise, after several titrations, erratic end-points will occur.

RESULTS AND DISCUSSION

Preliminary studies of the coulometric titration of 200–400 $\mu\text{eq.}$ of 8-quinolinol with bromine showed that the relative standard deviation was usually better than 0.2%.

When a supporting electrolyte containing only 0.2 M sodium bromide was employed, the dibromo derivative of 8-quinolinol separated during the titration and an erratic end-point was obtained. In order to keep the dibromo derivative soluble, it was necessary to employ 0.5 N or higher acidity for titrating about 400 $\mu\text{eq.}$ of 8-quinolinol in 70 ml of solution. The above finding is contrary to CARSON⁵ who reported that no end-point could be obtained with solutions in which the dibromo derivative was soluble. This contradictory observation is probably due to the different indicator systems employed.

When 8-quinolinol was titrated in the presence of ammonium molybdate (with supporting electrolyte, 1–2 N in acid and 0.2 M in NaBr), a precipitate formed during electrolysis (probably the 5,7-dibromo-8-quinolinolate of molybdenum). The use of citric acid, tartaric acid, and oxalic acid to prevent the precipitation was studied. For the recommended acidity (1–2 N), only oxalic acid proved to be effective.

The precision of the method can be estimated by considering the results obtained for pure silica. With the data obtained from pure silica in 1.5 N sulfuric acid, the deviations of the individual experimental "Correction factors" from their corresponding best fitted values obtained from the least squares method were employed to calculate the standard deviation. For 33 determinations over the range 10–25 mg of silica, the standard deviation was found to be 0.002 corresponding to a relative standard deviation of 0.2%.

The results obtained for silica in a number of glass, glass ceramic, and refractory materials by this method are given in Table II, and compared with the values obtained by the acid-dehydration gravimetric method. It can be seen that the results obtained for 17 different glass and glass ceramic compositions, two refractories, and one felspar are satisfactory. Of the 22 samples analyzed, 18 samples contained 40–80% of silica and 4 samples contained less than 10%. The agreement between the 2 different methods was within 0.6% absolute, which was reasonably good when one considers that the results compared were obtained not only by different methods but also by several analysts⁹.

In order to cope with certain potential interferences in the cases of some glasses, glass ceramics, and refractories, special studies with consequent procedural modifications were made. The results of these studies are discussed below for arsenic and antimony, zirconium and titanium, and barium and lead containing samples.

Arsenic- and antimony-containing samples

Since the procedure included the coulometric titration of 8-quinolinol with bromine, arsenic(III) or antimony(III) would interfere. It is known that fusion with alkali carbonate effects oxidation of many elements¹⁰. The oxidation potentials of the Sb(III)-Sb(V) and As(III)-As(V) couples in basic solutions are reported¹¹ to be about + 0.59 and + 0.67 V, respectively. It was expected therefore that trivalent antimony and arsenic would be oxidized to the pentavalent state during the potassium

TABLE II
RESULTS OF SILICA DETERMINATION

Type of sample	% SiO ₂		Difference
	Present method	Acid-dehydration method	
1. Soda Felspar	67.98, 68.03 Av. 68.01	68.03, 68.17 Av. 68.10	- 0.1
<i>Glass</i>			
2. SiO ₂ -Na ₂ O	71.13, 71.05 Av. 71.09	70.64, 70.70 Av. 70.57	- 0.5
3. SiO ₂ -Na ₂ O-K ₂ O	76.29, 76.19 Av. 76.24	75.85, 76.30, 76.16 Av. 76.10	+ 0.1
4. SiO ₂ -Na ₂ O-CaO	70.39, 70.30 Av. 70.35	70.04, 69.85, 69.88 Av. 69.92	+ 0.5
5. SiO ₂ -Na ₂ O-Al ₂ O ₃	72.78, 72.22 Av. 72.50	72.43	+ 0.1
6. SiO ₂ -Na ₂ O-CaO-MgO	73.37, 73.28 Av. 73.33	72.96	+ 0.3
7. SiO ₂ -B ₂ O ₃ -Na ₂ O-Al ₂ O ₃	80.36, 80.70 Av. 80.53	80.38	+ 0.1
8. SiO ₂ -B ₂ O ₃ -Na ₂ O-Al ₂ O ₃ - As ₂ O ₃ (0.8%)	77.81, 77.69 Av. 77.75	78.00	- 0.2
9. SiO ₂ -Al ₂ O ₃ -Na ₂ O-Sb ₂ O ₃ (1%)	60.45, 60.77 Av. 60.61	61.0, 61.3 Av. 61.2	- 0.6
10. SiO ₂ -Al ₂ O ₃ -Na ₂ O-Sb ₂ O ₃ (1%)	61.11, 60.93 Av. 61.02	61.2, 61.4 Av. 61.3	- 0.3
11. SiO ₂ -La ₂ O ₃ -Cs ₂ O-Li ₂ O-UO ₂ (7%)	43.05, 43.51 Av. 43.28	42.97, 42.89 Av. 42.93	+ 0.4
12. SiO ₂ -PbO (77%)-ZnO-B ₂ O ₃ - Al ₂ O ₃	1.41, 1.41, 1.42 Av. 1.41	1.39, 1.40 Av. 1.40	+ 0.01
13. SiO ₂ -PbO (77%)-ZnO-B ₂ O ₃ - Al ₂ O ₃	2.50, 2.50 Av. 2.50	2.54, 2.53 Av. 2.54	- 0.04
14. SiO ₂ -Na ₂ O-K ₂ O-Al ₂ O ₃ - Sb ₂ O ₃ (0.4%)-F (1%)-BaO (11%)	68.54, 68.54 Av. 68.54	69.14	- 0.6
<i>Glass ceramic</i>			
15. SiO ₂ -Al ₂ O ₃ -Li ₂ O-TiO ₂ (2%)	63.60, 63.33 Av. 63.46	63.72, 63.65 Av. 63.69	- 0.2
16. SiO ₂ -Al ₂ O ₃ -Li ₂ O-MgO- ZnO-TiO ₂ (5%)-As ₂ O ₃ (0.6%)	69.23, 69.65 Av. 69.44	69.2	+ 0.2
17. SiO ₂ -Al ₂ O ₃ -Li ₂ O-TiO ₂ (10%) ^a	59.44, 59.14 Av. 59.29	59.30, 59.47 Av. 59.39	- 0.1
18. SiO ₂ -Al ₂ O ₃ -MgO-Li ₂ O- ZnO-As ₂ O ₃ (0.5%)-ZrO ₂ (4%)	69.32, 69.07 Av. 69.20	69.55	- 0.4

Type of sample	% SiO ₂		
	Present method	Acid-dehydration method	Difference
19. SiO ₂ -Al ₂ O ₃ -Na ₂ O-TiO ₂ (6%) - BaO (6%) - As ₂ O ₃ (0.4%) ^b	42.59, 42.71 Av. 42.65	43.0	- 0.3
20. SiO ₂ -Al ₂ O ₃ -B ₂ O ₃ -TiO ₂ - MgO-Li ₂ O	61.24, 59.92 Av. 61.08	60.90	+ 0.2
<i>Refractory</i>			
21. SiO ₂ -Al ₂ O ₃ -MgO-Chrome Ore-TiO ₂ (5%) ^c	3.18, 3.24 Av. 3.21	3.32	- 0.1
22. SiO ₂ -Al ₂ O ₃ -MgO-Chrome Ore-TiO ₂ (5%) ^d	8.50, 8.38 Av. 8.44	8.40, 8.45 Av. 8.43	+ 0.01

^a 1 ml glycerol added before addition of ammonium molybdate.

^b 1.5 g Na₂SO₄ added before addition of ammonium molybdate.

^c 25 ml glycerol added before addition of ammonium molybdate.

^d 15 ml glycerol added before addition of ammonium molybdate.

carbonate-sodium tetraborate fusion. When about 100 mg of Sb₂O₃ was fused with K₂CO₃-Na₂B₄O₇ flux or 1 min, only 3.7 to 2.4% of the original Sb₂O₃ was recovered as Sb(III). Since the final concentrations (after melting) of arsenic and/or antimony rarely exceed 1%, this nearly complete (96%) oxidation effectively reduces the interference to a negligible value.

Arsenic(V) is reported¹ to react with ammonium molybdate and 8-quinolinol to form precipitates under certain conditions. However, it was demonstrated by running standard silica solutions spiked with 1-2% of arsenic pentoxide, that no precipitate was formed under the present conditions.

Zirconium- and titanium-containing samples

When hydrochloric acid medium is employed in the precipitation of silico-12-molybdate with 8-quinolinol, zirconium and titanium are reported¹ to hydrolyze (during the digestion at 60°) and interfere. However, precipitation of the 8-quinolinol complex in sulfuric acid as specified in the recommended procedure yielded silica results on glass ceramics containing up to 4% ZrO₂ (No. 18) and 5% TiO₂ (No. 16) with no evidence of interference.

When the titania content was as high as 10% (No. 17), hydrolysis was observed during the period for silico-12-molybdate complex formation. Although the hydrolyzed titanium products redissolved on addition of acid before precipitation, the hydrolysis seemed to carry down some silicon(IV) and cause incomplete formation of silico-12-molybdate. For example, when sample No. 17 was analyzed under the usual conditions the silica found ranged from 56.5 to 58.1% (actual value, 59.4%). This difficulty was overcome by adding 1 ml of glycerol to the solution before addition of ammonium molybdate. Glycerol was found to be more effective than sulfate ion for preventing the hydrolysis of titanium(IV). With the use of more glycerol the titanium-containing refractories (No. 21 and 22) were analyzed satisfactorily. With one of the refractories, the titania content was 1.6 times the silica content. (The application of the method to the determination of silica in zircon refractories is being investigated.) The refractory samples analyzed were fused with K₂CO₃-Na₂B₄O₇ (1:1) flux in a 150-ml platinum dish and the melts were dissolved in dilute sulfuric acid with the aid of a magnetic stirrer. After the addition of glycerol, the determina-

tion of silica was carried out by the regular procedure.

Although glycerol is oxidized by bromine in neutral solution¹², it is stable in acidic medium. Only a negligible blank was obtained when 1 ml of glycerol was diluted to 250 ml and a 10.00-ml aliquot was titrated as for a sample. When 15 and 25 ml of glycerol were employed, the blank titrations were found to be about 0.4 and 0.7 $\mu\text{eq.}$ of bromine, respectively. However, the refractories analyzed were low in silica, and the corrections required for the use of glycerol hardly affected the last figure of the results.

Barium- and lead-containing samples

In sulfuric acid medium, barium and lead are precipitated as sulfates, whereas in hydrochloric acid medium, they are precipitated as molybdates. The latter would seriously disturb the desired conditions for the formation of the silico-12-molybdate complex. The use of oxalic, tartaric, and citric acids to prevent the precipitation of barium molybdate was attempted; however, not only the barium precipitation was prevented but also an incomplete formation of silico-12-molybdate was observed (probably, due to the formation of a stronger complex between molybdenum(VI) and the organic acid). Actually, the sulfuric acid medium was found to be satisfactory. Although barium and lead were precipitated as sulfates, no loss of silica was observed, and the precipitated sulfates could be left in the solution, thus avoiding an extra filtration step.

The lead glasses analyzed (No. 12 and 13) were low in silica, and easily dissolved with dilute nitric acid. The sample was suspended in 30–40 ml of distilled water and 3 ml of 8 *M* nitric acid was added. After complete dissolution of the sample, the solution was diluted to about 100 ml. Then about 1 g of sodium sulfate dissolved in 10 ml of water was added to precipitate lead as lead sulfate. The determination of silica was otherwise carried out by the regular procedure.

In summary, the present method has been applied to a wide range of compositions, including Li, Na, K, Cs, Mg, Ca, Zn, B, Al, Ti(IV), Zr, Ba, Pb, As(V) (< 1%), Sb(V) (< 1%), La, U(VI), Cr(VI) and F(1%). Germanium(IV), vanadium(V), and phosphorus(V) are known to interfere by forming precipitates with ammonium molybdate and 8-quinolinol¹.

Among the advantages of this method is the fact that borax may be incorporated into the fusion flux, greatly facilitating the decomposition of samples which are otherwise difficult to attack by alkali carbonate alone. If borax is included in the flux used for the gravimetric determination of silica by dehydration, the boron must be removed by an arduous procedure involving volatilization of methyl borate¹⁰.

Finally, it should be mentioned that the method is rapid; about 3 h are required to finish duplicate determinations on one sample. Eight determinations can be completed by one analyst in an 8-h day.

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SUMMARY

A rapid method for the determination of silica in glasses, glass ceramics and

refractories is described. The utilization of direct coulometric titration of the excess of 8-quinolinol employed to precipitate the silico-12-molybdate complex, enables duplicate determinations in the presence of diverse ions to be completed in about 3 h. Studies of the optimum conditions indicated that the acidity and choice of acid were critical. For greatest versatility a sulfuric acid medium was better than hydrochloric or perchloric acids. The addition of glycerol allowed analysis of titanium-containing refractories. The accuracy of the method for a wide variety of materials is similar to that of the conventional acid-dehydration method.

RÉSUMÉ

On décrit une méthode rapide pour le dosage de la silice dans le verre, la céramique et les matériaux réfractaires. En effectuant un titrage coulométrique direct de l'hydroxy-8-quinoléine, ajoutée en excès pour précipiter le complexe silicomolybdique, on peut obtenir un double résultat en 3 h environ. L'acidité et le choix de l'acide sont importants. En présence de titane, il faut ajouter du glycérol. La précision de cette méthode est comparable à celle obtenue avec la méthode gravimétrique conventionnelle par insolubilisation.

ZUSAMMENFASSUNG

Es wird eine schnelle Methode zur Bestimmung von Kieselsäure in Gläsern, Glaskeramiken und Ofenmaterialien beschrieben. Mit 8-Oxychinolin wird der Silico-12-molybdatkomplex gefällt und der Überschuss direkt coulometrisch titriert. Es sind dadurch Doppelbestimmungen in Gegenwart verschiedener Ionen in einer Zeit von etwa 3 Std. möglich. Untersuchungen der optimalen Bedingungen zeigen, dass die Acidität und die Wahl der Säure entscheidend sind. Schwefelsäure ist für viele Zwecke besser geeignet als Salz- oder Perchlorsäure. Die Zugabe von Glycerin erlaubt die Analyse von titanhaltigen Ofenmaterialien. Die Genauigkeit der Methode ist für sehr unterschiedliche Materialien ähnlich dem konventionellen Verfahren, bei dem mit Säure eingedampft wird.

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ISONITROSOACETANILIDE AS AN ANALYTICAL REAGENT

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In earlier papers, a study of the reactivity of various isonitrosoacetarylides with inorganic ions was described and possible analytical applications were reported. Attempts were made to elucidate the effect of different substituents in the benzene nucleus on the behaviour of the functional group $A-NH-CO-CH=NOH$. The derivatives reported previously include the monohalogenated (with the various halogens in different positions)^{1,2}, methoxy- and ethoxy- (both in the *ortho* and *para* positions)³, carboxy-^{4,5}, N-methyl and N-ethyl⁶, dihalogenated⁷, methoxyhalogenated⁸ and alcohol derivatives⁹.

In this paper the reactivity of isonitrosoacetanilide is described. This is the simplest member of the isonitrosoacetarylides family. Because it has no substituents, it is interesting as a point of reference to estimate the influence of the various substituents as well as for its own reactions. The composition of some of its complexes is also described.

EXPERIMENTAL

Preparation of isonitrosoacetanilide

Isonitrosoacetanilide was prepared by the SANDMEYER synthesis¹⁰, as modified and described by MARVEL and HIERS¹¹. It was purified by repeated recrystallizations from ethanol, after boiling with active carbon (m.p. 175°).

Elementary analysis: calcd.: C 58.50%, N 17.09%, H 4.88%; found: C 58.65%, N 17.40%, H 5.03%.

Reactivity

Reagent. The substance was insoluble in benzene and ether, almost insoluble in water and rather soluble in many alcohols. Ethanol (solubility: 9.5%) was chosen as solvent to prepare a 1% solution of isonitrosoacetanilide.

Tested ions. The reactions of isonitrosoacetanilide with 49 metal ions in aqueous solution were studied. The metal solutions contained 1 g of metal ion per liter. The procedure was as follows. To 2 ml of the test solution were added 0.5 ml of the reagent solution and 0.25 ml of the 2 N solution used to adjust the medium between pH 1-13. The reagents used for this pH adjustment were nitric acid, acetic acid, acetic acid-sodium acetate, ammonia hydroxide and sodium hydroxide. Each of the tests was checked against a blank test.

It was observed that the order of addition of the reagents had a considerable effect on the sensitivity of the reactions: higher sensitivities were obtained when the reagent for pH adjustment was added last.

The reactions obtained and the corresponding sensitivities are indicated in Table I. Other ions tested were Ag(I), Pb(II), Tl(I), Hg(I), Hg(II), Bi(III), Cd(II), As(III), Sb(III), Sn(II), As(V), Sb(V), Au(III), Sn(IV), W(VI), Mo(VI), Pt(IV), Se(IV), Se(VI), Fe(II), Al(III), V(V), Cr(III), Tl(III), Ti(IV), Th(IV), Zr(IV), Ce(III), In(III), Be(II), Zn(II), Ca(II), Sr(II), Ba(II), Mg(II), Li(I), Na(I), K(I), Cs(I) and Rb(I).

TABLE I
REACTIONS OF ISONITROACETANILIDE WITH METAL IONS

Ion	Limit of dilution		Medium
	Precipitation	Coloration	
Cu(II)	—	1 : 200,000	NaOH
Pd(II)	1 : 250,000	1 : 400,000	HNO ₃
Fe(III)	—	1 : 50,000	HAcO—NaAcO
UO ₂ (II)	1 : 10,000	—	NH ₃
Ce(III)	1 : 20,000	1 : 20,000	NH ₃
La(III)	1 : 10,000	—	NH ₃
Mn(II)	1 : 100,000	—	NH ₃
Ni(II)	—	1 : 100,000	NH ₃
Co(II)	—	1 : 1,000,000	NH ₃

Most interesting reactions

Palladium. Palladium was the only ion which gave both precipitation and color reactions in an acidic medium; in an ammoniacal or alkaline medium these were not produced. The yellow precipitate formed on addition of the reagent solution to 2 ml of 0.1% (w/v) palladium solution followed by acidification with nitric acid, was powdery and acquired an orange color on drying at 45–50°. The dilution limit of the precipitation reaction, in diluted nitric acid medium, was 1 : 250,000. At higher dilutions in the same medium, no precipitate appeared, but a yellow coloration was maintained as far as a dilution limit of 1 : 400,000. In the other tested acidic media (acetic, hydrochloric) the limits of dilution were slightly lower. Both the precipitate and the color disappeared on making alkaline or on addition of sodium cyanide. None of the other cations tested interfered with the reaction, which is thus specific for palladium. However, the iodide ion, which gave a black precipitate of palladium iodide, did interfere with the reaction.

Cobalt. With a 0.1% (w/v) cobalt solution, a brown-orange precipitate appeared. As the dilution was increased, a brown-yellow colored solution was obtained, and, on further dilution, a yellow one. Both the precipitate and coloration disappeared on acidification. The precipitate disappeared on addition of potassium cyanide, but the coloration remained. The dilution limit of the reaction, in ammoniacal medium, was 1 : 1,000,000. This test was unsatisfactory in the presence of Cu, Fe(III), Mn and Ni, which reacted with the reagent under the same pH conditions as cobalt. Complex formation with cyanide prevented the interferences of copper and nickel.

Gravimetric study of the Pd-complex

To determine the composition of the precipitate formed with palladium, elementary analyses were carried out with the following average results: C 44.17%, H 3.70%, N 12.73%, Pd 25.50%. (Palladium was determined by ashing to the metal.) For $(C_8H_7O_2N_2)_2Pd$ the theoretical values are C 44.35%, H 3.69%, N 12.93%, Pd 24.61%. The results obtained experimentally thus agreed well with those expected for a 2:1 isonitrosoacetanilide-palladium complex.

Colorimetric study of the Co-complex

This study was carried out by the continuous variations method¹² and by the mole ratio method¹³. The latter method was performed at a constant cobalt concentration with varying isonitrosoacetanilide concentrations and also at a constant ligand concentration with varying metal ion amounts; the studies with constant ligand concentration gave clearer results.

For these colorimetric methods, an ethanolic $1.97 \cdot 10^{-3} M$ solution of isonitrosoacetanilide and an aqueous $1.72 \cdot 10^{-3} M$ solution of cobalt(II) nitrate were used. The concentration of the cobalt solution was determined gravimetrically as $NH_4CoPO_4 \cdot H_2O$. The absorbances were measured in an Engel filter colorimeter (Kipp & Zonen) with a high-sensitivity galvanometer and matched 16-mm diam. glass tubes. The readings were taken at pH 10 after 25 min for stabilization of the color, and with filter number 43 (maximum absorbance at 430 m μ).

The curves obtained are shown in Figs. 1 and 2. The results indicated that a 3:2 ligand-cobalt complex was formed.

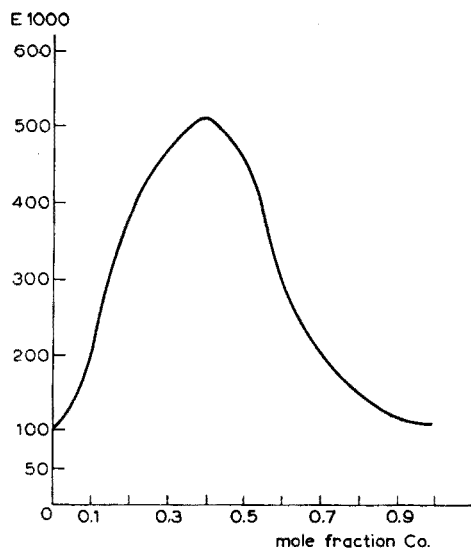


Fig. 1

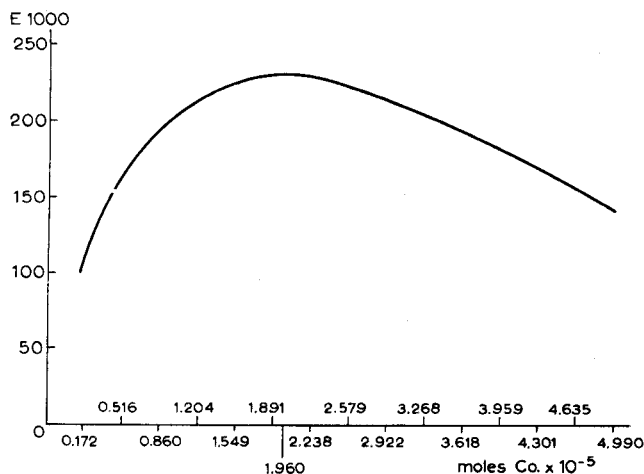
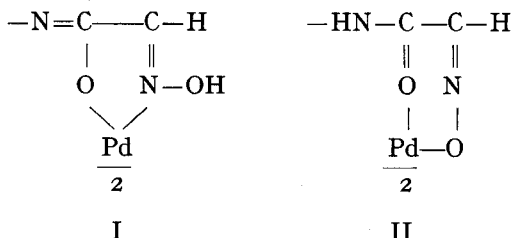


Fig. 2

Infrared study of the Pd-complex

The infrared spectrum of the palladium complex was measured in order to obtain some idea of the mode of action of the functional group $-\text{NH}-\text{CO}-\text{CH}=\text{NOH}$. It was hoped to elucidate—among the many possible forms of reaction—whether a five-member ring chelate such as I, which would be possible as a result of enolization, or a six-member chelate such as II, with participation of the oxime H, was formed.



Owing to the insolubility of the palladium complex in non-polar solvents the spectrum was determined on a KBr tablet, which limited its interpretation. However, a study of the spectrum inclined one to accept an enolization; the band at 3600 cm^{-1} and the extensive alteration of the spectrum in the $1700-1500 \text{ cm}^{-1}$ zone indicated a five-member ring rather than a six-member ring. This agrees with the fact that the N-substituted derivative⁶—in which this enolization is not possible owing to the absence of amide H—does not give the precipitation reaction with palladium in acidic medium, which is given by all the isonitrosoacetyl derivatives of primary amines. In order to determine whether it is the N or the H atom in the oxime group which acts, we are at present preparing the acetyl and alkyl derivatives of many isonitrosoacetylides.

RESULTS AND DISCUSSION

The reactivity of isonitrosoacetanilide tested against 49 ions, is of the order of the other isonitrosoacetarylides which we have previously studied. With few variations, these acetarylides give in ammoniacal medium color reactions with Co, Ni, Cu, Fe and Mn, and in acidic medium a precipitation reaction with Pd. This precipitation reaction is given by all the isonitrosoacetyl derivatives tested up to the present, except the N-substituted ones, such as N-methyl- and N-ethylisonitrosoacetanilide⁶.

Of the various derivatives tested so far, isonitrosoacetanilide is the only compound which reacts with lanthanum, cerium(III) and uranyl ions in ammoniacal medium, though very weakly. Another difference is that isonitrosoacetanilide gives a precipitate with manganese(II) in relatively concentrated solutions, whereas all the other derivatives give only colors.

The sensitivity of the reactions with Pd, Cu, Fe and Ni is less than that of the reactions of most of the other isonitrosoacetarylides substituted in the nucleus. The only highly sensitive reaction of isonitrosoacetanilide is that with cobalt in ammoniacal medium, the dilution limit of which reaches 1 : 1,000,000, *i.e.* about the same order of magnitude as with the 2-ethoxy-³ and the 4-carboxy-⁵ derivatives and higher than with the other isonitrosoacetarylides.

None of the soluble or insoluble complexes of isonitrosoacetanilide is extractable with water-immiscible solvents, which precludes their application for separation by extraction, whereas the metal complexes of some other derivatives, such as the alkoxy-, can be used for this purpose³. The gravimetric study of the palladium complex and the spectrophotometric study of the soluble cobalt complex indicate the same stoichiometry of the complexes as that previously established for the other derivatives².

The results show that the applications of isonitrosoacetanilide as reagent are not of great interest. The reaction with palladium in acidic medium, which has a dilution limit of 1 : 400,000 and is specific for this ion, is less sensitive than that of other compounds of this group; *p*-iodoisonitrosoacetanilide gives a precipitate at a dilution of 1 : 800,000 and is also specific¹. However, the study of isonitrosoacetanilide permits some other comparisons to be made with its substituted derivatives. It seems, in general, that substitution increases the sensitivity of many reactions and produces some good properties. For instance, the halogen substitution gives a high sensitivity with palladium; this sensitivity increases with the atomic weight of the halogen. Thus 2-chloroisonitrosoacetanilide gives a precipitate at a dilution of 1 : 90,000 and only a coloration at 1 : 100,000¹ and the 4-chloroisonitrosoacetanilide gives a precipitate at 1 : 350,000 and a coloration at 1 : 700,000¹, whereas 4-iodoisonitrosoacetanilide gives a precipitate at 1 : 800,000 which makes the reaction one of the most sensitive available for precipitation of this ion. The 4-iodo derivative is suitable for gravimetric determination of palladium even in the presence of gold and platinum².

This increase in sensitivity due to substitution with halogen also takes place in the reactions with cobalt and nickel. The mentioned halogen derivatives give dilution limits between 1 : 700,000 and 1 : 900,000¹. It is the same with the carboxy derivatives, 4-carboxy-⁵ and 2-carboxy-⁴, and even with the alkoxy derivatives³.

In regard to the position of substitution, it seems that the *para* position is more favorable than the *ortho* one; the sensitivities of the reactions of 4-carboxyisonitroso-

acetanilide with cobalt and manganese⁵ are greater than those of the 2-carboxy derivative⁴, though the sensitivities of the other ions remain almost unchanged. The sensitivities of 4-methoxy- and 4-ethoxyisonitrosoacetanilide are in general greater than those of the 2-methoxy- and 2-ethoxyisonitrosoacetanilide³. The same trend is observed in the reactions of palladium with 4-chloroisonitrosoacetanilide and 2-chloroisonitrosoacetanilide. The introduction in the nucleus of two chlorine atoms produces a decrease in reactivity; this is the case with the 2,3-dichloro-, 2,5-dichloro- and 3,4-dichloro derivatives⁸. The substitution of one of these chlorine atoms by other less electronegative substituents such as $-\text{OCH}_3$, restores the normal reactivity of the active group⁸. An attempt to note the reactivity of the trichlorinated derivatives failed, due to the impossibility of obtaining the corresponding derivative of the 2, 3, 5-trichloraniline which does not give the SANDMEYER synthesis.

The entrance into the molecule of substituents of obvious organic character, makes some complexes soluble in many water-immiscible solvents and permits their extraction, *e.g.* the palladium complexes of the alkoxyisonitrosoacetarylides³ and the copper and nickel complexes of the N-substituted derivatives⁶.

SUMMARY

In a continuation of earlier work on the reactivity of various isonitrosoacetarylides, the simplest of the series, isonitrosoacetanilide was examined. In acidic medium, this reagent gives a specific reaction with palladium (dilution limit 1 : 400,000), and in ammoniacal medium a very sensitive reaction with cobalt (dilution limit 1 : 1,000,000). The composition of the complexes involved was established as R_2Pd and R_3Co_2 . The effect of substitution on the reactivity is discussed.

RÉSUMÉ

Les auteurs ont examiné l'isonitrosoacétanilide comme réactif d'analyse. En milieu acide, il donne une réaction spécifique avec le palladium (limite de dilution 1 : 400,000); en milieu ammoniacal, une réaction très sensible avec le cobalt (limite de dilution 1 : 1,000,000). Composition des complexes formés: R_2Pd et R_3Co_2 . On a examiné l'influence de substitution sur la réactivité.

ZUSAMMENFASSUNG

In Fortsetzung früherer Arbeiten über die Reaktivität verschiedener Isonitrosoacetarylide wurde das einfachste dieser Reihe das Isonitrosoacetanilid untersucht. Im salzsauren Medium ergibt dieses Reagenz eine spezifische Reaktion mit Palladium (Grenzkonzentration 1 : 400,000) und im ammoniakalischen Medium eine sehr empfindliche Reaktion mit Kobalt (1 : 1,000,000). Für die Zusammensetzung der Komplexe wurde R_2Pd und R_3Co_2 gefunden. Der Einfluss der Substitution auf die Reaktivität wird diskutiert.

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A SEPARATION SCHEME FOR GALLIUM, INDIUM, THALLIUM, GERMANIUM, TIN AND LEAD BY SOLVENT EXTRACTION WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

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Gallium, indium, thallium, tin and lead often occur together naturally in minerals in conjunction with other more common elements. Efficient and convenient separations of certain combinations of the above-mentioned elements, *e.g.* indium and tin, indium and lead, and indium and gallium by precipitation methods have however proved difficult¹. Furthermore, some of these separations are of interest to the radiochemist since the elements in question may be produced from neighbouring elements in the periodic table or they are found, with the exception of thallium and lead, among the fission products resulting from the fission of certain heavy nuclei². On these grounds germanium has been studied in addition to the previously mentioned elements.

Liquid-liquid extraction can frequently provide more convenient and efficient separations than precipitation methods where the same main chemical reactions are involved. Accordingly an examination was made of the application of N-benzoyl-N-phenylhydroxylamine (BPHA) to the separation of the above-mentioned elements by solvent extraction methods. BPHA is a versatile organic reagent³; it has been used for the separation and gravimetric determination of gallium, indium^{4,5} and tin⁶. The precipitates formed by gallium and indium are soluble in chloroform⁴ and BPHA in chloroform has been examined⁷ as an extractant for lead. Preliminary experiments showed that tin and thallium are also extracted into chloroform solutions of BPHA.

In the present work the distribution of each element between various aqueous phases and a chloroform phase containing BPHA was examined and several convenient separations were found.

Phase distributions of the different elements were measured using radioactive tracers except in the case of lead where distributions were followed by compleximetric titration⁸. Radio-isotopes were also used to determine the efficiency of the separations, except for lead for which a spot test was applied⁹.

EXPERIMENTAL

Isotopes

Germanium-68 was kindly provided by Dr. D. J. SILVESTER (M.R.C. Cyclotron

Unit, Hammersmith Hospital, London) adsorbed on alumina from which a chromatographic column was prepared and carrier-free gallium-68 was 'milked' as required by the method of GREEN AND TUCKER¹⁰. The EDTA was most effectively removed from the gallium by taking the eluate to dryness, with hydrogen peroxide added, and heating the container to a dull red heat. Germanium-68 when required was desorbed from the alumina with 8 *M* hydrochloric acid and extracted into chloroform from which it was recovered by shaking with 2 *M* hydrochloric acid.

Indium-114m containing a known concentration of carrier indium was obtained from the Radiochemical Centre, Amersham, England.

Tin-113 was obtained by neutron irradiation of metallic tin in BEPO, Harwell. The 27.5-h tin-113 was allowed to decay away before use. Thallium-204 was also obtained by irradiation of thallium in BEPO.

EXPERIMENTAL

Reagents

Lead nitrate. A 0.1 *M* solution was prepared from reagent-grade salt, and standardized by compleximetric titration using xylenol orange indicator⁸.

N-Benzoyl-N-phenylhydroxylamine. This was supplied either by British Drug Houses or L. Light and Co. Samples with m.p. 120–121° were used directly; those with lower m.p. were recrystallized from hot water.

Chloroform. 'Laboratory Reagent Grade', containing 2% ethanol as preservative.

Acetic acid buffer pH 5.3. 80 g of anhydrous sodium acetate and 8 ml of glacial acetic acid were diluted to 1 l.

Apparatus

The thallium and indium samples were counted in liquid form (10 ml) in an annular type Geiger-Muller counter (Twentieth Century Electronics, type M6H). The other radio-isotopes, also in liquid form (2 ml) were counted using a well-type γ -scintillation counter, making use of the radiation resulting from positron annihilation in the case of gallium and the 0.393 MeV γ -ray of the 1.7-h indium daughter of tin-113. Germanium was determined indirectly by measuring the gallium-68 (half-life 68 min) after allowing sufficient time for the latter to come to equilibrium with the parent. The tin-113 was determined indirectly on the same basis.

pH measurements were made using a Doran 'Universal' pH meter standardized at pH 4.0 with 0.05 *M* potassium hydrogen phthalate. Mixing of the phases was performed in polyethylene bottles using a mechanical shaker of the vibrator type. The phases were separated in a glass separating funnel.

Outline of the procedure

Ten-ml samples (10.5 ml for indium and thallium) of the aqueous phase were equilibrated for a certain time with an equal volume of chloroform containing the BPHA. The effect of pH or acid concentration was first determined by shaking the two phases together for a time (usually 15 min) known to be longer than that necessary for equilibrium to be established. A 1% solution of BPHA in chloroform was used. For gallium, indium, lead and thallium, 0.5 ml of acetic acid-acetate buffer was added to the aqueous phase and the pH was adjusted with hydrochloric acid or ammo-

nia as required. For germanium hydrochloric acid was used and for tin hydrochloric or perchloric acid was employed. The extraction at the lowest optimum pH was then examined as a function of the BPHA concentration in chloroform keeping the equilibration times constant (15 min). With the minimum concentration of reagent in chloroform required to give maximum extraction the distribution of metal ions between the two phases was then determined as a function of time. In these experiments the concentration of metal ion varied from one metal to another but at least a 20-fold (molar) excess of reagent over metal ion was maintained. The maximum concentrations of each metal ion which could be extracted without impairing the extraction efficiency were thus obtained.

In these experiments, after equilibration and separation of the phases, the aqueous phase was washed twice with 10-ml portions of chloroform before withdrawing samples for counting or titrating. A check on the material balance was also frequently performed by measuring the activity transferred to the chloroform phase.

Separations

The separation of pairs of the elements was checked. A synthetic mixture of the two elements was taken and a radioactive tracer (except for lead) added for one member of the pair. The acidity was adjusted to the previously determined optimum value and the extraction performed. The inactive component thus separated was examined for radioactivity. The experiment was repeated with the other member of the pair labelled. From the results separation factors were calculated. Separations involving gallium, indium, thallium and lead were performed from acetic acid-acetate media. Tin was extracted either from 0.8 *M* hydrochloric acid or 4 *M* perchloric acid into BPHA in chloroform, and germanium from 8 *M* hydrochloric acid into chloroform alone. By these procedures germanium-68 was separated from gallium-68, and tin-113 from indium-113m, and the gallium and indium were allowed to decay away completely, the residual activity in each case thus providing a further check on the efficiency of the separation. In experiments with lead, a spot test with benzidine was used to check decontamination.

In each experiment in which a separation was attempted, two extractions of the aqueous phase with equal volumes of chloroform phase were carried out. The aqueous phase was then washed twice with equal volumes of chloroform. The organic phase was washed twice with the appropriate aqueous phase lacking only the metals in question.

RESULTS AND DISCUSSION

Figure 1 records the extraction behaviour of tin(IV) separately in solutions of hydrochloric and perchloric acids of varying concentrations. The reason for the sharp maximum in the extraction from hydrochloric acid is not clear and further work on the reactions of tin (including tin(II)) with BPHA in the presence of halide is in progress. Of the halides, only fluoride interferes seriously with the extraction. On the other hand, tin(IV) distribution follows a very different pattern in perchloric acid solution. Germanium is extracted well into chloroform in the absence of BPHA and some results thus obtained together with data taken from the work of BRINK *et al.*¹¹ are shown in Fig. 1; above 8 *M* in hydrochloric acid, germanium is very efficiently

extracted. It was found that germanium or tin(IV) is not extracted from perchloric acid solution into chloroform, and no extraction was observed (a) from a germanium solution 0.8 M in hydrochloric acid and 7 M in perchloric acid or (b) from a 2 M hydrochloric acid solution saturated with ammonium chloride (about 6 M in chloride ion). Germanium and tin in a mixture are conveniently separated by extracting the

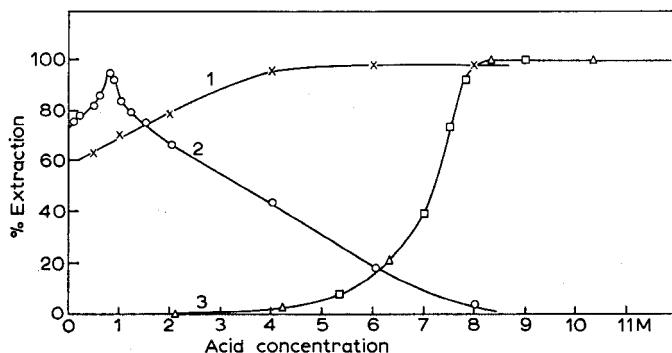


Fig. 1. Extraction of tin and germanium as a function of acid concentration. Curve 1, Sn from HClO_4 ; curve 2, Sn from HCl; curve 3, Ge from HCl. Δ values taken from BRINK *et al.*¹¹, \square this work. Extraction conditions: 1% BPHA for Sn, chloroform alone for Ge, equilibration time 15 min, Sn and Ge concns. were $1.3 \cdot 10^{-3} M$ and $10^{-3} M$ respectively. Data refer to single extractions with equal volumes of extractant.

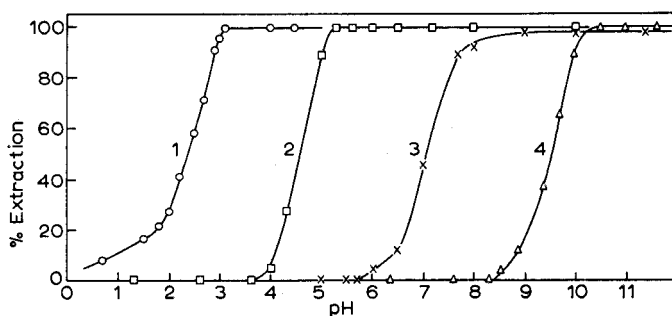


Fig. 2. Extraction from 0.05 M acetate-acetic acid as a function of pH; Ga (curve 1), In (curve 2), Pb (curve 3) and Tl (curve 4). For conditions of extraction see the footnotes to Tables I and II.

former from an 8 M hydrochloric acid solution. Tin(IV) may then be extracted efficiently if required either by neutralizing the raffinate with ammonia and making 4 M in perchloric acid, or reducing the acidity to 0.8 M in hydrochloric acid with ammonia. The former method is preferable if gallium is present, as in 0.8 M hydrochloric acid solution (containing additional chloride ion or not) slight extraction (about 0.3%) of this element occurs along with tin. Two extractions with an equal volume of a 1% solution of BPHA in chloroform remove tin efficiently under the conditions recommended.

The extractions of gallium, indium, thallium(I) and lead as a function of pH are shown in Fig. 2; acetate-buffered systems (0.05 *M* in acetic acid and acetate) are used. Gallium may be separated with maximum efficiency from the others by extraction at pH 3.1–3.8; indium from lead and thallium(I) at pH 5.3–5.6 and lead from thallium(I) at pH 7.8–8.2. Thallium(I) begins to be extracted above pH 8.2 and extraction is virtually quantitative above pH 10.5. Thallium(III) is not extracted up to pH 9.5 from an acetate medium; precipitation commences at about pH 9.8 and incomplete extraction is obtained.

The accumulated results show that by suitable choice of conditions all 6 elements can be separated from each other and this was confirmed by experiment. Extraction as a function of reagent concentration is recorded in Table I and the effect of time of equilibration is given in Table II. Table III summarises the optimum pH,

TABLE I
EXTRACTION AS A FUNCTION OF BPHA CONCENTRATION

BPHA concn. (%, w/v)	% Extraction ^a				
	Ga ³⁺	In ³⁺	Tl ⁺	Sn ⁴⁺	Pb ²⁺
0.025	—	30.2	—	—	—
0.05	—	50.4	—	—	—
0.10	21.3	69.9	55.7	17.4	31.3
0.20	50.1	81.1	81.9	39.9	48.8
0.30	60.8	84.3	86.1	58.1	60.3
0.40	79.3	86.7	90.8	75.3	68.9
0.60	88.4	90.3	95.3	84.1	82.1
0.70	91.7	93.1	99.7	88.3	87.7
0.80	94.1	96.5	99.7	90.7	90.4
1.0	99.4	99.2	99.7	94.4	97.4
1.5	99.4	99.2	99.7	94.4	97.4
2.0	99.4	99.2	99.7	94.4	97.4

^a Equal volumes of the two phases were equilibrated for 15 min. Extraction data refer to single extractions. Metal concentrations: Ga $6.0 \cdot 10^{-3} M$, In $1.0 \cdot 10^{-3} M$, Tl $5.0 \cdot 10^{-4} M$, Sn $1.3 \cdot 10^{-3} M$ and Pb $2.0 \cdot 10^{-3} M$.

TABLE II
EXTRACTION^a OF VARIOUS METAL^b IONS INTO EQUAL VOLUMES OF 1.0% BPHA IN CHLOROFORM

Time (min)	Ga ³⁺	In ³⁺	Tl ⁺ ^c	Sn ⁴⁺	Pb ²⁺
1	20.8	55.6	81.2	20.0	53.1
3	39.9	71.3	90.4	41.8	78.5
6	62.1	93.6	96.5	75.3	87.3
8	83.7	97.8	99.7	89.1	94.4
10	94.3	99.2	99.7	94.4	97.4
12	99.4	99.2	99.7	94.4	97.4
15	99.4	99.2	99.7	94.4	97.4

^a Expressed as a percentage of the total metal present in the system.

^b For metal concentrations see footnote to Table I.

^c Thallium extracted into a 0.7% solution.

TABLE III

OPTIMUM CONDITIONS FOR THE EXTRACTION OF VARIOUS METAL IONS

<i>Ion extracted</i>	<i>pH</i>	<i>BPFA concn. (% w/v)</i>	<i>Optimum equilibration time (min)</i>	<i>Maximum metal ion concn. (mg/10 ml)</i>	<i>% extracted^a</i>
Ga ³⁺	3.1	I	12	10	99.4
In ³⁺	5.3	I	10	10	99.2
Tl ⁺	10.5	0.7	8	8	99.7
Ge ⁴⁺	8 M HCl	0	15	10	99.8
Sn ⁴⁺	0.8 M HCl	I	10	10	94.4
	4 M HClO ₄	I	10	10	96.1
Pb ²⁺	9.0	I	10	12	97.4

^a In a single extraction with equal volumes of the two phases.

TABLE IV

SEPARATION FACTORS^a OBTAINED FOR VARIOUS PAIRS OF ELEMENTS

<i>Element A separated from B</i>	<i>Method of measuring</i>	<i>Separation factor</i>
Ga In	Radioactive In	10 ⁴
In Pb	Benzidine test	10 ⁴
Ga Pb	Benzidine test	10 ⁴
Ga Ge	⁶⁸ Ga decay	10 ³
In Sn	^{113m} In decay	10 ³
Sn Ga	Radioactive Ga	10 ³
Sn In	Radioactive In	10 ³
Sn Pb	Benzidine test	10 ⁴
Pb Tl	Radioactive Tl	6 · 10 ²

^a The ratio of the final amount of impurity (B) present in the separated sample (A) to the initial amount present in the mixture (A + B).

reagent concentration, time of equilibration, fraction of the total metal ion extracted into an equal volume of the chloroform phase in a single extraction and the maximum recommended concentration of elements applicable to these conditions. Table IV records separation factors obtained for pairs of elements separated under the conditions so described and it also contains results for the separation of gallium-68 from germanium-68 and indium-113m from tin-113 in which contamination was measured by allowing the short-lived daughters to decay away and measuring the residual activity.

For back-extraction into the aqueous phase, simple adjustment of acidity is adequate for gallium, indium, lead and thallium(I). For tin(IV) saturated oxalic acid in 3 M hydrochloric acid is efficient. As may be deduced from Fig. 1, germanium can be back-extracted into hydrochloric acid less than 4 M. It is also extracted into dilute perchloric acid.

All possible interferences from anions and cations are not known. Iron(III), which is extracted⁷ appreciably at about pH 1.0, and aluminium, which is precipitated

quantitatively³ in the pH range 3.6–6.4, would probably interfere with some of the proposed separations; the aluminium complex is readily extracted into chloroform. In hydrochloric acid solution antimony(III) is extracted efficiently from 1 *M* hydrochloric acid and again from concentrated hydrochloric acid or concentrated hydrobromic acid. Although there is a minimum in the distribution between the acidities mentioned, a satisfactory separation of antimony(III) from tin does not appear to be possible in such a medium (Fig. 1). Oxalate and tartrate would also upset the separation scheme.

We are grateful to Dr. D. J. SILVESTER for the provision of germanium-68 and one of us (A.D.S.) gratefully acknowledges financial assistance provided by H.E.H. The Nizam's Charitable Trust Fund, Hyderabad, India.

SUMMARY

Gallium, indium, thallium, germanium, tin and lead in mixtures containing up to 1 mg/ml of each element are extracted separately with *N*-benzoyl-*N*-phenylhydroxylamine (BPHA) and chloroform under suitable conditions. Germanium is extracted into chloroform alone from 8 *M* hydrochloric acid and tin(IV) from 0.8 *M* hydrochloric or 4 *M* perchloric acid into BPHA in chloroform. The remaining elements are extracted from 0.05 *M* acetic acid–acetate buffered solutions. Gallium is extracted at pH 3.1, indium at 5.3, and lead at 7.8. Good separations of all these elements from each other are thus quickly obtained. Optimum conditions for partition of each metal ion between the two liquid phases are given.

RÉSUMÉ

Les auteurs proposent un schéma de séparations des métaux suivants: gallium, indium, thallium, germanium, étain et plomb, par extraction au moyen de *N*-benzoyl-*N*-phénylhydroxylamine (BPHA) et chloroforme. Ge est extrait d'abord dans le chloroforme (milieu HCl 8 *M*); Sn(IV) dans BPHA + chloroforme (milieu HCl 0.8 *M* ou HClO₄ 4 *M*). Les autres éléments sont extraits en solutions tamponnées acide acétique/acétate, Ga au pH 3.1, In à 5.3 et Pb à 7.8 On obtient ainsi rapidement de bonnes séparations de tous ces éléments d'avec chacun des autres.

ZUSAMMENFASSUNG

Gallium, Indium, Tallium, Germanium, Zinn und Blei in Mischungen, die bis hinauf zu 1 mg/ml eines jeden Elements enthalten, können durch Extraktion mit *N*-Benzoyl-*N*-phenyl-hydroxylamin (BPHA) und Chloroform unter brauchbaren Bedingungen getrennt werden. Germanium wird mit Chloroform aus 8 *M* Salzsäure allein extrahiert und Zinn(IV) aus 0.8 *M* Salzsäure oder 4 *M* Perchlorsäure mit BPHA in Chloroform. Die zurückbleibenden Elemente werden aus 0.05 *M* essigsäuren acetat-gepufferten Lösungen extrahiert, und zwar Gallium beim pH-Wert 3.1, Indium bei 5.3 und Blei bei 0.8. Es lassen sich so alle Elemente gut und schnell voneinander trennen. Für die Verteilung jedes Metallions zwischen zwei flüssigen Phasen werden die optimalen Bedingungen angegeben.

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Anal. Chim. Acta, 32 (1965) 575-582

SHORT COMMUNICATIONS

Coprecipitation of substituted anilines with zinc ferrocyanide: analysis of *p*-aminobenzoic acid-procaine mixtures

A number of *p*-substituted anilines are of pharmaceutical importance; a convenient absorptiometric method for their determination involves diazotisation of the primary amino group and coupling^{1,2}, but this method is not specific to any member of the group and in pharmaceutical and biological materials two or more *p*-substituted anilines frequently occur together. Separations must therefore be carried out before individual compounds can be determined, or a more specific method of determination must be employed.

In the course of unpublished work connected with the analysis of penicillin solutions it was noted that procaine (2-diethylaminoethyl-*p*-aminobenzoate) was coprecipitated with zinc ferrocyanide. This appeared to offer a further method of separating *p*-substituted anilines. An investigation to ascertain specificity and quantitative relationships was therefore undertaken.

Experimental

Preliminary studies. It has been shown^{3,4} that titration of a zinc salt with potassium ferrocyanide in acid solution first causes the precipitation of zinc ferrocyanide, $Zn_2Fe(CN)_6$; further addition of potassium ferrocyanide converts this to potassium zinc ferrocyanide, $K_2Zn_3(Fe(CN)_6)_2$, the complete precipitation of which is generally taken as the end-point of the titration⁵. More recently GIBALO AND BYR'KO have indicated that only the latter compound is formed⁶.

Preliminary studies were made of the coprecipitation of procaine during the two possible stages above, with 0.1 *M* procaine solutions. It was found that there was

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no apparent difference in efficiency. However, it was considered essential to have a standardised procedure to ensure maximum reproducibility. The following was therefore adopted.

An aliquot (10 ml) of a solution containing 100 g of zinc acetate dihydrate and 50 ml of glacial acetic acid made up to 2 l with water, was placed in a 100-ml graduated flask. An aliquot of the sample solution (50 ml or less) was added, the solution being rinsed into the flask with a volume of distilled water from a measuring cylinder. The volume of water employed was 55 ml less the volume of sample solution taken, so that the precipitation of all samples took place in approximately the same volume of liquid. After mixing, the contents of the flask were treated with 10 ml of a potassium ferrocyanide solution (80 g of potassium ferrocyanide trihydrate and 1.6 g of anhydrous sodium carbonate dissolved in water and diluted to 2 l) added from a buret, with constant agitation to ensure thorough mixing. After standing for 5 min, the solution was made up to volume with water, mixed thoroughly and then allowed to stand for a further 15 min before filtration.

Absorptiometric determination. The procedure involving diazotisation and coupling with N-1-naphthylethylenediamine^{1,2} was adopted for the quantitative studies of coprecipitation. Other workers have shown that the time required for diazotisation and coupling varies with the amine concerned. SNELL AND SNELL¹ have listed the recommended times and show that of the compounds under consideration the longest periods are required for *p*-aminobenzoic acid, which needs 20 min for completion of diazotisation and a further 30 min for coupling. In order to obtain uniformity and to cater for unknown mixtures these times were adopted for all determinations. The procedure was as follows.

An aliquot of the amine solution contained in a 100-ml graduated flask was treated with 2 ml of 1:1 hydrochloric acid and 2 ml of 0.1% (w/v) sodium nitrite. After mixing, the solution was allowed to stand for 20 min and then treated with 2 ml of 0.5% (w/v) sodium sulphamate. It was mixed and allowed to stand for 3 min, and 2 ml of 0.1% (w/v) N-1-naphthylethylenediamine dihydrochloride was added. The flask was finally made up to volume with water and allowed to stand for 30 min. An aliquot was then placed in a cell and its absorption at 545 m μ measured by means of a Unicam SP600 spectrophotometer.

Studies of coprecipitation efficiency. Solutions 10⁻³ M with respect to each compound studied were prepared, using a small volume of dilute hydrochloric acid to dissolve the solid; 10-ml aliquots of these were subjected to the coprecipitation procedure. The final concentration of each substance was therefore 10⁻⁴ M.

After filtration 10 ml of each filtrate was subjected to absorptiometric determination to measure the amount remaining after coprecipitation. The results (Table I) show that the degree of coprecipitation varied greatly according to the species involved. Procaine was almost completely removed from solution whereas other materials such as sulphanilic acid, sulphanilamide and *p*-aminobenzoic acid suffered little loss. The application of the coprecipitation procedure is therefore limited to the separation of procaine and possibly sulphasomidine and sulphafurazole from a limited selection of substances, in the absence of materials whose coprecipitation efficiency falls in the intermediate range. In order to illustrate the applicability of the method, the determination of *p*-aminobenzoic acid and procaine in admixture was studied further.

Analysis of mixtures of p-aminobenzoic acid and procaine

The degree of coprecipitation of each substance from solution was investigated first. *p*-Aminobenzoic acid was found to suffer an almost constant loss of 5% over the concentration range studied ($5 \cdot 10^{-6} M$ to $5 \cdot 10^{-4} M$). A correction was therefore necessary in the analysis of *p*-aminobenzoic acid–procaine mixtures. The coprecipitation of procaine was almost quantitative at low concentrations; less than 1% of the procaine remained in solution after treatment of $< 8 \cdot 10^{-4} M$ procaine solutions; 5% of procaine remained in solution after treatment of $2 \cdot 10^{-3} M$ solutions.

TABLE I
COPRECIPITATION FROM 0.0001 *M* SOLUTIONS

	Optical density			Amine coprecipitated (w/w) (%)	
	Of untreated solns.	Of treated solns.	Average lowering		
Sulphanilic acid	0.462 0.462	0.466	0.459 0.460	0.464 0.003	0.6
Sulphanilamide	0.502 0.509	0.508	0.495 0.499	0.498 0.009	1.8
Irgafen	0.506 0.505	0.508	0.494 0.493	0.497 0.010	2.0
Sulphacetamide	0.514 0.511	0.513	0.495 0.496	0.493 0.018	3.5
Sulphaguanidine	0.514 0.516	0.518	0.484 0.485	0.486 0.031	6.0
<i>p</i> -Aminobenzoic acid	0.488 0.486	0.486	0.448 0.463	0.461 0.030	6.2
Irgamid	0.515 0.516	0.515	0.420 0.417	0.416 0.098	19
Sulphathiazole	0.481 0.475	0.475	0.391 0.383	0.380 0.092	19
Sulphadiazine	0.515 0.518	0.516	0.378 0.376	0.379 0.138	27
Sulphamethoxypyridazine	0.534 0.531	0.532	0.363 0.359	0.363 0.170	32
Sulphadimidine	0.533 0.534	0.536	0.295 0.282	0.294 0.244	46
Sulphamethizole	0.533 0.527	0.524	0.275 0.266	0.285 0.253	48
Sulphapyridine	0.444 0.446	0.448	0.198 0.212	0.205 0.241	54
Sulphaphenazole	0.343 0.344	0.341	0.118 0.115	0.120 0.225	66
Sulphamerazine	0.511 0.515	0.513	0.148 0.149	0.150 0.364	71
Sulphafurazole	0.328 0.326	0.328	0.051 0.052	0.051 0.276	84
Sulphasomidine	0.515 0.513	0.516	0.059 0.059	0.059 0.456	88
Procaine	0.416 0.416	0.417	0.004 0.003	0.003 0.413	> 99

Determinations of mixtures of the two substances were then carried out. Three solutions were prepared; all were $2 \cdot 10^{-3} M$ in procaine and contained $9.8 \cdot 10^{-5}$, $3.9 \cdot 10^{-4}$ and $9.8 \cdot 10^{-4} M$ *p*-aminobenzoic acid, respectively. In each case the *p*-aminobenzoic acid concentration was determined after precipitation of the procaine; a 5% correction factor was applied as mentioned above. The absorption of the original solution was also measured and the procaine obtained by difference. The results obtained are given in Table II.

TABLE II
SEPARATION OF PROCAINE AND *p*-AMINOBENZOIC ACID

Volume taken (ml)		<i>p</i> -Aminobenzoic acid ($\cdot 10^{-4} M$)		Procaine ($\cdot 10^{-4} M$)	
Original soln.	Filtrate	Added	Found	Added	Found
10	25	0.98	1.03	20	19.4
		0.98	1.03	20	19.6
		0.98	1.03	20	19.4
10	25	3.9	4.0	20	19.6
		3.9	4.0	20	19.6
		3.9	4.0	20	19.6
10	10	9.8	9.7	20	19.4
		9.8	9.6	20	19.6
		9.8	9.6	20	19.6

Discussion

The efficiency of coprecipitation of *p*-substituted anilines with zinc ferrocyanide varies greatly according to the species precipitated, as shown in Table I. It appears to bear a definite relationship to the length and complexity of the side chain. The mixture analysed (*p*-aminobenzoic acid and procaine) serves as an example, but other combinations could be similarly examined. It is, however, necessary to ascertain in each case the efficiency of coprecipitation so that an appropriate correction may be applied.

The result of the analysis of procaine-*p*-aminobenzoic acid mixtures (Table II) shows that satisfactory reproducibility is obtainable. That for procaine ($\pm 2\%$) compares favourably with results obtained without coprecipitation. The initial concentration of procaine should not exceed $8 \cdot 10^{-4} M$ under the conditions employed.

It is considered that the procedure developed in this work has interesting possibilities in pharmaceutical analysis. Further studies will be reported later.

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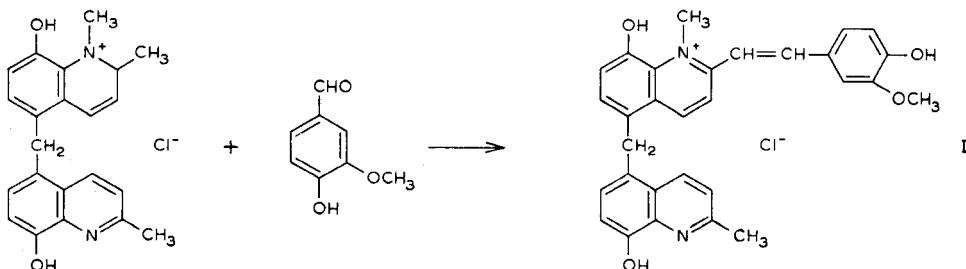
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A new solvatochromic chelating agent

In an effort to obtain a chelating agent that would show a larger change in color as a function of solvent polarity than those previously investigated¹⁻³, we have prepared 2-(4'-hydroxy-3'-methoxystyryl)-5-(8-hydroxy-5-quinaldylmethyl)-1-methyl-8-hydroxyquinolinium chloride (I) by the piperidine-catalyzed condensation of the N-methyl derivative of bis(8-hydroxy-5-quinaldyl)methane² with vanillin as shown below:



The new reagent contains a merocyanine-type function (the quaternary nitrogen and the side chain) to confer maximum solvatochromism and also an 8-quinolinol type of chelating center for metals. In alkaline solutions a change in the principal visible absorption maximum from high to low dielectric constants for the solvents exceeded 130 m μ (Table I), and in pyridine-water mixtures the band additionally showed an unusual change of character at 80% pyridine, splitting at this point into twin maxima with the longer wavelength component increasing as the shorter became submerged at higher pyridine content or lower dielectric constant. Comparison with the spectra of model compounds¹ suggests that this is the result of insufficient basicity of the solvent at low pyridine concentrations; *i.e.*, in the predominant form in moderately basic solution protons have been removed only from the oxygen atoms of the vanillylidene and 8-hydroxyquinaldyl moieties, whereas in the stronger base the proton is removed from the remaining hydroxyl as well.

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TABLE I

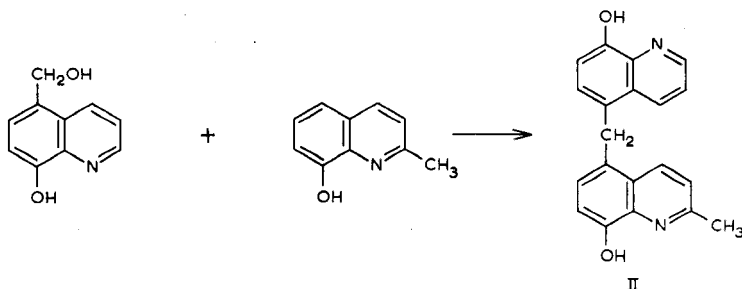
ABSORPTION SPECTRA OF COMPOUND I MERCYANINE AS FUNCTION OF SOLVENT POLARITY

Solvent	Dielectric constant (20°)	Principal maxima, $m\mu$ (log ϵ)
0.1 N HCl		325 (4.20), 414 (4.46) ^a
0.01 N KOH	80.4	375 (4.15), 478 (4.50) ^b
90% MeOH ^c	37.9	392 (4.09), 514 (4.57)
90% <i>n</i> -PrOH	29.8	397 (4.13), 525 (4.58)
90% isoPrOH	23.5	400 (4.15), 526 (4.59)
90% Acetone	25.9 ^d	405 (4.40), 530 (4.66)
Benzyl alcohol	13.1	385 (4.32), 545 (4.06)
CHCl ₃	4.8	389 (4.74), 611 (3.52)
30% Pyridine		— ^e 509 (4.58)
50% Pyridine		399 (4.14), 527 (4.57)
80% Pyridine		401 (4.38), 530 (4.23)
		561 (4.23)
86% Pyridine		— ^e 593 (3.95)
94% Pyridine		403 (4.57), 605 (3.91)
98% Pyridine		— ^e 609 (3.89)

^a Also ultraviolet maxima: 260 (4.70) and 281 (4.22) $m\mu$.^b Also ultraviolet maxima: 259 (4.48) and 290 (4.13) $m\mu$.^c All aqueous phases from this point on in the Table were 0.01 N in KOH and all non-aqueous phases were extracted from alkaline aqueous solutions.^d Although the dielectric constant is higher than for 90% isoPrOH, the Z-value, claimed to be a better solvent polarity measure, is lower: E. M. Kosower, *J. Am. Chem. Soc.*, 80 (1958) 3253.^e Not determined.

At pH 5 qualitative tests with I showed that insoluble chelates were formed with several metal ions, nickel, copper, zinc and cobalt all giving orange precipitates; at pH 9 these ions as well as magnesium, aluminum, and iron(III) formed red precipitates. The reagent was about 60 times more soluble in benzyl alcohol than in alkaline aqueous solutions, and the chelates also dissolved in this solvent. Although some striking color changes of the metal complexes in various solvents were noted, the desired effect of wide variations in color of chelates of different metals in a single solvent was not satisfactorily achieved and for this reason further study of the reagent was not undertaken.

In the course of this project we also made 5-(8-hydroxy-5-quinolylmethyl)-8-hydroxyquinaldine (II), a rather unusual bifunctional chelating agent in that one function could chelate with aluminum and the other (the 8-hydroxyquinaldine moiety) could not, at least if the two functions behaved like 8-quinolinol and 8-hydroxyquinaldine respectively, while toward other metals the performance of the two ends of the molecule should be quite similar. A qualitative test of this proposition was the formation of an olive chelate with II of copper ion, which forms a green chelate with 8-quinolinol and a brown one with 8-hydroxyquinaldine. In addition, II forms only a 3 : 1 reagent-metal chelate from a solution containing excess aluminum ion. It should be possible for this compound to form chelate polymers with suitable metals as similar reagents have been reported to do⁴⁻⁶. Attempts to quaternize one nitrogen in II in order to permit it to condense readily with aldehydes to give products similar to I did not succeed. The preparation of II followed the methods of FIEDLER⁷ for similar compounds:



Experimental

Preparation of reagents. (I) A mixture of 3.04 g (0.02 mole) of vanillin with 3.26 g (0.01 mole) of the betaine of 5-(8-hydroxy-5-quinolalidyl)methyl-1-methyl-8-hydroxyquinaldinium chloride² with 0.3 ml of piperidine as catalyst in 15 ml of methanol was refluxed for 30 min, during which time the product precipitated. It was filtered, washed with methanol and ether and then dissolved in methanol which was saturated with hydrogen chloride in order to precipitate the dihydrochloride. By two recrystallizations from 90% ethanol this yielded 1.24 g of I as the hydrate (m.p. 250° dec.). (Analysis: calcd. for $C_{30}H_{27}ClN_2O_4 \cdot H_2O$, N 5.26%; found, N 5.25%.)

(II) The reaction of 0.01 mole amounts of 5-hydroxymethyl-8-quinolinol with 8-hydroxyquinaldine in 10 ml of acetic acid by the dropwise addition of 6 ml of concentrated sulfuric acid was allowed to proceed for 2 days at room temperature. After heating for 2 h at 60° the mixture was poured over ice and neutralized with 20% sodium hydroxide. Steam distillation removed excess unreacted matter and recrystallization of the residue from xylene produced a 70% yield of II (m.p. 219–220°). (Analysis: calcd. for $C_{20}H_{16}N_2O_2$, N 8.86%; found, N 8.88%.)

The dihydrochloride was also prepared and analyzed: calcd. for $C_{20}H_{16}N_2O_2 \cdot 2HCl \cdot 2H_2O$, N 6.88%; found, N 6.73%.

Chelate compounds of II with copper(II) and aluminum ions were prepared by standard methods⁸, washed thoroughly with isopropyl alcohol, and dried at 70°. Analyses for metal were performed by ignition to the oxide. The calculated value for a 2:1 ratio of II to copper (precipitated from solution containing excess reagent) was 9.2% metal; and the result found was 9.2%. An attempt to produce a polymeric aluminum chelate by using a 3:2 ratio of II to aluminum ion produced only the 3:1 product calculated for 2.8% metal; the result found was 2.8%.

Spectra. Ultraviolet and visible regions were recorded with a Beckman DK-2 Spectrophotometer. Infrared spectra on potassium bromide pellets were obtained on a Baird AB-2 instrument; in addition to hydroxyl and aromatic bands in the infrared for II there were strong individually characteristic maxima at 12.1, 12.8 and 14.1 μ . Principal maxima observed in the ultraviolet spectra of II (and log e) were: 258 (4.94), 313 (3.62), 324 (3.61), and 3.71 (3.70) $m\mu$ in 0.1 N hydrochloric acid; and 258 (4.74), 344 (3.84), and 365 (3.82) $m\mu$ in 0.1 N sodium hydroxide.

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Ultrapurity analysis of zone-melted organic compounds*

In previous publications^{1,2} the concepts of "absolute" and "relative" methods of determining ultrapurity were introduced. Of the physical tests for ultrapurity, thermal analysis has been developed to a point of prominence as one of the most accurate and precise, absolute techniques for determining the total amount of impurities present in a sample without differentiation as to kinds of impurities. As applied to purity determinations, dynamic methods of thermal analysis^{3,4} involve the plotting of absolute temperature of a sample against time under specified conditions. At the melting point, too many extraneous factors are involved, so that the plateau or halt is usually not analyzed. A number of characteristics are involved in heating and cooling curves, and any of these may be related to the lowering of the freezing point equations. However, it should be noted that the mathematical techniques for handling solid solutions by the dynamic method have not yet been attempted (with the exception of known impurities) and these methods can only be applied to eutectics.

In general, the slope of a heating or cooling curve of one sample is compared to another sample acting as an "internal standard" thus giving a measure of impurities⁴. If the freezing point equations of the two samples are integrated between N_2 ' and N_2 '' they give:

$$T' - T'' = \frac{(RM_1 T'^2)}{1000\Delta H_f} (m_2'' - m_2')$$

where T' and T'' are the 2 freezing temperatures with concentrations expressed in molality. From this simplified equation, if the slopes of the heating or cooling curves of the two samples are known and the impurity *added* to the second sample is known, the original impurity in the first sample can be calculated.

Attention is focused here on the most recent procedure in the field and the modifications made in this laboratory to perfect a dynamic method.

Theory

HERRINGTON⁴ developed a procedure, which although it is not as accurate as

* This work is abstracted from a dissertation submitted to the Graduate School, University of Connecticut in partial fulfilment of the requirements for the Ph.D. degree.

calorimetric measurements (static methods of thermal analysis), approaches the requirements for ultrapure materials. However, it is extremely tedious and time-consuming, although with regard to equipment and theory, it is respectively inexpensive and straightforward. It was shown that the melting portion of the curve yields the most reliable data (see Fig. 1). In his procedure, HERRINGTON allowed the sample to equilibrate for 1 h and then increased the temperature at $0.2^\circ/\text{min}$ until the sample was 10° below its melting point. Readings were taken at 2-min intervals and continued until all the sample had melted. Thermocouple measurements were used and repeat experiments were carried out after the addition of known amounts of impurity in sequence. By plotting temperature *vs.* time, a series of melting curves was obtained.

The derivation of the equation used for calculating the mole per cent impurity of an ultrapure sample was given by HERRINGTON⁴.

The final equation makes use of the slope of the time-temperature curves and the mole per cents of impurity added:

$$\frac{\Delta T_1}{\Delta T_2} = \frac{n_1}{n_1 + n_2}$$

where ΔT_1 and ΔT_2 are the slopes of the time-temperature curves taken at equal time intervals for two samples, n_1 is the mole per cent impurity in the original ultrapure sample to be determined and n_2 is the known mole per cent of impurity added.

Modifications of this procedure in this laboratory included the following: (1) the use of a platinum resistance thermometer calibrated by the National Bureau of Standards and a G_2 Mueller Bridge, in place of thermocouple measurements; and (2) a heating rate of $0.016^\circ/\text{min}$ with an equilibration time of 5 h. These improvements increased the accuracy of the method to 6 significant figures in line with the accuracy

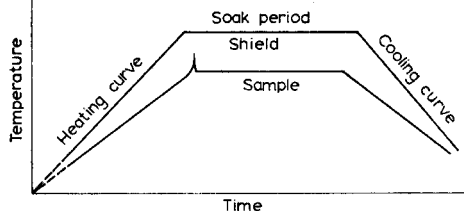


Fig. 1

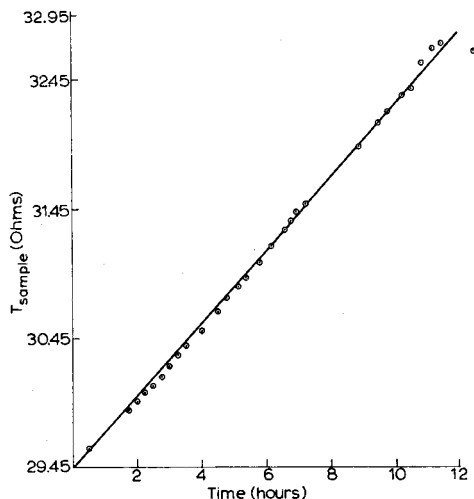


Fig. 2

of calorimetric measurements. However, the recording procedure was tedious since the temperature readings were taken manually.

Procedures

The exact specifications for the recording and automatic temperature control necessary for this method are given elsewhere²; the equipment would be readily accessible in any well-equipped analytical laboratory.

Two methods are commonly used for positioning the samples for absolute temperature measurements with a platinum resistance thermometer. The more difficult method involves a stirrer in the bed of solid material so that complete mixing accompanies the temperature readings. It is of equal value to place a thin layer of sample closely packed around the base of the thermometer (sensing area) and assume uniformity of sample. The latter method was applied in this investigation by using a test tube (filled with sample) whose diameter was only slightly larger than that of the resistance thermometer.

To determine accurately the *slopes* of the time-temperature curves, as required for the HERRINGTON formula, temperature readings were taken every 15 min. A large number of points (as many as 50) were obtained which could be refined by a least squares approximation to determine statistically the most probable slope of the curves. Although a number of such analyses were conducted as few as 7 temperature readings were sufficient to give the same accuracy (see Fig. 2).

The derivation of the least squares method utilized is given by VAN VOORHIS AND PETERS⁵. This method is applied to both the original sample and to the same sample with one or more independent additions of impurities. HERRINGTON showed that if a plot of (*T* sample) vs. (*T* sample plus impurity) was linear, the equations are valid and solid solutions are not formed. In this investigation, the validity of the method was checked by the above procedure and by comparison of results with phase solubility methods. Assuming an average molecular weight of impurities close to that of naphthalene, it was possible to show the equivalence of results of the thermal analysis and phase solubility measurements.

A typical calculation for the thermal analysis of a zone-melted sample (one pass) is given below.

$\Delta T_1 = \text{slope of original sample} = 0.003045$; $\Delta T_3 = \text{slope of sample} + \text{impurity} = 0.013764$; $n_2 = \text{mole per cent impurity added} = 0.18128\%$.

$$\Delta T_1 / \Delta T_2 = n_1 / (n_1 + n_2)$$

Thus $0.003045 / 0.012186 = n_1 / (n_1 + 0.181280)$ and $n_1 = 0.060403$ mole per cent.

$\Delta T_1 = \text{slope of original sample} = 0.00304$; $\Delta T_2 = \text{slope of sample} + \text{second impurity} = 0.017109$; $n_3 = \text{mole per cent of second impurity added} = 0.292489$.

$$\Delta T_1 / \Delta T_3 = n_1 / (n_1 + n_3)$$

Thus $(0.178034) = n_1 / (n_1 + 0.292489)$ and $n_1 = 0.063352$ mole per cent.

Results

The accuracy of the instrumentation is governed by the least accurate value obtained. The platinum resistance thermometer is certified by the National Bureau of Standards to $\pm 0.001^\circ$, although the instrument can be read to 0.0002° . The G_2

Mueller Bridge has an accuracy established by the Leeds and Northrup Company of $\pm 0.002\%$ of reading which when converted to temperature indicates an accuracy of $\pm 0.0016^\circ$. A small calculation indicates that the final accuracy of the values obtained for mole per cent impurities is accurate to $\pm 0.002\%$ of the value obtained. This error is negligible.

The experimental data for this thermal analysis method have been detailed elsewhere². Table I lists the results of thermal analysis measurements using the above procedures. Measurements were made on commercial (Fisher, Reagent Grade) naphthalene, zone-melted (one pass, non-ideal-equilibrium conditions) naphthalene, and zone-melted (thirty passes, non-ideal-equilibrium conditions) naphthalene.

TABLE I
THERMAL ANALYSIS RESULTS OF NAPHTHALENE SAMPLES

Source	Mole % impurities
Commercial Fisher Reagent Grade	2.69936
Zone-melted (one pass)	0.060403, 0.063352
Zone-melted (thirty passes)	0.000947, 0.000562

It is of interest to compare the findings of the National Bureau of Standards, the results of HERRINGTON and the data obtained in this laboratory for the mole per cent impurities found in ultrapure samples. The N.B.S. cites 0.04 mole per cent impurities for ultrapure naphthalene and 0.023 mole per cent impurities for benzene. HERRINGTON claims 0.005 mole per cent impurities for benzene and claims comparable values for ultrapure naphthalene although no figures have been published. In this laboratory, naphthalene has been ultrapurified to 0.000947 mole per cent impurities.

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Titrimetric determination of sulfate in sea-water

A rapid method of determining sulfate in sea-water and brines was required. The method of NAVONE¹ is quantitative for sulfate in waters containing less than 300 p.p.m. of chloride ion. Three indirect procedures were investigated in which EDTA-NH₄OH reagent² or disodium EDTA³, disodium EGTA⁴ or standard sodium hydroxide were used as titrants to measure the excess barium ion present in the filtrates, after filtration of barium sulfate precipitated from cation-free sea-water effluents, or to titrate benzidine sulfate⁵ precipitated at 0° from the decationized effluents.

Each method²⁻⁴ gave quantitative recoveries of about 50 mg of sulfate in known mixtures of approximately equal amounts of sulfate and chloride ions by precipitating the barium sulfate with 0.1 *N* barium chloride, or lead sulfate with 0.05 *N* lead nitrate, filtering, and titrating the excess of the respective barium or lead ion in the filtrate.

When cation-free sea-water effluents were evaporated to about 3 ml to volatilize hydrochloric acid, the sulfuric acid oxidized the organic material present, with partial loss of the sulfate. Treatment of the cation-free effluents with activated carbon did not improve the results of the sulfate determinations. Attempts were made to isolate sulfate from simple aqueous solutions of 25-50 mg of sulfate ion in dilute perchloric acid, by adsorbing on a 6.5-ml column of prepared aluminum oxide, and eluting with dilute sodium hydroxide, ammonium hydroxide, or aqueous ethylamine at 25° or 70-75°; total adsorption of the sulfate was obtained, but the recoveries were incomplete.

Reagents and chemicals

A 0.1 *N* (or 0.2 *N*) EDTA-ammonium hydroxide solution was prepared from 29.2 (or 58.4) g of EDTA by the method of VRESTAL AND HAVIR². The solution was adjusted to pH 5.40 using a pH meter, and diluted to 2 l with deionized water. It was standardized with calcium chloride solution prepared from pure calcium carbonate in the usual way.

Ammonium hydroxide-ammonium chloride buffer, pH 10, was prepared as described by SÏJDERIUS³. A borate buffer, pH 10, was prepared as described by RINGBOM *et al.*⁶.

A 0.1 *N* barium chloride solution was standardized both gravimetrically and by titration with 0.1 *N* EDTA-NH₄OH. Representative results were: gravimetric 0.1020 *N*; EDTA-NH₄OH 0.1022 *N*.

A 0.05 *N* disodium EGTA solution was prepared by dissolving 8.8397 g of EGTA (Geigy) in 46.5 ml of *N* sodium hydroxide, diluting to 1 l, and storing in a polyethylene bottle⁶. The reagent was standardized⁶ with 0.050 *N* calcium chloride, using 2.0 (or 3.0) ml of 0.0233 *M* zinc chloride, 25 ml of pH 10 borate buffer and 4 drops of eriochrome black T indicator.

A 0.174 *N* benzidine hydrochloride solution was prepared as directed⁵ by dissolving 22.40 g of twice-recrystallized, carbon-decolorized, vacuum-dried benzidine hydrochloride. The recrystallized benzidine hydrochloride gave white benzidine upon addition of dilute aqueous sodium hydroxide.

A 0.5% eriochrome black T solution in triethanolamine was prepared.

A 0.05 *N* sodium hydroxide solution was standardized with pure potassium biphthalate.

A 0.0233 *M* zinc chloride solution was prepared by dissolving 0.7616 g of C.P. granular zinc (20 mesh) in concentrated hydrochloric acid, evaporating to dryness, re-dissolving in 2 drops of 6 *M* hydrochloric acid and a few ml of deionized water, and diluting to 500 ml.

Procedures

Titrimetric method with EDTA-NH₄OH^{2,3}. Remove the cations from a 20–40 ml sample of mixed, clear, unfiltered sea-water, or a water sample containing about 50 mg of sulfate, by ion exchange on a column (0.75 × 20 in.) of Dowex 50 (H form) or Amberlite IR-120 (H form) at a flow-rate of about 1 ml/min. Wash the column with 100 ml of deionized water in 20–25 ml portions at a flow-rate of 1–2 ml/min. Precipitate the sulfate in the boiling effluent by slow dropwise addition of 17–25 ml of 0.1 *N* barium chloride, digest the precipitate for 30 min at 100°, filter from the hot (95–100°) mixture on a fine-porosity fritted glass crucible, wash the barium sulfate by decantation with three 20-ml volumes of 95–100° deionized water, and evaporate the filtrate to 20–25 ml. Cool, add 25 ml of the pH 10 ammoniacal buffer and 4 drops of eriochrome black T indicator (or 0.2 g of dry 1:250 eriochrome black T–potassium chloride mixture) and titrate with 0.1 or 0.2 *N* EDTA-NH₄OH to the blue end-point (with no purple tinge).

*Titrimetric benzidine sulfate method*⁵. Evaporate the cation-free sea-water effluent to 50–60 ml. Precipitate the benzidine sulfate at 0° for 30 min. Collect the (iced) benzidine sulfate in a fine-porosity glass crucible, wash with five 10-ml volumes of saturated benzidine sulfate solution at 0°, and titrate the benzidine sulfate with 0.05 *N* sodium hydroxide.

The gravimetric method for sulfate was applied in the usual way, using fine-porosity fritted glass crucibles.

Discussion

The results for sulfate in the sea-water samples are shown in Table I. The recoveries by the indirect EDTA-NH₄OH^{2,3} titration were 95.2–100.5%, based on the respective gravimetric data. The results obtained by the benzidine sulfate titrimetry were in fairly good agreement with the gravimetric data, the coefficient of variation being 1.4%. Interference by organic matter is believed to cause the indefinite end-points which were experienced in several of the EGTA titrations. A Kjeldahl determination showed the presence of 23.0 p.p.m. organic nitrogen in a sample (Campeche Bank). The phosphate content of the water samples was investigated qualitatively by heating 150-ml samples with ammonium molybdate, ammonium nitrate and nitric acid. A moderate yellow color was obtained in each case, indicating a trace of phosphate; but a precipitate was not formed. If phosphate were present in macro quantities, high sulfate results would be found owing to phosphate interference. The EDTA-NH₄OH titrimetric method can be recommended, although the average error of the results is about –2%.

The water samples were obtained by the cooperation of the Department of Oceanography and Meteorology of Texas A. and M. University and the courtesy of

TABLE I
DETERMINATION OF SULFATE IN SEA-WATER

Sample	Gravimetric	Titrimetric (p.p.m. SO ₄ ²⁻)		
		Benzidine sulfate	EDTA-NH ₄ OH	Di-Na EGTA
60 mi. SSE of Galveston	2787	2777	2741	2745
	2828			
	2779	2750	2731	2723
	2812			
	2795	2722	2742	2737
	2789			
	2787			
	2783	2764	2731	2737
Av. 2795				
Campeche Bank*	2731	2791	2734	No end-point
	2715	2785	2734	No end-point
	2722			
	2731	2788	2734	—
	2724			
	2694			
Av. 2720	746	734.4	No end-point	
Baffin Bay (Tex.)	777.8	741	729.8	No end-point
	767.5			
	767.5	744	727.3	—
	763.4			
	761.3			
Av. 767.5	1270	1244	Not detd.	
Galveston Jetties	1259	1269	1230	—
	1256	1270	1237	—
Galveston W. Jetty	Av. 1258	Not detd.	Not detd.	Not detd.
	2298	—	—	—
	2294	—	—	—
Freeport (Tex.)	Av. 2296	2878	2844	No end-point
	2868	2864	2836	No end-point
	2852	2850	—	—
	Av. 2860	Av. 2864	2840	—

* Campeche Bank water contained 23.0 p.p.m. organic nitrogen. Some sea-water samples were lost during construction and could not be replaced.

Dr. ED IBERT and JAMES SLOWEY. The courtesy of the Companies who gave chemicals and materials is gratefully acknowledged.

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Fluorescent gallium complexes extractable by benzene from 6 N hydrochloric acid*

Gallium forms a fluorescent complex with rhodamine B in 6 N hydrochloric acid, which is extracted by benzene. ONISHI AND SANDELL¹ as well as CULKIN AND RILEY² have studied this chelate, but did not attempt to determine the group or groups responsible for the formation of the complex. Several other compounds of basically the same functional groups have been advanced as reagents for gallium³⁻⁵ and other metals^{6,7}. In a study of this reaction we found that acridine red, which does not have the benzoic acid group, would also serve as a reagent for gallium with results similar to those with rhodamine B. Further experiments showed that the bridge oxygen in rhodamine B may be replaced with nitrogen or sulfur and similar results obtained with gallium. These results are shown to assist in location of the coordination of gallium in the complex.

Reagents

GaCl₃ solution. 0.1659 g of gallium metal was dissolved in 250 ml of 1 N hydrochloric acid (9.5 μ moles Ga/ml).

Flaveosine (C.I. 46060). The necessary intermediates for the preparation of flaveosine were made as follows.

(1) *m*-Nitrodiethylaniline. An adaptation of a modified method⁸ of KROLL for the production of *m*-nitrodimethylaniline was followed. *N,N*-Diethylaniline (89.2 g) was added with stirring to 254 ml of concentrated sulfuric acid kept below 25° by the addition of dry ice directly into the solution. Concentrated sulfuric acid (40 ml) and 40 ml of concentrated nitric acid were mixed in a 200-ml beaker and cooled to 5°. This mixed acid was added slowly to the amine sulfate at a temperature between 5 and 10°. The reaction mixture was stirred for 2 h at this temperature. The mixture was then poured into 200 ml of ice water, and 400 ml of concentrated ammonia liquor were added below the surface while the temperature was kept below 25° by the addition of dry ice. The *p*-isomer which formed was filtered; the solution was neutralized to the congo red end-point with about 330 ml of ammonia liquor as above. An ether extraction of the aqueous solution, followed by ether evaporation and vacuum distillation of the remaining oil, yielded 66 g of pure *N,N*-diethyl-*m*-nitroaniline (b.p. 135° at 0.7 mm Hg).

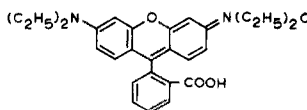
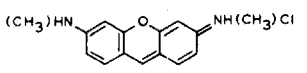
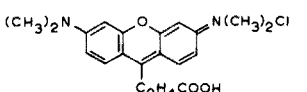
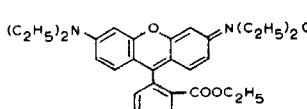
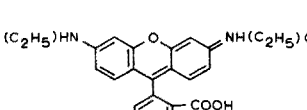
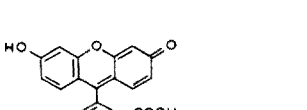
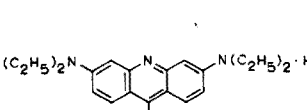
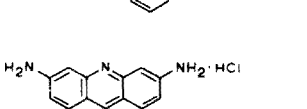
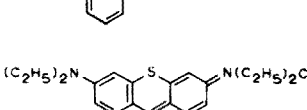
(2) *m*-Aminodiethylaniline. *m*-Nitrodiethylaniline (15 g) was added to 100 ml of 95% ethanol in a Parr bomb. About 2 g of palladium-charcoal catalyst was added, the bomb swept free of air by displacement with hydrogen, and the mixture shaken under hydrogen pressure. The absorption of hydrogen continued until the theoretical amount of hydrogen had been absorbed. The solution was filtered, the alcohol evaporated under reduced pressure (water aspirator), and the blue oil which remained vacuum-distilled at 4 mm of Hg and 117°. The yellowish white amine was collected and stored under nitrogen. Exposure to air caused a strongly blue discoloration.

m-Aminodiethylaniline (10 g) was reacted according to the procedure of GRANDMOUGIN AND LANG⁹ to prepare successively *m*-diethylaminoacetanilide, diacetyldiaminodiethylanilinephthalein, and finally flaveosine. The flaveosine was crystallized from 95% ethanol in orange yellow needles (m.p. 333°).

* Taken in part from the thesis submitted by R. J. ARGAUER to the Graduate School of the University of Maryland (June, 1963) in partial fulfillment of the requirements for the Ph.D. degree.

TABLE I

BENZENE EXTRACTION OF FLUORESCENT COMPOUNDS FROM 6 N HCl WITH GALLIUM PRESENT

Color index no. and name	Structure	Comment	Ref.
C. I. 45170 Rhodamine B		Extracts ^a	1,2
C. I. 45000 Acridine red		Extracts ^b	
C. I. 45050 Rhodamine S		Extracts ^a	4
C. I. 45175 Rhodamine 3B		Extracts ^a	3
C. I. 45150 Rhodamine 6G		Extracts ^a	5
C. I. 45350 Fluorescein		No extraction ^b	
C. I. 46060 Flaveosine		Extracts ^c	
3,6-Diamino-9-(o-carboxyphenyl) acridene hydrochloride		No extraction ^c	
Thiopyromine		Extracts ^c	11

^a Literature cited.^b Available commercially.^c Prepared in this laboratory.

3,6-Diamino-9-(o-carboxyphenyl)acridine. The method of MEYER AND OPPELT¹⁰ was followed. Fluorescein (20 g) was dissolved in 60 ml of concentrated ammonia liquor and poured into a glass 100-ml test tube; the tube was placed in a steel bomb, which was heated for 8 h at 180–200° (194°). After cooling the bomb to room temperature, the excess ammonia was decanted, and the residue dissolved in concentrated hydrochloric acid. The solution was cooled and filtered, and the filtrate poured with stirring into excess concentrated ammonia liquor and ice. The precipitate which formed was redissolved in hydrochloric acid and reprecipitated in ammonia liquor. The compound was dried over phosphorus pentoxide.

Thiopromine. This compound was prepared by the method of BIEHRINGER AND TOPALOFF¹¹.

Screening compounds for reactivity and extractability

Information concerning 3 compounds known to form extractable gallium complexes was found in the literature. The remainder of the compounds given in Table I were tested as follows. One ml of a 0.2% solution of the respective compound in 6 N hydrochloric acid was diluted to about 6 ml with 6 N hydrochloric acid. About 10 ml of benzene was added and the solution shaken for about 2 min. In no case was fluorescence evident in the benzene phase. A solution of gallium in 1 N hydrochloric acid containing approximately 50–100 μg of gallium was added and the mixture reshaken for 2 min. Table I lists the results obtained.

Discussion

Substituent groups and coordination in the rhodamine B-gallium complex. Rhodamine B has 4 centers available for coordination: the COOH group, two $\text{N}(\text{C}_2\text{H}_5)_2$ groups, and a bridge oxygen. Published results with rhodamine 3B and rhodamine S (Table I) indicate that both the carboxylic acid group and the phenyl ring substituted at the 9 position probably are not necessary for complex formation. Our results with acridine red also confirm this point. Experiments with rhodamine 6G indicate that an ethylamine group substituted in place of the diethylamine group does not hinder the extraction of the complex. Flaveosine (nitrogen in place of the bridge oxygen in rhodamine B) forms an extractable gallium complex. Fluorescein with gallium showed no extraction with benzene, which demonstrates that an amino group is necessary for complex formation. The compound, 3,6-diamino-9-(o-carboxyphenyl)acridine, also failed to extract in the presence of gallium. This indicates that primary amino groups substituted in place of alkyl or dialkyl amino groups do not permit the formation of a complex with gallium which is sufficiently stable for extraction into benzene. The following conclusions are reached. The o-carboxyphenyl group attached at the 9 position in rhodamine B is not needed for a gallium complex to form. The non-bonding pair of electrons on the nitrogen atom of substituent amino groups contributes to the formation of the complex with gallium. In primary amino groups, the non-bonding electron pair is not sufficiently basic to form a stable, extractable complex with gallium.

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Anal. Chim. Acta, 32 (1965) 596-599

BOOK REVIEWS

M. R. F. ASHWORTH, *Titrimetric Organic Analysis. Part I. Direct Methods*, Chemical Analysis Series, Vol. 15, Interscience Publishers, New York, 1964, xx + 501 pp., price 132 s.

The author calls this book a miniature Beilstein for titration of organic materials, and it is as a rapid guide to the original literature that it will be valuable. This first volume deals with direct titrations only; indirect methods will be compiled in a second volume. In the first section of this volume, general aspects of titration methods such as reaction rates and visual and instrumental methods of end-point detection, are considered briefly; in the second, the available direct titrimetric methods for the determination of functional groups and compounds are classified according to the reagent used. For example, in the part headed "Perchloric acid" 341 references are listed chronologically and the tabulated data show what is determined, the reagent solvent, the reaction medium and the method of end-point detection. The third section is essentially a guide to section 2, the groups and compounds determined being listed alphabetically. It will certainly surprise most organic chemists to realize that so many materials can be determined by a straightforward titration.

The value of the book is rather difficult to assess. It will be useful as a comprehensive compilation of the relevant literature up to 1961, but is flawed by the lack of information on titrant strengths and on the amounts of material determined; however, likely interferences are apparent from the method of tabulation. From the initial elementary outline of titration processes, the author proceeds rapidly to the somewhat rash assumption that most readers will be able to undertake their own critical evaluation of the methods listed. Such an evaluation would be impossible without recourse to the original literature. Nevertheless, this compilation will save many hours of tedious searching for references and should therefore be available in all academic and industrial institutes concerned with organic analysis.

A. M. G. MACDONALD (Birmingham)

Anal. Chim. Acta, 32 (1965) 599

ALFRED J. MOSES, *Analytical Chemistry of the Actinide Elements*, International Series of Monographs on Analytical Chemistry, Vol. 9, Pergamon Press, Oxford, 1963, 137 pp., price 45/-.

This short text (98 pages plus appendices and index) is by the Head Chemist of Atomics International, Canoga Park, California. In his preface the author says "This monograph presents a number of pertinent techniques for the analysis of actinides . . .". With this part of the sentence the reviewer agrees; but not with the remainder ". . . and provides sufficient information to guide the analyst in modifying procedures to meet special situations".

The book merely skims through a wide range of techniques, none of which can be covered thoroughly in the space available, and the result is that a feeling of dissatisfaction is left with the reader because he is simply redirected to other references. That feeling is not helped by occasional odd statements which indicate the author's unfamiliarity with some parts of his subject, *e.g.* in chapter VIII on analysis by emission spectroscopy, "Samples often need to be purified prior to analysis. Suitable techniques for purification include *carrier distillation*, ion exchange and solvent extraction" (reviewer's italics).

This book can be recommended only as a brief introduction to the analytical chemistry of the actinides, not as an authoritative text.

A. A. SMALES (Harwell)

Anal. Chim. Acta, 32 (1965) 600

Analysis and Characterization of Oils, Fats and Fat Products, Vol. 1, Edited by H. A. BOEKENOOGEN, Interscience Publishers—John Wiley and Sons Ltd., New York, 1964, xiii + 421 pp., price 84 s.

The appearance of the first volume of a new work on the analysis of fats is a matter of some importance. In a foreword the Editor explains that the object of the venture is to assist workers in keeping up-to-date in a field which is rapidly expanding, by providing chapters on selected subjects of an analytical nature.

The present volume contains nine contributions, the first of which is by Dr. J. BALTES: classical methods including the quantitative determination and separation of components and the evaluation of chemical constants. This is followed by a chapter devoted to the assay of essential fatty acids, which is divided into a rather diffuse review of all possible methods (15 pp.) and a description of methods (18 pp.) selected by the author for application. Some of the methods mentioned such as polybromide number and thiocyanogen value are of questionable value in the assay of essential fatty acids and although gas chromatography is discussed at some length no reference is made to the important question of standardisation of the apparatus. The application of urea in fat analysis includes some suggested analytical tests. There is a full account of dilatometry by workers at Vlaardingen and G. F. LONGMAN discusses the analysis of monoglycerides and related emulsifiers. Other contributions include the determination of foats in oils, nuclear magnetic resonance, spectroscopy and the use of ion exchange in the analysis of detergents. A rather different type of contribution is offered on the analysis of butter and cheese. Information given here is more detailed and is of special interest in comparison with methods in use in other countries (*e.g.*

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British Standard 769: 1961 (with amendment in 1962) for butter and 770: 1963 for cheese).

Although there may be some lack of uniformity in the manner in which different authors have approached their particular topic, the volume should be invaluable to all those actively concerned with fat chemistry and analysis.

W. D. RAYMOND (London)

Anal. Chim. Acta, 32 (1965) 600-601

ROGER G. BATES, *Determination of pH. Theory and Practice*, John Wiley and Sons, New York-London-Sydney, 1964, xv + 435 pp., price £ 5.0.0.

This book is a revised and enlarged version of the well known monograph *Electrometric pH Determinations* published in 1954 by the same author.

An outstanding contribution of the previous work was a bridging of the gap between thermodynamically exact but experimentally impractical pH scales and the experimentally convenient but thermodynamically undefined pH meter reading. This combination of thermodynamic rigor with experimental practicality is continued and extended in the present book. In particular, attention is paid to high precision pH standards and to acidity measurements in mixed solvents and in totally non-aqueous ones.

As reflected in the change of title, the new work has been extended to include colorimetric pH measurements with acid-base indicators. A discussion of salt effects and solvent effects on indicator colors is particularly welcome. The discussion of measurement equipment is "addressed to the chemist rather than to the engineer" and thus is limited to the underlying principles rather than to details of circuitry. The discussion of the theory of glass electrode behavior is somewhat sparse. It is hoped that in a future edition, more attention can be paid to the theory of foreign cation effects and the so-called "acid error" in relation to anion effects.

This book will undoubtedly be recognized as the standard reference work on pH measurements, and as such it deserves a place on the reference shelf of every chemist working in solution chemistry.

H. A. LAITINEN (Urbana)

Anal. Chim. Acta, 32 (1965) 601

PUBLICATIONS RECEIVED

H. A. FLASCHKA, *EDTA Titrations: An Introduction to Theory and Practice*, 2nd Edition, Pergamon Press, Oxford, 1965, 144 pp., price 42 s.

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ANNOUNCEMENT

AMERICAN CHEMICAL SOCIETY; FIRST MIDDLE ATLANTIC REGIONAL MEETING

The First Middle Atlantic Regional Meeting will be held on Thursday and Friday, February 3 and 4, 1966, at the Sheraton Hotel in Philadelphia. This Meeting will be the first of an annual series, replacing the former Delaware Valley and Metropolitan Regional Meetings. Dr. Walter Clavan, Pennsalt Chemicals Corporation, is the General Chairman for this first meeting.

The co-sponsoring ACS local sections (and respective meeting co-chairmen) are: Delaware (Dr. E. J. VANDENBERG, Hercules Research Center), Lehigh Valley (Dr. A. J. DIEFENDERFER, Lehigh University), Monmouth County (Dr. W. PFEFFERLE, Engelhard Industries, Inc.), New York (Dr. P. REGNA, The Squibb Institute for Medical Research), North Jersey (Dr. W. L. HAWKINS, Bell Telephone Laboratories, Inc.), Philadelphia (Dr. W. CLAVAN), Princeton (Dr. G. J. KENT, Rider College and Dr. A. LUTZ, American Cyanamid Co.), Southeastern Pennsylvania (Dr. L. H. DUNLAP, Armstrong Research and Development Center), South Jersey (Dr. D. M. NACE, Socony Mobil Oil Co.) and Trenton (Dr. E. H. HOUSE, Trenton Junior College).

There will be nine scientific divisions for the presentation of papers. These (with their respective chairmen) are: Analytical Chemistry (Mr. O. I. MILNER, Socony Mobil Oil Co.), Chemical Education (Dr. A. BREYER, Beaver College), Industrial and Engineering Chemistry (Mr. M. SITTFIELD, Marcus Sittenfield and Associates), Inorganic Chemistry (Dr. A. G. MACDIARMID, University of Pennsylvania), Medicinal and Biochemistry (Dr. J. L. RABINOWITZ, Veterans Administration Hospital), Organic Chemistry (Dr. C. W. JEFFORD, Temple University), Petroleum Chemistry (Dr. H. SHALIT, Atlantic Refining Co.), Physical Chemistry (Dr. J. VARIMBI, Bryn Mawr College) and Polymer Chemistry (Mr. J. BRODNYAN, Rohm and Haas Co.).

Further information may be obtained from Dr. WALTER CLAVAN, Pennsalt Chemicals Corporation, Technological Center, King of Prussia, Penna. 19406 (U.S.A.).

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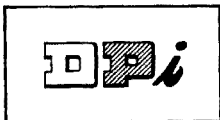
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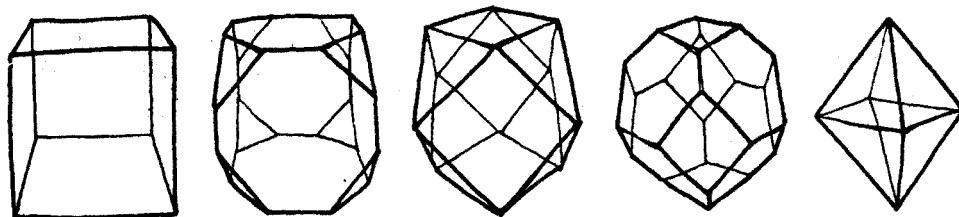


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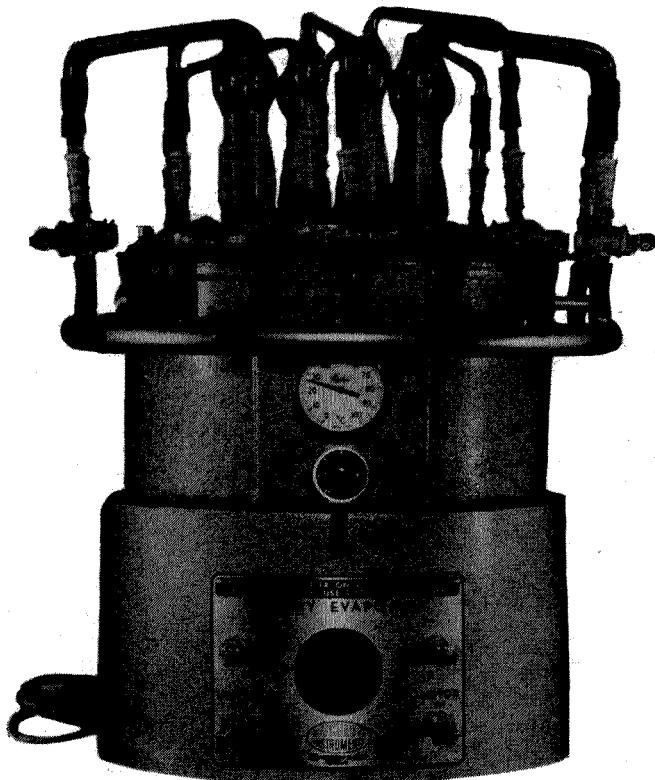
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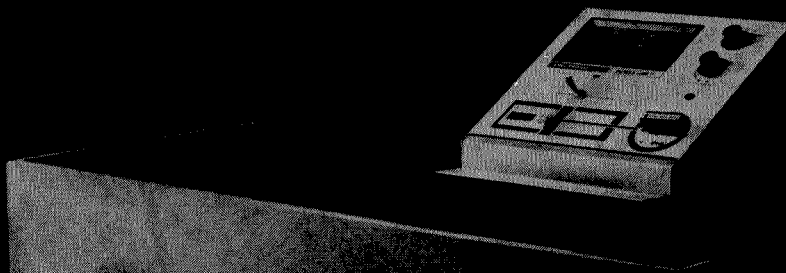
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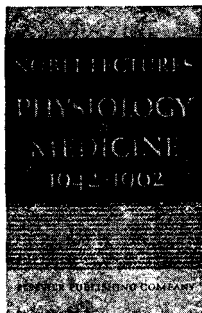
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