Residue Reviews

Residues of Pesticides and
Other Foreign Chemicals
in Foods and Feeds

Rückstands-Berichte
Rückstände von Pesticiden und
anderen Fremdstoffen in
Nahrungs- und Futtermitteln

Edited by
Francis A. Gunther
Riverside, California

Volume 26: Contents

Pesticide regulations and
residue problems in Japan,
K. Fukunaga and Y. Tsukano
Determination of organophos-
phorus pesticides in water,
G. Zweig and J. M. Devine
Toxicity and hazards to man,
domestic animals, and wildlife
from some commonly used auxin
herbicides, J. M. Way
A specific gas chromatographic
method for residues of organic
nitrogen pesticides, C. C. Cassil,
R. P. Stanovick, and R. F. Cook
Significance of organochlorine
insecticide residues in fresh
plants as possible contaminants
of milk and beef products,
J. G. Saha
Potential interferences in
certain pesticide residue
analyses from organochlorine
compounds occurring naturally
in plants, J. W. Hylin,
R. E. Spenger, and F. A. Gunther

With 14 figures. VII, 142 pages.
1969. Cloth DM 40,—; US $ 10.00

Volume 27: Contents

The regulation of pesticides in
Italy, P. de Pietri-Tonelli

Polycyclic aromatic hydrocar-
bons (polynuclears) in smoked
foods, D. J. Tilgner and H. Daun
On the problem of the harmful
effect of DDT and its mechanism
of action, Yu. S. Kagan,
S. I. Fudel-Ossipova,
B. J. Khaikina, U. A. Kuzminskaya,
and S. D. Kovtun
The metabolism of diene-
organochlorine (cyclodiene)
insecticides, G. T. Brooks

With 6 figures. VII, 143 pages.
1969. Cloth DM 38,—; US $ 9.50

Volume 28: Contents

Insecticide residues in
California citrus fruits and
products, F. A. Gunther

With 38 figures. VII, 127 pages.
1969. Cloth DM 38,—; US $ 9.50

Volumen 29: Special Volume —
Symposium on Decontamination
of Pesticide Residues in
the Environment

Atlantic City Meetings of the
American Chemical Society,
September 1968
Contents:

Introduction to the symposium:
Decontamination of pesticide
residues in the environment,
G. K. Kohn
Attenuation of pesticidal
residues on seeds, G. K. Kohn
The decontamination of animal
feeds, T. E. Archer and
D. G. Crosby
Reduction of parathion residue
on celery, N. P. Thompson
Accelerated removal of pestici-
des from domestic animals,
B. J. Liska and W. J. Stadelman
Effects of processing on
pesticides in foods, B. J. Liska
and W. J. Stadelman
Canning operations that reduce
insecticide levels in prepared
foods and in solid food wastes,
R. P. Farrow, E. R. Elkins,
W. W. Rose, F. C. Lamb,
J. W. Ralls, and W. A. Mercer
Chemical and thermal methods
for disposal of pesticides,
M. V. Kennedy, B. J. Stojanovic,
and F. L. Shuman, Jr.
Some research approaches,

toward minimizing herbicidal
residues in the environment,
C. L. Foy and S. W. Bingham
Decontamination
of pesticides in soils,
P. C. Kearney, E. A. Woolson,
J. R. Plimmer, and A. R. Isensee
Interaction of diquat and
paraquat with clay minerals and
carbon in aqueous solutions,
S. D. Faust and A. Zarins
Kinetics of hydrolysis of
diazinon and diazoxon,
H. M. Gomaa, I. H. Suffet,
and S. D. Faust
Biodegradation kinetics of
2,4-dichlorophenoxyacetic acid
by aquatic microorganisms,
R. B. Hemmett, Jr.
and S. D. Faust

With 46 figures. VIII, 213 pages.
1969. Cloth DM 54,—; US $ 13.50

Volume 30: Contents

Distribution of pesticides in
immiscible binary solvent
systems for cleanup and identi-
fication and its application in
the extraction of pesticides from
milk, M. Beroza, M. N. Inscoe
and M. C. Bowman
Factors affecting the extraction
of organochlorine insecticides
from soil, M. Chiba
Cumulative table of subjects
covered, volumes 21—30
Comprehensive and cumulative
subject-matter index,
volumes 21—30
Cumulative author index,
volumes 21—30
Cumulative list of volumes 1—30
List of promised forthcoming
papers by short titles

With 11 figures. X, 169 pages.
1970. Cloth DM 58,—; US $ 14.50

Springer-Verlag
Berlin
Heidelberg
New York

Talanta

An International Journal of Analytical Chemistry

ห้องสมุด กรมวิทยาศาสตร์

PRACTICAL ANALYSIS OF HIGH-PURITY CHEMICALS—I

PREPARATION AND CHARACTERIZATION OF HIGH-PURITY EDTA

A. J. Barnard, Jr., E. F. Joy, K. Little and J. D. Brooks
Research Analytical Services, J. T. Baker Chemical Company,
Phillipsburg, New Jersey 08865, U.S.A.

Summary—Advanced laboratories have requirements for high-purity chemicals with less than 500 ppm total impurities (ultrapure chemicals) and with broad analytical definition of each lot. Some economically feasible approaches to the practical analysis of such chemicals, both inorganic and organic, are delineated. Compounds used in the study of lunar samples and in other advanced programmes are noted. EDTA, as the free acid, has been prepared by dissolution in water with base and precipitation by addition of acid. The product has been broadly characterized. Precision assay is achieved by weight titrimetry, potentiometrically as a triprotic acid and photometrically as a chelating agent. Other tests applied include elemental analysis, ash, loss on drying, particulate matter, and tests for nitrilotriacetate, arsenic, and chloride. Boron, silicon, and trace metals are determined by emission spectrography. Many of the procedures are applicable to other high-purity organic chemicals.

A "PURIFIED" chemical during the first half of the 19th century meant little more than that the product had been either recrystallized or redistilled, with no analytical assessment of quality. For reagent-grade chemicals analytical definition has progressed over the past one hundred years from feeble attempts at semiquantitative expression to the determination of up to 15 or more impurities.[1]

High-purity chemicals with 500 ppm or less of total impurity, often called "ultrapure" chemicals,[2] constitute a present-day challenge. In recent years a number of such chemicals have been offered in laboratory-use quantities. The rule of *caveat emptor* has often prevailed because suppliers have commonly confirmed the quality of a lot, if at all, by a single technique (*e.g.*, emission spectrography for inorganic compounds and gas chromatography for organic ones). High-purity chemicals, both inorganic and organic, with broad analytical definition of each lot, represent the direction of advance. Uses for such products include analytical reagents for exacting trace analysis and characterization of complex materials, such as lunar and geochemical samples, standards for various analytical methods, and reagents for advanced materials research and diverse biochemical studies.

Since knowledge of purification processes is now extensive, the preparation of many high-purity chemicals presents less of a problem than their analysis and storage. In the development of an economically profitable line of broadly defined, high-purity chemicals not only must the preparation and storage be considered from the standpoint of cost, but also the strategies adopted for the analysis. Some analytical approaches to this *practical* analysis of high-purity chemicals are summarized in Table I and most have now been applied to over 50 such products, prepared in 1–200 kg lots.

TABLE I.—SOME METHODS FOR THE PRACTICAL ANALYSIS OF HIGH-PURITY CHEMICALS

Major constituent and assessment of purity	Minor and trace constituents	Physical properties	General tests
Coulometry*	Activation analysis*	Chemical microscopy	Ash
Differential scanning calorimetry	Atomic-absorption photometry	Density	Insoluble matter
Elemental organic analysis	Emission spectrography	Differential thermal analysis	Loss on drying
High-resolution gas chromatography	Extraction-spectro-photometry	Electrical conductivity (low-level)	pH of solution
Phase solubility analysis	Flame emission photometry	Infrared spectra	Residue after evaporation
Precision gravimetry	Fluorometry	Melting point	Trace particulate matter
Precision weight titrimetry (instrumental end-point detection)	Gas chromatography	Refractive index	
	Mass spectrometry*	Specific rotation	
	Nuclear magnetic resonance*	UV-visible spectra	
	Polarography		
	Spot tests		
	Thin-layer chromatography		
	Titrimetry (electrometric or photometric end-point detection)		
	Turbidimetry		
	UV-visible-IR spectrophotometry		

* Not yet applied in our laboratories.

Precision assay by gravimetry or weight titrimetry offers the same success that it has long had for the evaluation of primary standard materials. Weight titrations to a photometric end-point, based on the formation of a metal complex with EDTA have been applied successfully to precision assay (see below). Gas chromatography is applicable to many classes of organic compounds, even high-melting polycyclic hydrocarbons, and can detect as little as 0·01% of an impurity. Subtraction from 100 thereby provides a "GC assay" value to 99·99%.

Differential scanning calorimetry (DSC) is promising for the assessment of chemicals that undergo melting without significant decomposition.[3] Computer processing[4] of the enthalpy-temperature data has been found to reduce labour costs markedly. At mole purities above 99·99% the premelting zone from which the impurity value is derived becomes so small that the purity assigned becomes markedly dependent on the assumptions in the calculations. The practical upper limit of the DSC technique may therefore be about 99·95%, although numerical values as high as 99·99% have been secured for some zone-refined compounds. The DSC technique is "blind" to solid solution formation and therefore should not be used as a sole criterion of purity, especially for chemicals purified by zone refining since this process is less effective when solid solutions form.[5] In our laboratories, for example, for an aromatic hydrocarbon purified by multipass zone refining the DSC technique indicated a mole purity of 99·96%, but gas chromatography gave a single impurity peak corresponding to 1·76%.[6]

Phase solubility analysis[7] is of special value for the assessment of thermally unstable, non-ionic compounds, such as urea.[8] This technique requires little equipment and allows determination of as little as 0·05% (by weight) of impurity.

For trace elements, survey emission spectrography has proved the most valuable single technique. By use of the recently introduced five-level standards with an internal standard,[9] over 40 elements can be evaluated routinely with favourable precision and accuracy. The limits of detection can be improved by preconcentration: organic compounds can be ashed; impurities in inorganic compounds can be collected by the 8-quinolinol–thionalide–tannic acid–indium system, especially if these reagents are used in a high-purity form; liquids such as volatile mineral acids can be evaporated. The limits of detection attained *via* these preconcentration techniques are listed in Table II for 10 key elements. Atomic absorption, especially with preconcentration, is valuable for particular elements.

TABLE II.—DETECTION LIMITS IN D.C.-ARC SPECTROGRAPHY, *ppm*

Element	Ashing*	Collection†	Evaporation‡
Ca	1	0·01	0·0001
Cr	0·1	0·002	0·001
Co	0·1	0·01	0·001
Cu	0·01	0·001	0·0001
Fe	0·02	0·002	0·001
Pb	0·2	0·02	0·001
Mg	0·002	0·0002	0·00005
Ni	0·1	0·02	0·001
Na	2	—	0·001
Zn	2	0·2	0·001

* 50-fold concn.
† 500-fold concn. *via* use of 8-quinolinol-thionalide-tannic acid system
with indium.
‡ 10000-fold concn. by evaporation of an acid.[13]

For inorganic compounds of high purity, the determination of anions and non-metal impurities has often been neglected. So-called "spectrographic grade" chemicals may contain significant anionic impurities. In our experience a costly metal carbonate of alleged 99·99+% purity by emission spectrography was found by acid-base titrimetry to assay only 77·7%; this discrepancy was traced to the presence of over 20% of the metal nitrate.[10] Conventional methods for the determination of anions[1] can be refined by optimizing conditions and by the use of purified reagents to give the detection limits shown in Table III.

Thin-layer chromatography on flexible sheets coated with various adsorbents is valuable in the control of high-purity organic chemicals. A sample can be put on a variety of such sheets and developed rapidly with a number of solvents. Appearance of a spot other than that of the major component immediately indicates that an impurity is present.

For organic liquids, low-level electrical conductivity measurements are valuable. Since literature values for a given compound can range over one or more orders of magnitude, the technique is best used only for the specification of minimum purity.

The general tests summarized in Table III and commonly employed with laboratory-use chemicals[1] can be of value with high-purity chemicals. Evaluation of the residue on evaporation should be considered for any organic liquid purified by preparative gas chromatography to ensure that no substantial bleed of the high-boiling liquid stationary phase has occurred. Some suppliers have overlooked such

TABLE III.—DETECTION LIMITS FOR ANIONS AND FOR SOME GENERAL TESTS

Test	Sample size, g	Detection limit, ppm
Arsenic (As)*	5	0·05
Bromide (Br) in presence of chloride†	2	1
Halide (as Cl)§	5	1
Phosphate (PO₄)‡	5	1
Sulphur compounds (as SO₄)§	8	0·5
Ash (sulphated)¶	5	20
Loss on drying¶	5	10
Particulate matter‖	10	10

* Evolution and silver diethyldithiocarbamate photometry.
† Hypochlorite oxidation, bromination of p-rosaniline, and photometry.
§ Turbidimetry.[1]
‡ Heteropoly blue photometry.
¶ Ref. 1.
‖ Membrane filtration and gravimetry.

contamination by limiting the final control to analytical gas chromatography. Any significant residue can be examined by infrared or other appropriate techniques. Similar remarks apply to materials purified by liquid adsorption chromatography, especially if large volumes of eluent have been used.

High-purity mineral acids, including hydrochloric, hydrofluoric, nitric, perchloric, and sulphuric acids, are used for the dissolution of diverse materials, including lunar samples.[11,12] The introduction of high-purity acids with certificates of actual lot analysis is a significant development. Many trace elements can be determined by emission spectrography after evaporation of the acid under contamination-free conditions (see Table II).[13] The containers for such products (borosilicate glass, or fluorocarbon polymer for hydrofluoric and perchloric acids) are preleached with acid and the filled containers are stored in a cold room at 0° until shipped. In this way purity on delivery corresponds closely to purity on analysis.

Phosphoric acid is a non-volatile acid and so not readily purified. Phosphorus pentoxide, however, can be sublimed to give high purity. The resulting product serves for the preparation of the high-purity phosphoric acid used to dissolve lunar and geochemical samples, especially for isotope abundance studies.[11] Mass spectrometric evaluation of this oxide by a number of laboratories indicates that a lead content of less than 1 ppM (parts per milliard) has been attained. Twelve trace metals have been determined in this oxide, following the technique of Kuzmin and co-workers[14] by neutralization of the derived phosphoric acid and extraction with high-purity 8-quinolinol; the organic extract is evaporated, mineralized, and subjected to d.c.-arc spectrography. In this way all twelve of the metals were found to be present at less than 0·1 ppm and ten of them at less than 20 ppM.[13]

Some high-purity analytical reagents have been prepared; 8-quinolinol has been purified to a total multivalent metal content of less than a few ppm and characterized by over 35 determinations and tests. This chelating agent has proved valuable as an analytical collector (with indium) and as an extractant in trace metal analysis (see above). EDTA, as the free acid, has also been purified (see below).

Standards constitute an important application for high-purity chemicals. Noteworthy has been the large scale production of "ultrapure" calcium carbonate. Remarkably, the strontium content could be reduced to a few ppm. This product is suitable as a primary acid-base and chelometric standard, and has now been certified by the National Bureau of Standards[15] as a clinical standard for calcium.

HIGH-PURITY EDTA

EDTA represents one of the most versatile organic compounds introduced during the past 30 years. As the free acid and simple salts, it finds tonnage application across the entire spectrum of the chemical, food, and pharmaceutical industries.[16,17] In the laboratory, EDTA finds extensive use as a chelating agent[18] and is usually employed in a purified or reagent grade. For the latter grade, specifications and associated procedures have been published by a number of groups.[1,19-21] Additionally a number of analytical studies have made of determination of the nitrilotriacetate (NTA) content of the product[22-26] and of the trace metal content.[27-29]

Interest has developed in an EDTA product of highest purity and close analytical definition. On one hand there is interest in a high-assay product low in nitrilotriacetate content, suitable for use as a chelometric standard, and allowing the simple, direct preparation of an EDTA solution of known concentration. On the other hand need exists for an EDTA product extremely low in multivalent metal content for use as a masking agent in analysis and in the crystallization of ultrapure salts, and as a reagent in enzyme and diverse biochemical studies.

The preparation and analytical definition of high-purity EDTA, as the free acid, has been undertaken in the framework of the extensive programme described in the introduction to this paper.

PREPARATION OF HIGH-PURITY EDTA

The commercial production of EDTA and related compounds has long involved purification based on the solubility of the sodium salts in water and the low solubility of the free acids. The solubility of EDTA as the free acid has been reported[31] to be 0·050 g/l. in water and to increase from 0·6 to 2·5 g/l. in 0·01–1·0M hydrochloric acid. The conjoined use of an alcohol in the purification may be of help in reducing the amounts of NTA and intermediates present.[32] Such approaches are utilized in producing EDTA to meet reagent-grade specifications. For the production of high-purity EDTA, as the free acid, the reagent grade disodium salt dihydrate is a feasible starting material. The laboratory procedure given below involves starting with 300 g of this salt, but has been successfully scaled up to the use of 10 kg. All operations must be conducted with meticulous attention to possible contamination and all laboratory ware must either be thoroughly leached with concentrated hydrochloric acid or be treated with a hot, strongly alkaline solution of EDTA. All dilutions should be made with doubly distilled water.

Procedure for preparation of high-purity EDTA

1. Dissolve 300 g of reagent grade disodium (ethylenedinitrilo)tetra-acetate dihydrate ('Baker Analyzed', Commodity No. 8993 or equivalent) in 3·3 l of water by shaking in a polyethylene bottle. Fit a 5-l. borosilicate filter flask with a Millipore filtration assembly and filter the solution through a 0·25-μm solvent-resistant membrane filter (Millipore No. UGWP04700). Transfer the filtrate to a 4-l. polyethylene beaker and add slowly reagent-grade hydrochloric acid (1 + 1, about 250 ml) until the pH is 1·5–2·0 (pH paper). Separate the precipitated EDTA, using a 5-l. borosilicate filter flask with a 126-mm porcelain Buchner funnel and a circle of hardened filter paper (Whatman No. 41H). Wash well with water.

2. Place the product from the previous step in a 4-l. polyethylene beaker, add 3·3 l. of water and then enough reagent-grade 50% sodium hydroxide solution (about 80 ml) from a polyethylene container to dissolve the EDTA and to bring the solution to pH 4·5–5·5 (pH paper). To ensure that the minimum amount of base is used, add it very slowly while stirring vigorously. Again precipitate EDTA with hydrochloric acid (1 + 1) and collect and wash as in step 1.

3. Repeat the operations of step 2 three more times. If the process must be interrupted for an extended period, finally wash the EDTA on the filter with acetone and then twice with ether, then dry in air or vacuum, and store under nitrogen or argon.

4. Dissolve the product from the final precipitation of step 3 with sodium hydroxide as described in step 2. Using a membrane filter as described in step 1, filter the solution and examine it under appropriate illumination to ensure that particulate matter is virtually absent. Precipitate EDTA as described in step 2. Allow the precipitate to settle with the beaker covered.

5. Decant the supernatant liquid, transfer the precipitate to a 2-l. polyethylene beaker, and slurry with 1 litre of water free from particulate matter. Cover the beaker tightly with polyethylene foil and allow to stand overnight at room temperature. Collect the precipitate on a 126-mm porcelain Buchner funnel fitted with a circle of Dacron filter material cut from an E & D Sparkler filter No. 940, (Keeler Co., Wyomissing, Pa.) or equivalent. Wash well with water.

6. As in step 5, again slurry the collected wet precipitate with water, allow to stand for 30 min, collect the precipitate on a Dacron filter, and wash well with water. Repeat this cycle four times. After the final collection, wash the precipitate with water until the washings are chloride-free (silver nitrate test), then twice with reagent-grade acetone, and twice with reagent-grade ether. Air-dry the resulting powder, taking care to protect it from contamination. Store the product in a polyethylene bottle under nitrogen or argon. The yield is 175–180 g.

Remarks. In the production of high-purity chemicals, almost all products, inorganic or organic, are routinely isolated and stored under a protective atmosphere of either nitrogen or argon. Whether this precaution is actually required for high-purity EDTA has not been established. As for all high-purity materials any proposed transfer or subdivision of the final analytically defined product must be considered carefully in order to ensure that the product will not be contaminated.

CHARACTERIZATION OF HIGH-PURITY EDTA

Adequate analytical definition of high-purity EDTA for diverse use involves establishment of the EDTA content through assay or elemental analysis or both, the application of various general and specific methods and tests, and the determination of key trace elements. All of the procedures developed can be described as both practical and economically feasible. Many of the approaches, moreover, are immediately applicable to many other high-purity organic chemicals.

Assay

The evaluation of a standard material by precision titrimetry is often based on a difference approach: in the simplest case, to a weighed amount of the standard a weighed amount of a reagent of unambiguous purity is added, that is either slightly greater or less than that required for complete reaction. This small difference is then measured by a conventional volume-based titration, often with a dilute solution of either the standard or the reagent as titrant. The difference approach has now been applied to EDTA in the free acid form in two ways: its titration as an acid and as a chelating agent.

Assay via *acid–base titrimetry*. A conventional potentiometric acid–base titration of EDTA has been performed by various workers, especially in fundamental studies. From the acidity constants of EDTA (1×10^{-2}; $2 \cdot 1 \times 10^{-3}$; $6 \cdot 9 \times 10^{-7}$; $7 \cdot 4 \times 10^{-11}$)[33] it is apparent that it can be titrated as either a diprotic or a triprotic acid.

A weighed amount of EDTA is taken and brought beyond the third equivalence point by addition of sodium hydroxide solution from a weight-burette. The excess of base is titrated conventionally with dilute hydrochloric acid to a potentiometric end-point. The dilute hydrochloric acid is prepared by dilution of a stock solution standardized by precision silver chloride gravimetry.[34] Additionally this stock solution is used for the standardization of the sodium hydroxide solution *via* weight titrimetry.

Assay via *titration as a chelating agent*. The difference approach can also be applied to precision chelometric titration of high-purity EDTA. A weighed amount

of calcium carbonate is reacted with a substoichiometric amount of EDTA. The small excess of calcium in the solution, buffered to pH 9·5, is titrated photometrically with a solution of a weighed amount of the same EDTA dissolved and diluted to known volume. Calmagite (3-hydroxy-4-[(6-hydroxy-*m*-tolyl)azo]-1-naphthalene-sulphonic acid)) serves as the indicator.[35] A phototitrator essentially of the design of Flaschka and Sawyer[36] is employed.

Ringbom[37] has shown how mathematical analysis can be applied to the selection of conditions for a chelometric titration to a photometric end-point. Calculation indicates that the photometric titration of calcium with EDTA at about pH 9·5
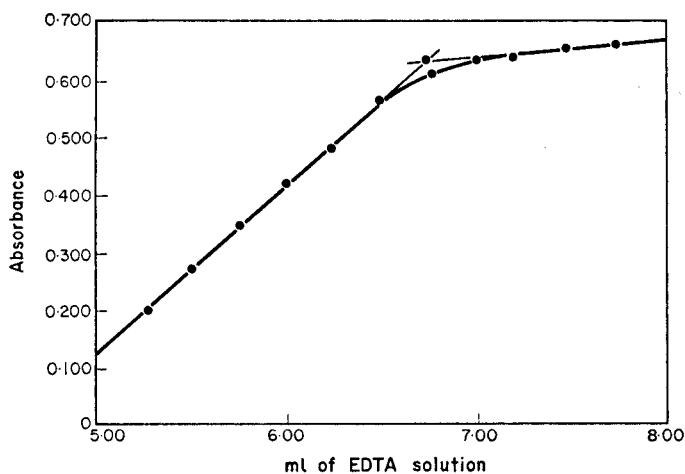
FIG. 1.—Typical photometric titration curve in precision assay of EDTA as chelating agent (see text).

($\log K_{CaY} = 9·7$, $pCa_{eq} \sim 5·7$) with Calmagite as the indicator ($pCa_{trans} = 3·2$) should have an adequate "break point". A typical titration curve is shown in Fig. 1.

Elemental analysis

As with many organic products, elemental analysis is applied as a preliminary, inexpensive method to ensure that no blunder had occurred during the preparation. Carbon and hydrogen are determined by a conventional micro-combustion technique and nitrogen by a micro-Kjeldahl procedure.

Ash (sulphated)

The conventional determination of the ash (that is, the residue on ignition), often with sulphuric acid added, is a valuable proximate method; however, with materials of low ash content a large sample must be ignited to yield weighable amounts of ash. This limitation becomes most serious with high-purity chemicals because of the preparative cost.

Loss on drying

Experience gained over some years in the examination of reagent-grade EDTA indicates that 105° is a suitable temperature for determination of the loss on drying. Selection of this temperature is supported by differential thermal analysis and thermo-gravimetric studies by Wendlandt.[38]

Nitrilotriacetate content

For use as a chelometric titrant, EDTA must have a sufficiently low nitrilotriacetate content. The presence of this weaker chelating agent has an adverse effect on the colour change of the metal indicator in some titrations[23] and may influence the titre of an EDTA solution toward different metals.[23,24] Indeed, as little as 1 % NTA in EDTA can be determined by titration with different metals at suitable pH values and with appropriate metal indicators.[25] Potentiometric indication allows an NTA content as small as 0·5 % to be recognized.[23]

Daniel and LeBlanc[22] have reported that 1 % or more NTA in EDTA can be detected both by infrared analysis and by spectrophotometric measurements of the chelates with various metals. However, none of these methods is as sensitive as the polarographic examination of the cadmium–NTA wave, which precedes that for the cadmium–EDTA wave. This method was introduced by Daniel and LeBlanc[22] who reported that as little as 0·03 % w/w of NTA could be determined in EDTA. The method was modified and simplified by Farrow and Hill;[24] by use of a larger sample and a cathode-ray polarograph, NTA down to 0·002 % in EDTA was determined by those workers. The polarographic approach has been adopted in the specifications for reagent-grade EDTA.[1,19] The procedure given by *Reagent Chemicals*[1] employs d.c. polarography and in our hands a limit of detection of 0·02 % NTA has been established.

Freeman and his associates have summarized in an informal report[26] some experiments on the silylation of EDTA with bis(trimethylsilyl)acetamide and gas chromatographic examination of the reaction products; a peak attributed to nitrilotriacetic acid was resolved at a content of 1 %. Such silylation has been briefly restudied by us with the aim of extension to smaller NTA contents. However, the complexity of the reaction mixture and the size of the blank made quantification of the results impossible.

Thin-layer chromatography

It was hoped that thin-layer chromatography might be useful in the detection of trace organic impurities, especially NTA; however, no separations of EDTA and NTA were achieved with a variety of adsorbents and simple solvent systems. Heinerth[39] recently reported the resolution of these compounds on a silica gel plate, with a 5:5:1:1 mixture of dichloromethane–ethanol–aqueous ammonia–water for development, and the copper(II)–PAN complex for visualization. In our laboratories, this separation was confirmed; no impurity spot was found with high-purity EDTA, but NTA could be detected only at a content of 1 % or above.

Particulate matter

The particulate matter, that is, the insoluble matter, is evaluated by membrane filtration gravimetry after dissolution of the EDTA in aqueous ammonia.

Arsenic

Arsenic is determined by the silver diethyldithiocarbamate method of Vašak and Šedivec[40] following destruction of organic matter, effected essentially by the general wet ashing procedure recommended by Middleton and Stuckey,[41] employing

96% nitric acid but with the addition of a small amount of sulphuric acid to ensure that arsenic losses are negligible. The procedure is somewhat tedious, but allows the determination of arsenic down to 50 ppM.

The recent findings of Dubois and co-workers[42] have resolved some of the problems initially encountered in the application of this photometric method to extremely low arsenic contents. These workers identified difficulties associated with the presence of silver(I) in excess of that required for the formation of the 1:1 silver diethyldithio-carbamate complex. They also established that when the reagent is recrystallized from pyridine–water, the absorbance maximum is shifted to 525 nm from the longer wavelengths suggested by earlier workers.

Chloride

Since the preparation of high-purity EDTA involves the addition of hydrochloric acid, determination of the trace chloride content of the product is mandatory. A conventional silver chloride procedure with visual comparison of the turbidity with that of standards is applicable; however, it was found that hydrogen peroxide must be added to avoid the otherwise observable reduction of silver.

Trace elements by emission spectrography

Photometric methods have been devised for the determination of copper[27] and iron[27,28] in EDTA. Various trace metals have been determined polarographically, copper, lead, cadmium, and zinc after ashing of the sample, and iron directly.[29] The determination of ten or more trace elements in individual samples not only would be costly in development and working time but might require as much as 2–10 g of the expensive product for each element. Survey emission spectrography after ashing has been applied routinely to the determination of the trace element content of many high purity compounds. Ashing procedures have been reviewed critically by Koch and Koch-Dedic.[43] The procedure employed in the present work involving moistening with sulphuric acid and this pre-ashing treatment appears sound and well founded.

EXPERIMENTAL

For all precision operations use only Class A volumetric ware at or near calibration temperature. All dilutions should be made with doubly distilled water.

Reagents

Hydrochloric acid, 1M. Standardized gravimetrically with high-purity silver as described by Strouts, Wilson and Parry-Jones,[34] exercising all the care and precautions recited by those authors. Store the solution in a heavy-wall polyethylene bottle. Express concentration as mole/kg.

Hydrochloric acid, ~0·5M. Transfer a suitable weight of the 1M acid (~50 g) via a weight-burette to a 100-volumetric flask and dilute with water to the mark. Express the concentration in terms of g of 1M acid per ml.

Sodium hydroxide, 1M. Prepare a 1-litre quantity of approximately 1M sodium hydroxide from reagent-grade 50% sodium hydroxide solution and freshly boiled distilled water. Since not all of the solution is used immediately, divide it between several 250-ml screw-cap polyethylene bottles. Screw each cap on fully, invert the bottle, and squeeze to verify that the cap makes an effective seal. Wrap the cap and bottle neck with polyvinyl chloride tape. Standardize the solution against the 1M hydrochloric acid by precision weight titrimetry with potentiometric indication, following the recommendations of Strouts and co-workers.[34] Express concentration as mole/kg.

Calcium carbonate. Use calcium carbonate of primary standard quality and take the assay value into account. Preferably establish the assay by acid–base weight titrimetry against the 1M hydrochloric acid.

High-purity aqueous ammonia. Bubble high-purity ammonia gas from its cylinder first through an ammoniacal solution of EDTA and then through water and with good cooling absorb in water contained in a polyethylene bottle. Continue the operation, taking care to avoid suck-back, until saturation is approached (sp. gr. 0·900).

Ammoniacal buffer, pH 10. Mix 70 g of reagent grade ammonium chloride and 570 g of high-purity aqueous ammonia and dilute with water to 1000 ml. Store in a polyethylene bottle.

Calmagite indicator powder. Grind 0·20 g of Calmagite with 2·0 g of sucrose to a fine powder, with a mortar and pestle.

High-purity EDTA, 0·05M. Weigh 3·77 g of the EDTA under evaluation to the nearest 0·1 mg, dissolve it in about 175 ml of water with addition of high-purity aqueous ammonia, and dilute in a 250-ml volumetric flask with water to the mark.

Inert gases. Use high-purity nitrogen. Alternatively use carbon dioxide-free air scrubbed with sulphuric acid and then passed successively through a soda-lime tower and a smaller tower filled with Ascarite.

Apparatus

Modified titration flask. Take a 500-ml wide-mouth conical flask. At a point 80 mm from the bottom seal in a 6-mm outside diameter right-angled tube. One end of the tube should extend through the flask wall to form a short side-arm and the other end nearly to the bottom of the flask, but well off-centre so that free movement of a magnetic stirring bar is possible and flow from a burette will not fall on the tube. (If a flask fitted with a standard taper ground-glass neck is used, the modified flask can be used to advantage in titrations where carbon dioxide is evolved, by attaching an extension consisting of a full length standard taper inner joint.)

Phototitrator. Use a phototitrator of the design of Flaschka and Sawyer[36] or equivalent.

Procedures

Assay of EDTA by acid–base titration. Put 3·3–3·5 g of the EDTA, weighed approximately, into a 100-mm long vial having a polyethylene "snap" cap, dry with the cap off at 105° for 2 hr, and allow to cool to room temperature in a desiccator. Weigh the sample by difference (to 0·1 mg) into a modified 500-ml titration flask with the side-arm capped with either a closed length of plastic tubing or a rubber policeman. Transfer the sample by holding the vial upright in utility tongs held vertically, inverting the flask over the vial so that the vial mouth reaches to the bottom of the flask, and then up-ending the vial and flask together so that the vial contents fall to the flask bottom without dusting.

Add about 250 ml of water, insert a magnetic stirring bar, and start the flow of either high-purity nitrogen or carbon dioxide-free air. Continue the magnetic stirring and flow of gas for about 15 min. Introduce a thin combination calomel-glass electrode pair connected to an expanded-scale pH-meter. Continue the stirring and passage of gas during the titration. Slowly add the standardized 1M sodium hydroxide by means of a 60-ml weight-burette until pH 9·0–9·1 is reached. Since EDTA as the free acid is water-insoluble and dissolves only slowly as base is added, take care that all of the sample dissolves, especially any particles that may creep up the flask walls. Record, to the nearest mg, the weight of the sodium hydroxide delivered. Now back-titrate with the ∼0·5M hydrochloric acid delivered from a 10-ml burette (0·02-ml divisions) in exactly 1-ml increments. Record the pH value attained after each addition from the start to below pH 7. Calculate the end-point volume by means of second differences in the pH values. Conduct the assay at least in triplicate.

Assay of EDTA by chelometric titration. Weigh approximately 5·86 g of the EDTA into a tall-form weighing vial, dry with the cover off at 105° for 2 hr, and allow to cool in a desiccator. Weigh by difference a sample of the standard calcium carbonate (1·0 g) to 0·01 mg into a 150-ml tall-form beaker containing a magnetic stirring bar. With 10 ml of water wash down the beaker walls and with stirring slurry the carbonate. Cover the beaker with a watch-glass and lift it momentarily to add 10 ml of reagent-grade hydrochloric acid. Complete the dissolution with stirring. Weigh by difference the dried EDTA (5·85 g) to 0·01 mg into the solution and stir briefly. Add dropwise high-purity aqueous ammonia until pH 7·0 is attained. Now add pH 10 ammoniacal buffer with stirring until pH 9·5 is just reached. Transfer the solution quantitatively to the sample cell of the phototitrator and dilute with water to about 100 ml. Position the borosilicate glass stirrer in the cell and adjust the stirring rate so that air bubbles do not occur. Use the 665-nm filter and adjust the galvanometer scale reading to zero for the dark-current and to 100 for the solution. Now add 0·050 g of Calmagite indicator powder and stir until dissolution is complete. Titrate with the 0·05M solution of the high-purity EDTA being evaluated, using a 10-ml burette with 0·02-ml divisions.

Record the transmittance readings after each titrant addition. Plot on linear graph paper either absorbance values (taken from a transmittance–absorbance conversion table) or the logarithms of the scale readings against the volume of EDTA solution added. Alternatively plot on semilogarithmic paper the scale readings (log) against the volume of titrant (linear). Since the end-point region used covers only 2 or 3 ml in a total solution volume of over 100 ml, volume corrections are unnecessary.

The end-point corresponds to the intersection of the extrapolations of the inclined and second horizontal portions (see Fig. 1).

Perform the assay at least in triplicate.

Elemental analysis. Determine carbon and hydrogen by conventional microcombustion techniques and nitrogen by a micro-Kjeldahl procedure. Theoretical values for $C_{10}H_{16}N_2O_8$ are 41·01% C, 5·52% H, and 9·59% N.

Ash (sulphated). Use a 5·0-g sample of the EDTA and the procedure given in *Reagent Chemicals*[1] for the determination of the residue after ignition. With this sample weight a sulphated ash content as low as 0·002% can be determined.

Loss on drying. Weigh a 4-g sample of the EDTA to the nearest 0·01 mg, dry for 2 hr at 105°, and reweigh after cooling in a desiccator.

Nitrilotriacetate. Follow the procedure given in *Reagent Chemicals*.[1] The limit of detection by this procedure is 0·02% NTA. The scan need not be confined to the prescribed range, but can be extended over the entire possible range; no spurious wave should occur.

Particulate matter. Slurry a 10·0-g sample of EDTA with 180 ml of water and add sufficient reagent-grade aqueous ammonia (2·3 ml) to effect dissolution; both the water and aqueous ammonia used should be filtered through membrane filters just before use. The pH should be below 7·0. Then use the general gravimetric procedure of the Millipore Corporation,[44] using a 25-mm diameter 0·80-μm membrane filter. Use of a 10-g sample allows the determination of less than 5 ppm by weight of particulate matter.

Arsenic. Weigh a 5·00-g sample of EDTA into a 500-ml iodine flask and add 20 ml of doubly distilled water, 2 ml of reagent-grade sulphuric acid and 10 ml of 70% reagent-grade nitric acid. Place a small short-stem glass funnel in the mouth of the flask. Since the initial reaction can proceed vigorously, warm the flask on a steam-bath until reaction starts, remove promptly, and allow to stand until the reaction terminates.

For the following operations use a hot-plate reliably adjusted to 300°, confirmed, for example, by a surface spot-check thermometer. Evaporate to fumes, partially cool the flask to allow addition of 2 ml of 90% reagent-grade nitric acid, and again evaporate to fumes. Repeat this addition of 2 ml of 90% nitric acid four more times or until there is no darkening of the reaction mixture. Finally, to remove nitric acid, remove the small funnel from the flask mouth and twice add 10 ml of water, evaporating to fumes after each addition.

Cool the solution and transfer it quantitatively with water to the arsine generator flask (conventional design) and determine the arsenic content by the method of Vašák and Šedivec.[40] Read the absorbance at 525 nm, preferably using a 50-mm cell, against the silver diethyldithiocarbamate reagent solution. Run a reagent blank for the entire procedure and correct the absorbance. Read the result from a standard curve, but run a standard with each group of samples to check the validity of the curve. Use of a 5-g sample allows the determination of an arsenic content as low as 50 ppM.

Chloride. Add 5·0 g of the EDTA to 35 ml of water and add sufficient reagent-grade aqueous ammonia (~3 ml) to dissolve the sample. Now add sufficient reagent-grade nitric acid to bring the pH to 3·5, stir, add 0·5 ml of reagent-grade 30% hydrogen peroxide, stir, and add 1 ml of 0·1M silver nitrate. After 5 min compare visually the turbidity developed with that of chloride standards prepared to include 3·5 ml of aqueous ammonia and 0·5 ml of 30% hydrogen peroxide and with nitric acid added to pH 3·5. Use of a 5-g sample allows determination of a chloride content as low as 5 ppm.

A refinement of this procedure was also studied in which sufficient nitric acid is added to precipitate EDTA as the free acid, the precipitate is separated by filtration, and washed with a small volume of dilute nitric acid. The combined filtrate and washings are used in the procedure as given. Since identical results were obtained, this refinement seems unnecessary.

Trace elements by emission spectrography. Transfer 2·5 g of the EDTA to a porcelain evaporating dish, moisten with 2 ml of high-purity concentrated sulphuric acid, and pre-ash under contamination-free conditions in a pre-ashing chamber.[45] Then add 25 mg of ultrapure or spectrographic grade lithium carbonate to the residue and ash in a muffle furnace, starting at room temperature, progressively raising the temperature to 450°, and continuing at this temperature overnight. Transfer the cooled residue to a weighed polystyrene vial. Add sufficient lithium carbonate to give a total weight of 50 mg and mix in a vibrator mill for 30 sec. Transfer 10 mg of the mixture to the crater of a preformed high-purity graphite electrode [3/16-in. (5-mm) neck, 3/16-in. (5-mm) deep crater], and use a ¼-in. (6-mm) preformed high-purity graphite counter electrode. Excite with a direct current of 15 A for 120 sec, maintaining a 4-mm gap throughout the burn. Record the 245–460 nm wavelength region on an spectrum analysis plate.

Develop, fix, rinse, and dry the plates in a conventional manner. Read the lines in the 245·0 to 387·5 nm region as well as strontium at 407·8 nm, calcium at 422·7 nm, and barium at 455·4 nm, against commercial standards in lithium carbonate. For key elements found absent, record the basic sensitivity as a "less than" value.

The key elements routinely read are listed for one lot in Table IV. These values were obtained with three-level commercial standards augmented by a fourth standard prepared by dilution of the lowest of those standards. The limits of detection for ten elements, employing 50-fold concentration by ashing as in the procedure above, are presented in Table II. If greater precision is desired, the recently introduced five-level spectrographic standards with indium as an internal standard can be used[9] and line-pair ratios can be measured densitometrically. Internal-line standards of this improved type are being routinely applied to other materials now under study in this laboratory.

TABLE IV.—CERTIFIED VALUES FOR ONE LOT OF HIGH-PURITY EDTA*

Assay ($C_{10}H_{16}N_2O_8$) after drying at 105°C for 2 hr		Metallic impurities (ppm)†† (Contd.)	
Potentiometric acid–base weight titration	100·0$_2$%†	Barium	<0·04
		Beryllium	<0·01
Chelometric weight titration with photometric indication§	100·0$_4$%‡	Bismuth	<0·1
		Cadmium	<0·2
		Calcium	0·1
		Chromium	<0·1
Elemental analysis		Cobalt	<0·1
		Copper	0·02
Carbon (theory 41·01%)	41·3%; 41·3%	Gallium	<0·1
Hydrogen (theory 5·52%)	5·6%; 5·5%	Germanium	<0·2
Nitrogen (theory 9·59%)	9·6%; 9·6%	Gold	<0·2
Ash (sulphated)	0·003%	Indium	<0·02
Loss on drying at 105°C for 2 hr	0·07%	Iron	0·1
		Lead	<0·2
Nitrilotriacetate content¶	0·02%	Magnesium	0·01
Particulate matter (after dissolution in aqueous ammonia)	0·003%	Manganese	<0·02
		Molybdenum	0·02
		Nickel	<0·1
		Niobium	<0·2
Non-metallic impurities (ppm)		Silver	0·01
Arsenic**	<0·05	Sodium	25
Boron††	<0·2	Strontium	0·1
Halide (as Cl)	30	Tin	<0·1
Silicon††	0·01	Titanium	0·02
		Vanadium	<0·02
Metallic impurities (ppm)††		Zinc	<2
Aluminium	0·03	Zirconium	<0·1
Antimony	<1		

* Actual lot analysis, Lot UHC 331, ULTREX®, (Ethylenedinitrilo)tetraacetate Acid, J. T. Baker Chem. Co., as packaged under argon in vials. The data support assignment of a 100·0% EDTA value to the product as a chelometric standard.

† Average value for 5 determinations: 100·1$_0$, 99·9$_3$, 100·0$_5$, 100·0$_3$% and 100·0$_6$%.

§ Weighed amount of ULTREX® Calcium Carbonate, Lot UMO 450, assay 99·99% CaCO$_3$; reacted with a substoichiometric weighed amount of the EDTA. The small excess of calcium in the solution, ammoniacally buffered to pH 9·5, titrated photometrically with a standard EDTA solution, with Calmagite as indicator.

‡ Average value for 3 determinations: 100·0$_6$, 100·0$_4$, and 100·0$_3$%.

¶ By d.c.-polarographic assessment of the cadmium–NTA wave (-0.94 V vs. S.C.E.).

** By evolution and silver diethyldithiocarbamate photometry.

†† By d.c.-arc spectrography.

RESULTS AND DISCUSSION

Values, obtained by the procedures detailed above, for one lot of high-purity EDTA are summarized in Table IV. It will be seen that the agreement for replicates in the two assay procedures is excellent. The loss on drying, 0·07%, for this lot, is for the air-dried material. Obviously this content could be reduced by either vacuum-drying of the product or its heating at 105° for a suitable time; these operations would have to be conducted under contamination-free conditions. For the nitrilotri-acetate, the value assigned for the smallest clearly discernible wave-height in the

polarogram under the conditions of the procedure is 2 mm, and corresponds to 0·02% NTA. The lot described here showed a wave-height less than this and was conservatively assigned the value of 0·02% NTA. Significant reduction of the halide content (30 ppm) by more persistent washing in the final step of preparation has been unsuccessful. Sodium at 25 ppm is the only metal impurity present significantly above the 1-ppm level. Most of the common metals are present, if at all, at concentrations below the basic sensitivity for them of the spectrographic procedure adopted.

The total amount of EDTA required for the conduct of the various procedures described is about 80 g. Obviously the detection limits of certain of the procedures might be improved by use of larger samples. However, economic considerations speak against this since for a 1-kg lot about 8% is already consumed in the analytical characterization. Some improvement might be secured by using a single portion of the EDTA for more than one determination. However, our experience indicates that if such a portion is carried consecutively through several procedures contaminants accumulate and high blanks result, thereby off-setting any advantages gained.

The question arises as to what else might be attempted in the way of further routine characterization of high-purity EDTA. Gas chromatography after silylation has failed (see *Nitrilotriacetate* in the introduction). According to our results and those of Wendlandt,[38] the temperature of decomposition as measured by thermal analysis appears to have no simple relation to purity.

Mercury is not reported in the spectrographic analysis since this element is probably largely volatilized in the ashing process.[43] For this element highly selective photometric determination based on extraction with dithizone at pH 4–5 with EDTA present to mask any elements might be considered.[46] Silver is the only significant interference reported. In our hands, with various high-purity inorganic salts, the method has given satisfactory results for mercury contents of 1–5 ppm. Conceivably this extraction–photometric method might be adapted for analysis of EDTA.

For the detection and quantification of trace elements spark-source mass spectrometry might also be considered.

One of the problems encountered in this work was how to dissolve the sample of EDTA for analysis. The free acid form of EDTA is relatively insoluble in water and only slightly soluble in many organic solvents, both common and exotic. Usually the free acid is dissolved in water by the addition of sodium or potassium hydroxide, and occasionally with aqueous ammonia. Sodium and potassium hydroxides are as yet not available with sufficiently low multivalent metal content, and reagent-grade aqueous ammonia supplied in glass bottles is high in silica content. Where a solution of the sodium salt is desired, high-purity sodium carbonate can be used. To a water slurry of EDTA an equimolar amount of anhydrous sodium carbonate is added in small portions with precautions to avoid loss by effervescence. To eliminate most of the carbon dioxide the mixture is stirred until reaction ceases and is then warmed briefly and aerated with nitrogen or filtered air for 20 min. The resulting solution has a pH of 4·4–4·5. If dissolution is still incomplete at the required EDTA concentration, additional sodium carbonate or hydroxide is added till pH 5·0 is reached. When a solution of the ammonium salt is to be made, ammonia gas is either bubbled directly into a cooled EDTA slurry or is absorbed (with cooling) in water and the resulting solution used promptly (see under *Reagents*). These two approaches should be of interest for any application of EDTA where low multivalent metal content is

mandatory. Indeed these approaches should be considered whenever reagent-grade EDTA, as the free acid, is to be utilized in the laboratory.

For a standard material, the rate of moisture pick-up on exposure to air should be small. For the lot described in Table IV, a portion of the powder was dried at $105°$ for 2 hr and 3 g of this dried material, weighed to the nearest 0.01 mg, were loosely spread over an area of 1.6×10^{-3} m² on the bottom of a weighing bottle. The open bottle was kept at 50% relative humidity (saturated calcium nitrate solution) and room temperature. After 24 hr the weight had increased by less than 0.01% and then remained essentially constant over a 5-day period.

Zusammenfassung—Hochentwickelte Laboratorien benötigen Chemikalien hoher Reinheit mit weniger als 500 ppm Gesamt-Verunreinigungen (ultrareine Chemikalien) mit ausführlichen analytischen Angaben für jede Partie. Wirtschaftlich durchführbare Methoden zur praktischen Analyse solcher Chemikalien, sowohl im anorganischen als auch im organischen Bereich, werden skizziert. Bei der Untersuchung von Mondproben und anderen hochentwickelten Untersuchungsprogrammen werden verwendete Verbindungen werden erwähnt. EDTA wurde durch Lösen in wasser mit Base und Fällen mit Säure als freie Säure hergestellt und ausführlich charakterisiert. Eine Präzisionsgehaltsbestimmung wird durch Wägetitration, potentiometrisch als dreibasige Säure und photometrisch als Chelatbildner erreicht. Andere Prüfungen sind Elementaranalyse, Veraschung, Gewichtsverlust beim Trocknen und Staub sowie Proben auf Nitrilotriacetat, Arsen und Chlorid. Bor, Silicium und Spurenmetalle werden durch Emissionsspektrographie bestimmt. Viele der Verfahren lassen sich auf andere organische Chemikalien hoher Reinneit anwenden.

Résumé—Les laboratoires de niveau supérieur ont des exigences pour des produits chimiques de haute pureté avec moins de 500 *p.p.m.* d'impuretés totales (produits chimiques ultra-purs) et avec une large définition analytique de chaque lot. On délimite quelques progrès réalisables économiquement vers l'analyse pratique de tels produits chimiques, tant inorganiques qu'organiques. Les composés utilisés dans l'étude d'échantillons lunaires et dans d'autres programmes avancés sont notés. L'EDTA, à l'état d'acide libre, a été préparé par dissolution dans l'eau avec une base et précipitation par addition d'acide. Le produit a été grossièrement caractérisé. Le contrôle de précision est réalisé par titrimétrie pondérale, potentiométriquement en tant qu'acide triprotique et photométriquement en tant qu'agent chélatant. D'autres essais appliqués comprennent l'analyse élémentaire, les cendres, la perte au séchage, la matière particulaire, et des recherches de nitrilotriacétate, d'arsenic et de chlorure. Le bore, le silicium et les métaux à l'état de traces sont déterminés par spectrographie d'émission. Un grand nombre des techniques sont applicables à d'autres produits chimiques de haute pureté.

REFERENCES

1. *Reagent Chemicals—American Chemical Society Specifications*, 4th Ed., Am. Chem. Soc., Washington, D. C., 1968.
2. J. K. Kennedy and G. H. Moates, *Ultrapurification*, in M. Zief and W. R. Wilcox, eds., *Fractional Solidification*, Vol. 1, pp. 463–473. Dekker, New York, 1967.
3. N. J. DeAngelis and G. J. Papariello, *J. Pharm. Sci.*, 1968, **57**, 1868; C. Plato and A. R. Glasgow, Jr., *Anal. Chem.*, 1969, **41**, 330.
4. G. L. Driscoll, I. N. Duling and F. Magnotta, paper presented at 155th Natl. Meeting, Am. Chem. Soc., San Francisco, April 1968.

5. M. Zief and W. R. Wilcox, eds., *Fractional Solidification*, Vol. 1, Dekker, New York, 1967; M. Zief, ed., *Purification of Inorganic and Organic Materials*, Dekker, New York, 1969.
6. E. F. Joy, J. Bonn and A. J. Barnard, Jr., unpublished work.
7. T. Higuchi and K. A. Connors, *Advan. Anal. Chem. Instrum.* 1965, **4**, 117.
8. R. Schaffer, National Bureau of Standards, personal communication; E. F. Joy and A. Foulds, unpublished work.
9. G. Chaplenko and L. Casper, paper presented at Pittsburgh Conf. on Analyt. Chem. and Appl. Spectroscopy, Cleveland, March 1969; Spex Industries, Inc., L-5 Standards, No. 10045.
10. M. Zief, *Am. Laboratory*, 1969, No. 10, 55.
11. M. Tatsumoto and J. N. Rosholt, *Science*, 1970, **167**, 461.
12. R. C. Murphy, G. Preti, M. M. Nafissi-V and K. Biemann, *ibid.*, 1970, **167**, 755.
13. N. Kershner, E. F. Joy and A. J. Barnard, Jr., unpublished work.
14. N. M. Kuzmin, G. I. Zhuravlev, I. A. Kuzovlev, A. N. Galaktionova and T. I. Zakharova, *Zh. Analit. Khim.*, 1969, **24**, 429.
15. NBS Standard Reference Material 915; cf. *NBS Technical News Bulletin*, 1969, **53**, 160.
16. S. Chaberek and A. E. Martell, *Organic Sequestering Agents*, Wiley, New York, 1959.
17. R. L. Smith, *The Sequestration of Metals*, Macmillan, New York, 1959.
18. G. Schwarzenbach and H. Flaschka, *Die komplexometrische Titration*, 5th Ed., Enke, Stuttgart, 1965.
19. *'AnalaR' Standards for Laboratory Chemicals*, 6th Ed., AnalaR Standards Ltd., London, England, 1967.
20. *Czechoslovak Fine Chemicals Standards*, 2nd Ed., Chemapol, Prague, 1960.
21. *Japanese Industrial Standards Handbook, Reagent Chemicals*, Nippon Kikaku Kyokai, Tokyo, 1961.
22. R. B. Daniel and R. B. LeBlanc, *Anal. Chem.*, 1959, **31**, 1221; cf. R. B. LeBlanc, *ibid.*, 1959, **31**, 1840.
23. R. N. P. Farrow and A. G. Hill, *Analyst*, 1965, **90**, 210; cf. R. G. Monk, *ibid.*, 1966, **91**, 597.
24. *Idem, ibid.*, 1965, **90**, 241.
25. D. L. Fuhrman, G. W. Latimer, Jr. and J. Bishop, *Talanta*, 1966, **13**, 103.
26. D. H. Freeman, ed., *Natl. Bur. Std. Technical Note* 459, pp. 27–29, Dec. 1968.
27. F. Vydra and R. Přibil, *Chemist-Analyst*, 1962, **51**, 76.
28. K. Nakhara and T. Danzuka, *Bunseki Kagaku*, 1964, **13**, 20.
29. O. Yu. Lavrova and N. M. Dyatlova, *Vestn. Tekhn. i Ekon. Inform. Nauch.-Isslid. Inst. Tekhn.-Ekon. Issled. Gos. Kom. Khim. i Neft. Prom. pri. Gosplane SSSR*, 1963, No. 4, 43; *Chem. Abstr.*, 1965, **62**, 12*f*.
30. E. V. Anderson and J. A. Gaunt, *Ind. Eng. Chem.*, 1960, **52**, 190; *Modern Chemical Processes*, Vol. VII, pp. 20–26. Reinhold, New York, 1963.
31. P. N. Palei and N. I. Udal'tsova, *Zh. Neorgan. Khim.*, 1960, **5**, 2315; *Chem. Abstr.*, 1962, **56**, 13620.
32. W. J. Blaedel and H. T. Knight, *Anal. Chem.*, 1954, **26**, 741.
33. L. G. Sillén and A. E. Martell, *Stability Constants of Metal-ion Complexes*, Spec. Publn. No. 17, Chemical Society, London, 1964.
34. C. R. N. Strouts, H. N. Wilson and R. J. Parry-Jones, *Chemical Analysis; The Working Tools*, 2nd Ed. Vol. I, pp. 200–201. Clarendon Press, Oxford, 1962.
35. F. Lindstrom and H. Diehl, *Anal. Chem.*, 1960, **32**, 1123.
36. H. Flaschka and P. Sawyer, *Talanta*, 1961, **8**, 521.
37. A. Ringbom, *Complexation in Analytical Chemistry*, pp. 108–122. Wiley, New York, 1963.
38. W. W. Wendlandt, *Anal. Chem.*, 1960, **32**, 848.
39. E. Heinerth, *Fette Seifen Anstrichm.*, 1968, **70**, 495; *Anal. Abstr.*, 1969, **17**, 3577.
40. V. Vašák and V. Šedivec, *Chem. Listy*, 1952, **46**, 341.
41. G. Middleton and R. E. Stuckey, *Analyst*, 1954, **79**, 138.
42. L. Dubois, T. Teichman, C. J. Baker, A. Zdrojewski and J. L. Monkman, *Mikrochim. Acta*, 1969, 185.
43. O. G. Koch and G. A. Koch-Dedic, *Handbuch der Spurenanalyse*, pp. 130–155. Springer, Berlin, 1964.
44. Millipore Corporation, Brochure ADM70, *Microchemical and Instrumental Analysis*, pp. 50–52, 1963.
45. R. E. Thiers, *Separation, Concentration, and Contamination*, in J. H. Yoe and H. J. Koch, Jr., eds., *Trace Analysis*, pp. 637–666. Wiley, New York, 1957.
46. H. Friedeberg, *Anal. Chem.*, 1955, **27**, 305.

EXTRACTIONS WITH LONG-CHAIN AMINES—I

EXTRACTION OF SOME METAL–XYLENOL ORANGE COMPLEXES INTO METHYLTRIOCTYLAMMONIUM CHLORIDE (ALIQUAT 336-S)

RUDOLF PŘIBIL and VLADIMÍR VESELÝ
Laboratory for Analytical Chemistry, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia

Summary—The extraction of traces of metals forming intensely coloured complexes with Xylenol Orange in acidic medium (p H0–3) has been studied. For such extractions in the presence of sulphates, chlorides and nitrates, a solution of methyltrioctylammonium chloride (Aliquat 336-S) in chloroform has been used. It is shown that it is possible to detect small amounts of gallium in indium and *vice versa*, and titanium or zirconium in thorium. These reactions should be capable of adaption to spectrophotometric determinations. The principle of the extraction of metals as their complexes with various metallochromic indicators is briefly discussed.

AMONGST the many new reagents which have been synthesized for complexometric purposes during the last decade, Xylenol Orange (XO)[1,2] and Methylthymol Blue (MTB)[3] have been popular because of their sensitive reactions and very sharp colour change. Both have also been used for the colorimetric determination of at least twenty metals (see Table I), the low selectivity being partly overcome by choice of proper conditions (pH, masking agents). The extraction of highly coloured ion-association, ternary or uncharged complexes has also proved very useful by allowing the development of sensitive and simple colorimetric procedures. We have assumed that similar extraction of intensely coloured complexes of XO, MTB and other compounds of this type would be a welcome contribution to analytical chemistry.

All these complexes are anionic and all attempts to extract them directly with common organic solvents have failed. Recently Moore has found that methyltrioctylammonium chloride (Aliquat 336-S) is able to extract some complexes of such aminopolycarboxylic acids as EDTA, DTPA and HEDTA.[4,5] We can expect that complexes of XO or MTB could also be extracted with a suitable solution of this amine or of other high molecular weight amines which are now on the market (Alamine, Hyamine, Arquad, Zephiramine, *etc*).

Preliminary experiments were very promising. In some cases the extraction of XO–metal complexes proceeded smoothly under proper conditions (pH and presence of suitable anion), in some cases the metal complexes were extracted not at all or only partly. For example, indium is extracted from acidic solution very easily in the presence of sulphate or chloride but gallium is not. Similarly, zirconium and hafnium are extracted, but thorium is not. Also the action of masking agents in some cases differs from that in aqueous solutions. The extracted $Ti–XO–H_2O_2$ complex does not react with fluoride in chloroform–amine medium. Such selective extractions permit successive separation of trace metals and their colorimetric determination either in the aqueous or the organic phase.

TABLE I.—OPTIMAL CONDITIONS FOR COLORIMETRIC DETERMINATION OF METALS
WITH XO

Metal	Acidity	Validity of Beer's law $\mu g/25$ ml	Reference
Zr	$0.2N$ H_2SO_4	5–63	6
	$0.5–1.0M$ $HClO_4$	—	7
Ga	pH 1.2–1.7	0–60	8
	pH 1.5–2.5	5–140	9
	pH 2	—	10
In	pH 3–4	5–80	11
Bi	$0.08–0.15N$ H_2SO_4	20–100	12
	$0.1–0.2M$ $HClO_4$	0–250	13
	$0.1N$ HNO_3 or $HClO_4$ or HCl	10–80	14
Th	pH 2.7–3.3	2–80 per 10 ml	15
Tl	$0.25–0.7M$ acetic acid	20–150	16
Ti	pH 3–4.5	—	17
Ti + H_2O_2	$0.04–0.06M$ $HClO_4$	7–70	18
Cr	pH 1.9–2.2	0–30	19
	pH 3	—	20
Al	pH 3.4	0–50	21
	pH 3.8	0–60	22
	pH 3.4	5–25	23
Fe	$0.04–0.06M$ $HClO_4$, HCl	5–50	24

In this paper we discuss the general conditions for extractive separation of some metal–Xylenol Orange complexes into a chloroform solution of Aliquat 336-S and some examples of qualitative detection of traces of metals. Further applications are also discussed briefly.

EXPERIMENTAL

Reagents

Amine hydrochloride solution. Chloroform solutions (5% w/w) of methyltrioctylammonium chloride (approx. $0.1M$) were prepared by dissolution of 50 g of Aliquat 336-S in 1 kg of chloroform. Aliquat 336-S (General Mills Inc., Kankakee, Illinois, U.S.A.) is R_3CH_3NCl, where R is an aliphatic amine with 8–10 carbon atoms, with octylamine predominating (90–95%).

Metal ion solutions. Solutions ($5 \times 10^{-2}M$ and $5 \times 10^{-4}M$) of metal salts were prepared by proper dissolution of the nitrates or chlorides (acidified if necessary).

Xylenol Orange, $10^{-3}M$ solution. Prepared daily by dissolution of 70 mg of the reagent (Lachema, Brno) in 100 ml of redistilled water.

Other reagents. These include $0.1N$ hydrochloric, nitric and sulphuric acids either alone or $0.1M$ in potassium chloride, potassium nitrate or sodium sulphate respectively. Buffer solutions of pH 3.0 and 4.6 were prepared from acetic or chloroacetic acid and sodium hydroxide. Solutions at pH 5–5.5 were prepared from acid solutions of metals by adding a 5% solution of hexamine.

RESULTS

Extraction of XO-complexes

Xylenol Orange as a complexometric indicator is used only in acidic solutions from pH 0 up to pH 5–5.5. Above this pH coloured forms of the indicator such as H_2XO^{4-}, HXO^{5-} and XO^{6-} are formed. Complex formation is strongly dependent on the pH of the solution. Generally speaking, the lower the pH, the more selective are the reactions of Xylenol Orange. For this reason we have studied the extraction from relatively acidic solutions (pH below 3), where only a few elements react with XO. Table I includes the values of optimal pH for colorimetric determination of elements

with XO. Other elements which react at pH >4 (bivalent metals, rare earths, *etc*) are not included. These are also extracted into a chloroform solution of Aliquat.

A great number of preliminary experiments, where the influence of pH and concentration of anions (nitrate, chloride, sulphate) on complex formation and extraction was studied, led to the adoption of the following procedure.

General procedure

To a test-tube, a solution containing 50 μg of metal was added and acidified with 5 ml of acid ($0·1N\ H_2SO_4/0·1N\ Na_2SO_4$ or $1M\ HCl/0·1M\ KCl$ or $0·1M\ HNO_3/0·1M\ KNO_3$) and diluted to 10 ml with redistilled water. After addition of 1 ml of $0·001M$ XO the test-tube was warmed for 5 min in a boiling water-bath. After cooling, the solutions were extracted with 10 ml of the Aliquat solution in chloroform by vigorous shaking for 10 sec. After phase separation, the colour observed eventually gave rise to a precipitate at the interface. The observations were evaluated as follows:

(a) Quantitative extraction was indicated by a colourless or slightly yellow water phase and an intensely coloured organic phase. After addition of more XO the water phase became intensely yellow and a second extract was colourless or slightly yellow (free XO).

(b) In partial extractions, both phases were coloured (orange, red or violet). By repeated extraction with additional XO, the degree of extraction could be roughly estimated.

(c) Where no extraction took place, even of traces, the organic phase was yellow (free XO).

Table II shows the behaviour of some elements in the presence and absence of some masking agents (bromide for Tl and Bi, fluoride for Zr and Th).

TABLE II.—EXTRACTION OF XYLENOL ORANGE COMPLEXES WITH ALIQUAT

Ion	0·1N HCl + 0·1M KCl	0·1N H₂SO₄ + 0·1M Na₂SO₄	0·1N H₂SO₄ + 0·1M Na₂SO₄ +10% KBr	+10% KBr/ 1M NH₄F*	0·1N HNO₃ + 0·1M KNO₃ +10% KBr	+10% KBr/ 1M NH₄F*
Bi	O	+	O	O	O	O
Ga	—	—	—	—	—	—
Hg(II)	P	+	P	O	—	O
In	+	+	+	+	O	O
Fe(III)	P	P	—	—	—	—
Sc	O	O	O	O	O	O
Fe(II)	O	O	O	O	O	O
Th	O	O	O	O	—	O
Zr	+X	+	PX	O	OX	O
Cu(II)	O	O	O	O	O	O
Al	O	—	—	O	O	O
Pb	O	O	O	O	O	O
Ni	O	W	O	O	O	O
Co(II)	O	O	O	O	O	O
Ti(IV) + H₂O₂	—	+	—	P	P	—
Ti(IV)		+				
Mo(VI)		O				
W(VI)		O				
V(V)		+				

* After extraction in the presence of KBr, the phases were left in contact, NH₄F added, and the phases were shaken again.

+ Extraction into the organic phase.

— No extraction.

X Hydrolysis.

P Partly extracted.

O No reaction with Xylenol Orange.

W Very feebly extracted.

These results are worth studying because quantitative extractions should allow the development of new colorimetric procedures for traces of these elements. With Xylenol Orange we are able to detect less than 1 μg/ml. Because of shortage of Aliquat in our laboratory we have worked out only a few simple qualitative procedures.

Qualitative detection

Detection of gallium in the presence of indium. To a solution containing at least 10 μg of Ga add 5 ml of 0·1 N H₂SO₄/0·1M Na₂SO₄ and dilute to 10 ml with water. Warm the solution in a boiling water-bath, and add 1 ml of 0·001M XO. Allow to cool and shake vigorously for 10 sec with 10 ml of Aliquat solution. An orange-red colour in the water phase indicates the presence of gallium. An intense red colour in the organic phase indicates the presence of indium. This test is reliable up to the ratio In:Ga = 5000 (0·02% Ga).

The extraction can be repeated. Usually the chloroform extract is colourless. If we add to the separated aqueous phase 1 ml of 1M ammonium fluoride and shake again with Aliquat, the Ga–XO complex is extracted (fluoride masks traces of Zr, Hf, Ti and simultaneously raises the pH), and can be stripped by adding 0·5 g of potassium bromide to the aqueous phase and shaking again.

Detection of indium in the presence of gallium. The procedure described above can be used provided that the gallium is not in large excess. To the cold solution containing at least 15 μg of In add acid and water as above, then 1 ml of XO and 10 ml of Aliquat reagent. The red extract indicates the presence of indium, the aqueous phase is an intense orange. Indium can be detected up to ratio Ga:In = 250 (0·4% In).

Detection of gallium in the presence of bismuth. To the solution containing at least 10 μg of Ga add 1 g of potassium bromide and proceed as described above. An orange-red colour in the water phase indicates the presence of gallium. The limit of detection is 0·1% Ga.

In all these tests thallium, thorium and bivalent metals do not interfere. Iron does not interfere if it is first reduced with ascorbic acid.

Detection of zirconium in the presence of thorium. Take a solution of zirconium and thorium sulphates containing at least 10 μg of Zr, adjust the sulphuric acid concentration to 0·5N, add 1 ml of 0·001M XO and warm the solution in a boiling water-bath for 5 min. The solution becomes red-orange during warming. After cooling extract the solution with 5–10 ml of Aliquat reagent. An intensely red or red-violet chloroform phase indicates the presence of zirconium. The detection limit is 0·02% Zr.

In the presence of chloride and nitrate zirconium is hydrolysed during the procedure, but its presence is indicated by the appearance of a red-violet ring at the interface. The sensitivity remains the same.

Detection of titanium in the presence of thorium. To the solution of titanium and thorium in 0·1N sulphuric acid (containing at least 6 μg of Ti) add 1–2 drops of 30% hydrogen peroxide and 1 ml of 0·001M XO. Warm the solution in a boiling water-bath; the solution turns orange or intense red depending on the Ti concentration. Allow it to cool and extract with 5 ml of Aliquat reagent. An intensely red extract indicates the presence of titanium. The aqueous phase remains orange (Th). On addition of 0·5 ml of 1M ammonium fluoride, and shaking again, the orange colour of the aqueous phase disappears, but the colour of the organic phase does not change (Ti–XO–H₂O₂–Aliquat does not react with fluoride). The detection limit is 0·07% Ti.

If the solution contains more than 10 mg of thorium, then after addition of peroxide the thorium is precipitated, the extract becomes very cloudy and colour detection fails.

DISCUSSION

The experiments reported above are the first attempt to extract and successively separate the highly charged complexes of Xylenol Orange. Similar behaviour has been observed with Methylthymol Blue (useful as an indicator at pH 1–11), Glycine-thymol Blue (selective for copper), and many others. Such extractions are dependent not only on pH and the chemical composition of the solution to be extracted, but also on the amine used. Extractions proceed differently with different extractants, *e.g.,* Aliquat, simple trioctylamine (Alamine) or tetradecyldimethylbenzylammonium chloride (Zephiramine). In addition, various metals can be suitably extracted as anionic complexes (or as simple anions such as CrO_4^{2-}, MnO_4^-) and determined

directly with a specific reagent in the organic phase, with high sensitivity. Quantitative studies are now in progress.

Zusammenfassung—Die Extraktion von Metallspuren wurde untersucht, die in saurem Medium (pH 0–3) mit Xylenolorange intensiv farbige Komplexe bilden. Für solche Extraktionen wurde in Gegenwart von Sulfaten, Chloriden und Nitraten eine Lösung von Methyltriotylammoniumchlorid (Aliquat 336-S) in Chloroform verwendet. Es wird gezeigt, daß man kleine Mengen Gallium in Indium und umgekehrt sowie Titan oder Zirkonium in Thorium nachweisen kann. Man sollte diese Reaktionen für spektrophotometrische Bestimmungen einrichten können. Das Prinzip der Extraktion von Metallen als Komplexe mit verschiedenen Metallfarbindikatoren wird kurz diskutiert.

Résumé—On a étudié l'extraction de traces de métaux formant des complexes intensément colorés avec l'Orangé Xylénol en milieu acide (pH 0–3). Pour de telles extractions on a utilisé, en la présence de sulfates, chlorures et nitrates, une solution de chlorure de méthyltriocytylammonium (Aliquat 336-S) en chloroforme. On montre qu'il est possible de détecter de petites quantités de gallium dans l'indium et *vice versa*, et le titane ou le zirconium dans le thorium. Ces réactions devraient pouvoir être adaptées aux déterminations spectrophotométriques. On discute brièvement du principe de l'extraction de métaux à l'état de complexes avec divers indicateurs métallochromes.

REFERENCES

1. J. Körbl, R. Přibil and A. Emr, *Collection Czech. Chem. Commun.*, 1957, **22**, 961.
2. J. Körbl and R. Přibil, *Chemist-Analyst*, 1956, **45**, 102.
3. *Idem, Collection Czech. Chem. Commun.*, 1958, **23**, 873; *Chem. Listy*, 1957, **51**, 1061.
4. F. L. Moore, *Anal. Chem.*, 1965, **37**, 1235.
5. *Idem, ibid.*, 1966, **38**, 905.
6. K. L. Cheng, *Talanta*, 1959, **2**, 61.
7. *Idem, Anal. Chim. Acta.* 1963, **28**, 41.
8. M. Otomo, *Bull. Chem. Soc. Japan*, 1965, **38**, 624.
9. P. P. Kish and M. I. Golovei, *Zh. Analit. Khim.*, 1965, **20**, 794.
10. R. Doicheva, S. Popova and E. Mitropolitska, *Talanta*, 1966, **13**, 1345.
11. N. Ishiwatari, H. Nagai and Y. Toita, *Bunseki Kogaku*, 1963, **12**, 603.
12. K. L. Cheng, *Talanta*, 1960, **5**, 254.
13. T. Sakai, *Nippon Kinkozu Gakkaishi*, 1966, **30**, 175.
14. H. Onishi and N. Ishiwatari, *Bull. Chem. Soc. Japan*, 1960, **33**, 1581.
15. B. Buděšinský, *Collection Czech. Chem. Commun.*, 1961, **26**, 231.
16. M. Otomo, *Bull. Chem. Soc. Japan*, 1965, **38**, 1044.
17. *Idem, ibid.*, 1963, **36**, 1577.
18. *Idem, ibid.*, 1963, **36**, 1342.
19. K. Tonosaki, M. Otomo and K. Tanaka, *Bunseki Kagaku*, 1966, **15**, 683.
20. K. L. Cheng, *Talanta*, 1967, **14**, 875.
21. J. Dvorǎk and E. Nývltová, *Mikrochim. Acta*, 1966, 1082.
22. D. T. Pritchard, *Analyst*, 1967, **92**, 103.
23. M. Otomo, *Bull. Chem. Soc. Japan*, 1963, **36**, 809.
24. K. L. Cheng, *Talanta*, 1959, **3**, 147.

INTERACTION OF PALLADIUM WITH SULPHAGUANIDINE

W. F. RITTNER, A. GULKO and G. SCHMUCKLER

Department of Chemistry, Technion, I.I.T., Haifa, Israel

Summary—The formation constants of palladium with chloride ions have been determined by a new approach to the interpretation of the ultraviolet spectra. The interaction of $PdCl_4^{2-}$ with sulphaguanidine (SG) has been interpreted and evaluated quantitatively. The formation constants of the mixed ligand complex $Pd(SG)_2Cl_2$, were determined spectrophotometrically. The stability constants for the stepwise formation of the palladium chloride complexes are: $\log k_1 = 3\cdot48$; $\log k_2 = 2\cdot79$; $\log k_3 = 2\cdot35$; $\log k_4 = 1\cdot1$, and for the interaction of $PdCl_4^{2-}$ with SG, $\log k_1 = 5\cdot42$; $\log k_2 = 4\cdot38$.

SULPHAGUANIDINE (SG), well known as a drug, was found by the authors to be a reagent with distinct selectivity for palladium. In slightly acidic aqueous media it yields an insoluble crystalline complex of the composition $Pd(SG)_2Cl_2$. SG belongs to a group of compounds having the general formula $RYC(NH)NH_2$ where $Y =$ —CH_2—, —S—, —O— or —NH—, and R = an alkyl, aryl or polymeric matrix, all of which have previously been found to possess some affinity for platinum metals as well as for gold.[1] This suggests the possibility of preparing selective ion-exchange resins by incorporating this type of ligand into a polymeric matrix. The present work will deal with the stability aspects of the palladium–SG complex, in order to yield an understanding of the processes that will take place in the polymeric matrix.

Since a mixed complex is formed, $Pd(SG)_2Cl_2$, separate discussions are needed for its two constituent parts, namely the palladium chloride system and the interaction of that system with SG.

EXPERIMENTAL

Methods

All stability constants were determined spectrophotometrically on samples equilibrated for 2 days and having a pH of 2 and an ionic strength of $1M$ (sodium perchlorate).

Palladium chloride system. A certain quantity, 5 ml, of $1\cdot17 \times 10^{-3}M$ ammonium tetrachloro-palladate(II) was measured into a series of 50-ml standard flasks. Enough sodium chloride solution was added to each flask for its final concentration to vary from 10^{-4} to $1\cdot0M$. After pH and ionic strength adjustments the samples were diluted to 50 ml and equilibrated for 2 days. The spectra of these samples, which are shown in Fig. 1, were taken on a Perkin–Elmer Spectrophotometer No. 350, in the region 200–400 nm, with 10-mm silica cells.

In order to obtain the numerical data for ε_4 (the molar absorptivity of the $[PdCl_4^{2-}]$ species) at 278 nm, the absorbance must be measured at a high free chloride concentration, namely $3M$. But under these conditions, with the palladium concentration chosen, the absorbance signal saturates the recorder at wavelengths shorter than 223 nm. This measurement was therefore carried out separately and does not appear in Fig. 1.

Sulphaguanidine. Equal quantities, $1\cdot67$ mg, of SG were introduced into a series of 100-ml standard flasks. Different quantities of perchloric acid were added to these samples so as to get a variation in pH from $0\cdot2$ to $6\cdot70$. The spectra of these solutions were recorded in the region 200–400 nm and are shown in Fig. 2.

Palladium chloride–SG system. For determination of k_1, various amounts of SG were placed in a series of 50-ml standard flasks each of which contained $9\cdot4 \times 10^{-4}M$ ammonium tetrachloro-palladate(II) and $0\cdot988 \times 10^{-2}M$ hydrochloric acid. The spectra of these solutions in the visible region (350–600 nm) were recorded and are shown in Fig. 3. Absorbance measurements for k_1 were taken at 402 nm.
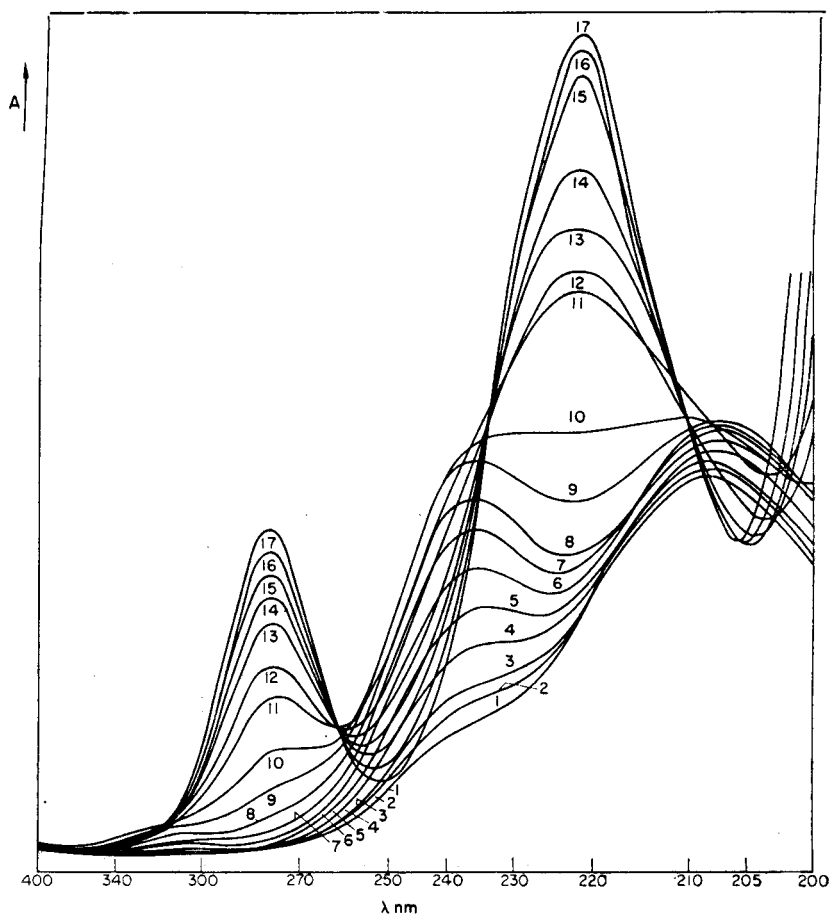
FIG. 1.—Spectral changes during the reaction of palladium with chloride ions.
Added chloride concentration: (1) 0; (2) $10^{-4}M$; (3) $2 \times 10^{-4}M$; (4) $5 \times 10^{-4}M$; (5)
$9 \times 10^{-4}M$; (6) $1.5 \times 10^{-3}M$; (7) $2.5 \times 10^{-3}M$; (8) $5 \times 10^{-3}M$; (9) $10^{-2}M$; (10)
$2 \times 10^{-2}M$; (11) $4 \times 10^{-2}M$; (12) $6 \times 10^{-2}M$; (13) $0.1M$; (14) $0.14M$; (15) $0.2M$;
(16) $0.3M$; (17) $1.0M$.

For the method of corresponding solutions, in order to determine the free ligand concentration
[A], two sets of palladium chloride solutions were prepared: $C_M' = 5.63 \times 10^{-4}M$ and $C_M'' =$
$3.75 \times 10^{-4}M$. A series of 50-ml standard flasks was prepared containing solution of concentration
C_M' and another series with concentration C_M''. To each of the flasks were added amounts of $1.126 \times$
$10^{-4}M$ SG varying from 1 to 12 ml, and the volumes were made up to 50 ml. Absorbance measure-
ments were taken at 390 nm in 10-mm silica cells.

For the method of continuous variations the ligand-to-metal ratio was determined by measuring
absorbances at 390 nm for various mixtures with [metal] + [ligand] = $2.21 \times 10^{-3}M$.

RESULTS AND DISCUSSION

Palladium chloride system

Many halide complexes of palladium are known, which have the general formula
PdL_2X_2, where L may be dimethylsulphoxide, thiocyanate, trialkylphosphine deriv-
atives, etc, and X is a halide.[2] The complex formed between SG and palladium chlo-
ride also belongs to this general type. In such complexes two chloride ions of the
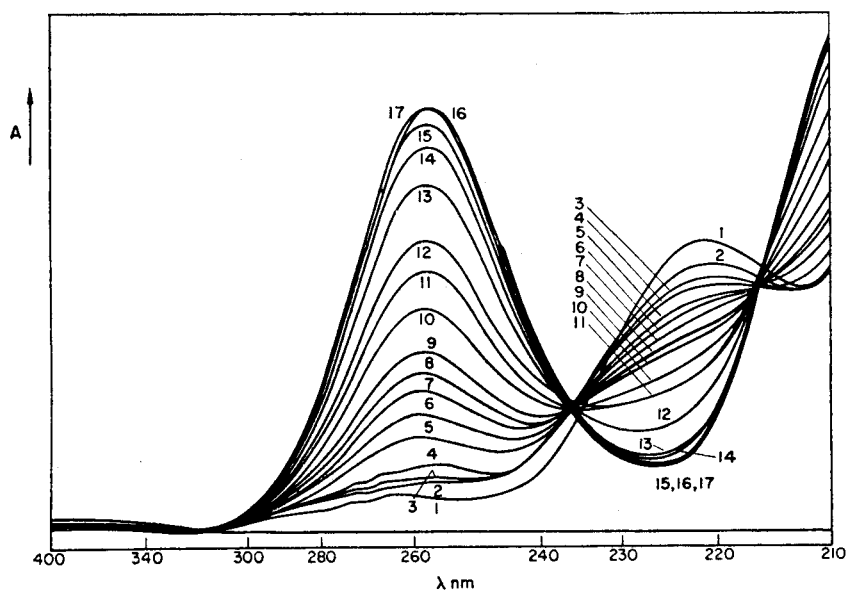
FIG. 2.—Spectral changes of sulphaguanidine with pH.
pH of solutions: (1) 0·2; (2) 1·03; (3) 1·22; (4) 1·40; (5) 1·64; (6) 1·80; (7) 2·01; (8) 2·09; (9) 2·20; (10) 2·35; (11) 2·48; (12) 2·62; (13) 2·95; (14) 3·42; (15) 3·70; (16) 4·77; (17) 6·70.
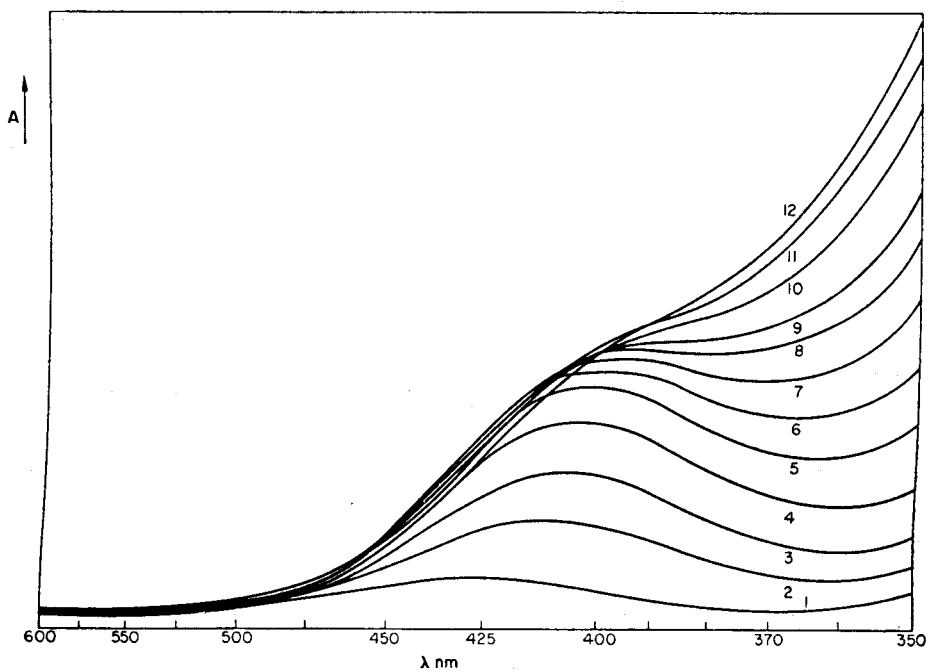
FIG. 3.—Spectral changes during the addition of SG to a palladium chloride solution. Concentration of Pd: $7·5 \times 10^{-4}M$; ratio SG/Pd: (1) 0; (2) 0·25; (3) 0·5; (4) 0·75; (5) 1·0; (6) 1·25; (7) 1·5; (8) 1·75; (9) 2·0; (10) 2·5; (11) 3·0; (12) 3·5.

original $PdCl_4^{2-}$ are apparently bound very strongly, while the other two can be easily substituted by other ligands.

The stepwise formation of the chloro-complexes of palladium in solution has already been studied potentiometrically[3] and spectrophotometrically.[4-9] The numerical results obtained differ considerably, while the values obtained for k_3 and k_4 seem to be too high in most of them. The photometric determinations of the stability constants consisted of measurements taken at the weak d-d transition peak (400 nm). Measurements at this wavelength are not very accurate because all the palladium chloride species absorb in this region and there are only slight differences in their peak intensities. The ultraviolet spectra under conditions of stepwise formation of the chloro-complexes offer more detailed and accurate information. Figure 1 illustrates a well resolved spectrum consisting of three different absorption peaks and two isosbestic points.

The peaks appearing in this spectrum can be definitely assigned to three species: $[PdCl_2(H_2O)_2]$ at 208 nm; $[PdCl_3(H_2O)^-]$ at 208 and 236 nm, and a shoulder at 278 nm; $[PdCl_4^{2-}]$ at 223 and 278 nm.

In Fig. 1 the $[PdCl_4^{2-}]$ species is clearly seen to be formed at high chloride concentrations, with its absorption maximum at 278 nm. Curves 1–9 mainly represent the formation of the lower chloro-complexes, the $[PdCl^+]$ and $PdCl_2$ species. Curve 10 is different in shape because at that chloride concentration the quantities of $[PdCl_3^-]$ and $[PdCl_4^{2-}]$ begin to become more appreciable. Curve 11 represents the following concentrations of the various palladium species: $PdCl_4^{2-}$ 31%, $PdCl_3^-$ 62%, $PdCl_2$ 7%. Beyond curve 11 there is a sharp rise in the concentration of $PdCl_4^{2-}$ and a decrease in that of $PdCl_3^-$ and the formation of the well defined absorption peaks at 223 and 278 nm is observed. No changes in the curve were found above $3M$ chloride concentration, which makes the existence of co-ordination numbers higher than 4 very unlikely.[4,6,10,12]

Determination of k_3 and k_4. The formation constant of the fourth chloro-complex,

$$k_4 = \frac{[PdCl_4^{2-}]}{[PdCl_3^-][Cl^-]} \tag{1}$$

can be determined from the data in Fig. 1. For the calculation of k_4 the assumption is made that in the range of chloride concentrations between $4 \times 10^{-2}M$ and $3M$ the system contains only $[PdCl_4^{2-}]$ and $[PdCl_3^-]$. This assumption is supported by the appearance of an isosbestic point at 261 nm, which indicates the existence of an isolated equilibrium between two species. The equation for the system at the 278 nm peak is

$$A = \varepsilon C_M = \varepsilon([PdCl_4^{2-}] + [PdCl_3^-]) = \varepsilon_4[PdCl_4^{2-}] + \varepsilon_3[PdCl_3^-], \tag{2}$$

where A is the absorbance measured at 278 nm, C_M the total concentration of palladium, and ε, ε_3, ε_4 the molar absorptivities of the mixture, $PdCl_3^-$ and $PdCl_4^{2-}$ respectively.

Rearranging equation (2) and multiplying by C_M yields

$$(\varepsilon_4 C_M - \varepsilon C_M)[PdCl_4^{2-}] + (\varepsilon_3 C_M - \varepsilon C_M)[PdCl_3^-] = 0. \tag{3}$$

By substitution of $A_0 = \varepsilon_4 C_M$ (for the absorption measured at the maximal chloride concentration of $3M$ where the only species present is $[PdCl_4^{2-}]$), and $A = \varepsilon C_M$, we arrive at a straight-line correlation between the absorption measured at 278 nm

and the free chloride concentration:

$$A = (A_0 - A)[\text{Cl}^-]k_4 + \varepsilon_3 C_M, \tag{4}$$

A plot of A vs. $(A_0 - A)[\text{Cl}^-]$ gives a straight line. Similar expressions were developed by Newman and Hume[14,15] in their studies on the formation constants of the bismuth–chloride system. From the slope and the intercept of this line k_4 and ε_3 can be calculated. The experimental results were treated by least-squares methods and gave the following values and standard deviations:

$$k_4 = 12 \cdot 3 \pm 0 \cdot 8$$

$$\varepsilon_3 = \frac{0 \cdot 222 \pm 0 \cdot 042}{C_M \times 10} = 190 \pm 36 \ \text{l.mole}^{-1}\text{mm}^{-1}.$$

For the calculation of k_3 the same approach as for k_4 was used, and the measurement was also carried out at 278 nm. The chloride concentrations were lower and therefore the existence of the PdCl_2 species had to be taken into account. The basic equation has the form of equation (3) with the addition of the absorption of the PdCl_2 species:

$$(\varepsilon_4 C_M - A)[\text{PdCl}_4{}^{2-}] + (\varepsilon_3 C_M - A)[\text{PdCl}_3{}^-] + (\varepsilon_2 C_M - A)[\text{PdCl}_2] = 0. \tag{5}$$

ε_3 and k_4 are now known and if we substitute:

$$[\text{PdCl}_4{}^{2-}] = k_3 \cdot k_4[\text{PdCl}_2][\text{Cl}^-]^2$$

$$[\text{PdCl}_3{}^-] = k_3[\text{PdCl}_2][\text{Cl}^-]$$

into equation (5) and divide by $[\text{PdCl}_2]$, the following equation is obtained:

$$A = \{(A_0 - A)k_4[\text{Cl}^-]^2 + [\varepsilon_3 C_M - A][\text{Cl}^-]\}k_3 + \varepsilon_2 C_M. \tag{6}$$

The graphical correlation of the measured absorption vs. the term in the brackets yields a straight line the slope of which gives the value 224 for k_3, and the intercept the value of ε_2, which is negligibly small.

Determination of k_2 and k_1. The k_1 and k_2 equilibria exist in the regions of lower chloride concentration. In those regions the assumption that the total chloride concentration is equal to the free ligand concentration is not valid. It was therefore decided to use Bjerrum's[16] more general approach, which makes use of the formation function:

$$\bar{n} = N - \frac{d \log \alpha_n}{d \log [A]} = \frac{C_A - [A]}{C_M}, \tag{7}$$

where $\bar{n}$ = the average number of chloride ions bound to palladium, N = maximal co-ordination number, α_n = degree of formation of an individual complex $[\text{PdCl}_n^{2-n}]$, $[A]$ = free chloride ion concentration, C_A = total chloride concentration, C_M = total palladium concentration.

Equation (7) can be used for the graphical construction of the formation function. C_M is known ($1 \cdot 17 \times 10^{-4}M$), and from the spectral data at 278 nm α_n can be calculated, for the special case of $[\text{PdCl}_4{}^{2-}]$, as a function of chloride concentration, as follows:

$$\alpha_4 = \frac{A/A_0 - \varepsilon_3/\varepsilon_4}{1 - \varepsilon_3/\varepsilon_4}. \tag{8}$$

The formation curve for the Pd–Cl system was constructed, and the following stepwise formation constants were calculated, to a first approximation, at the points $\bar{n} = n - \frac{1}{2}$:

$$k_n = \frac{1}{[A]_{n-1/2}} \tag{9}$$

$$\log k_1 = 3\cdot48$$
$$\log k_2 = 2\cdot79$$
$$\log k_3 = 2\cdot00$$
$$\log k_4 = 0\cdot96$$

These values agree fairly well with those obtained by Burger and Dyrssen,[6] who used different experimental methods; k_3 and k_4, in particular, are in fair agreement with those calculated by the foregoing method and with Jörgensen's low value for k_4.

The ligand sulphaguanidine

The ultraviolet spectra of aqueous sulphaguanidine solutions in the pH range 1–7 were recorded between 210 and 400 nm and are illustrated in Fig. 2. This spectrum demonstrates the existence of two species in equilibrium:

$$SG + H^+ \rightleftharpoons SGH^+. \tag{10}$$

Above pH 3 the basic species SG with an absorption maximum at 258 nm is predominant. At higher acidities a protonated species is formed with a maximal absorption peak at 222 nm. Isosbestic points at 217 and 236 nm support the simple equilibrium shown in equation (10). In solutions more acidic than pH 1 a higher protonated species of the type SGH_2^{2+} may form, as evidenced by the shift of the isosbestic point.

The dissociation constant of the monoprotonated SG was found potentiometrically by Bell and Roblin[17] to be $pK_a = 2\cdot75$. In the present work, Fig. 2 was used to determine this constant in the same manner as that adopted for the Pd–Cl system. Equation (11) is analogous to equation (4) for the special case of the SG system in different pH media.

$$A = \frac{k_a}{k_w} \{(A_0 - A)[OH^-]\} + \varepsilon_{HA} \cdot C_{HA}, \tag{11}$$

where A = the absorption measured at 258 nm, A_0 = the maximum absorption of SG at 258 nm, ε_{HA} = the extinction coefficient of the protonated ligand at 258 nm, k_w is the ionic product for water.

The slope of the straight line obtained gives the value $pk_a = 2\cdot32 \pm 0\cdot02$, which seems to be more accurate than the former value.

The reaction between palladium chloride and sulphaguanidine

On addition of sulphaguanidine to a palladium chloride solution the yellow colour of the solution immediately became more intense. With palladium concentrations higher than $10^{-3}M$ a yellow crystalline precipitate slowly formed, with composition $[PdCl_2(SG)_2]$. The ligand-to-metal ratio was determined experimentally by Job's method, and the palladium-to-chloride ratio by elemental analysis.

Precipitation was carried out in acidic solution (pH 2) in order to avoid hydrolysis of the palladium ions. The acidity of the solution increased slightly during this process, because of displacement of protons from the protonated SG.

The conditions of complex formation between palladium and SG were studied in solution below the limit of precipitation, by measuring the d-d transitions of the Pd–Cl system occurring at 400 nm.

Determination of formation constants. The numerical value of the first formation step,

$$K_1 = \frac{[PdCl_2(SG)]}{[PdCl_2][SG]} \tag{12}$$

can be determined by gradually adding small quantities of SG until a palladium:SG molar ratio of 1:1 is reached. The spectra illustrated in Fig. 3 show the complex formation below the limit of precipitation, and indicate that at a wavelength of 402 nm there are no changes in absorption above the 1:1 ligand-to-metal ratio. The species appearing in equation (12) were evaluated by making the following substitutions:

$$A_1 = \varepsilon_0 M_0 + \varepsilon_1 [PdCl_2(SG)] = \varepsilon_0 [M_t - PdCl_2(SG)] + \varepsilon_1 [PdCl_2(SG)]$$
$$= \varepsilon_0 [M_t - SG_t] + \varepsilon_1 [SG_t] \tag{13}*$$

where A_1 = the absorption measured at 402 nm, ε_0 = the molar absorptivity of $[PdCl_4{}^{2-}]$ at 402 nm, ε_1 = the molar absorptivity of $[PdCl_2(SG)]$ at 402 nm, M_0 = concentration of the chloro-complexes of palladium which did not react with the ligand, M_t = total palladium concentration, SG_t = total ligand concentration, $[SG]$ = free ligand concentration (*i.e.*, not bound to palladium).

ε_1 can be determined experimentally from equation (13), and the concentration of the species $[PdCl_2(SG)]$ can now be expressed as a function of measurable quantities:

$$[PdCl_2(SG)] = M_t - M_0 = \frac{A_1 - \varepsilon_0 M_t}{\varepsilon_1 - \varepsilon_0} \tag{14}$$

$$M_0 = \frac{\varepsilon_1 M_t - A_1}{\varepsilon_1 - \varepsilon_0}. \tag{15}$$

The free SG concentration can now also be expressed by measurable quantities:

$$[SG] = \left[SG_t - \frac{A_1 - \varepsilon_0 M_t}{\varepsilon_1 - \varepsilon_0} \right] \Big/ D \tag{16}$$

where D is a pH correction term for the ligand and is equal to $(1 + [H^+]/k_a)$

$$[PdCl_2] = \frac{M_0}{G} = \frac{\varepsilon_1 M_t - A_1}{(\varepsilon_1 - \varepsilon_0)G} \tag{17}$$

* Equation (13) is valid under the specific conditions of $SG_t < M_t$, when it can be assumed that all the SG is associated with palladium.

where G is a correction term for $[PdCl_2]$ as a function of chloride concentration and is given by

$$G = \frac{1}{k_1 k_2 [Cl^-]^2} + \frac{1}{k_2 [Cl^-]} + 1 + k_3 [Cl^-] + k_3 k_4 [Cl^-]^2. \qquad (18)$$

Substitution of equations (14), (16) and (17) into equation (12) yields

$$K_1 = \frac{A_0 - \varepsilon_0 M_t}{(\varepsilon_1 M_t - A_1)} \frac{(\varepsilon_1 - \varepsilon_0)}{(\varepsilon_1 - \varepsilon_0)(SG)_t + (\varepsilon_0 M_t - A_1)} \cdot D \cdot G \qquad (19)$$

The experimental plot of equation (19) is a straight line and yields the numerical value $(3·13 \pm 0·14) \times 10^5$ for the first stability constant K_1, the correction terms at pH 2 and chloride concentration $0·988 \times 10^{-2} M$ being $D = 3·18$ and $G = 3·74$.

Since by spectrophotometric measurements at 402 nm only K_1 could be determined, it was decided to use Bjerrum's general equation since it enables both K_1 and K_2 for the palladium–SG system to be determined.

However, the general Bjerrum equation $\bar{n} = (C_A - [A])/C_M$ can be used only if there is an appreciable difference between the total ligand concentration C_A and the free ligand concentration $[A]$. The free ligand concentration was determined by the method of corresponding solutions.[11] This method is based on the assumption that if two solutions of different C_M and C_A show the same absorbance, the distributions of all complex species in both solutions are equal. According to Bjerrum the free ligand concentration can then be calculated by the formula

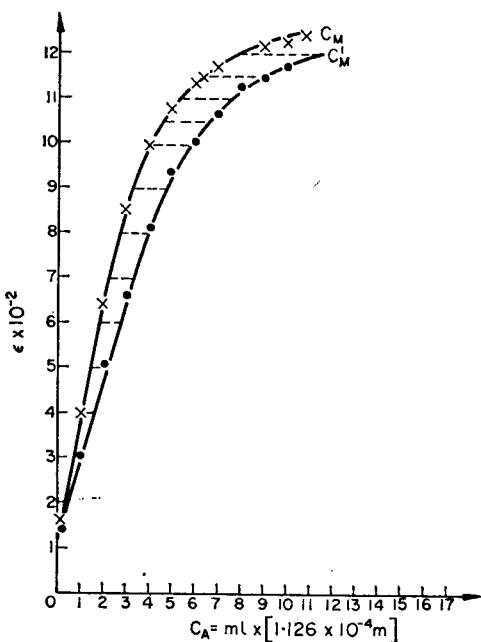$$[A] = \frac{C_\mu' C_A'' - C_M'' C_A'}{C_M' - C_M''}. \qquad (20)$$

FIG. 4.—Determination of [A] by the method of corresponding solutions.
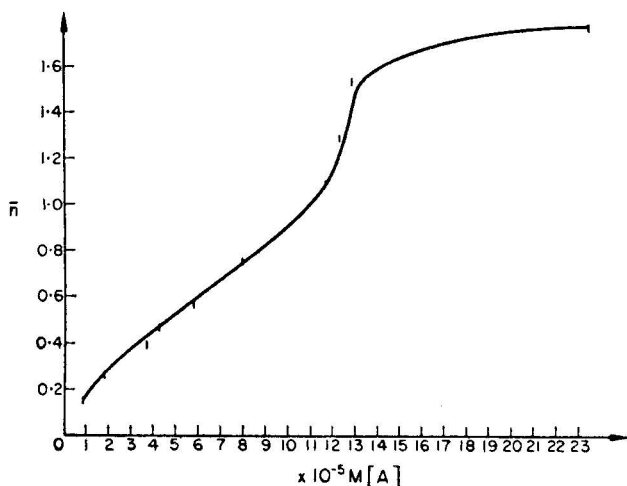
FIG. 5.—Formation curve for the interaction of palladium chloride with SG.

The free ligand concentrations for different C_A and C_M, as determined experimentally, are illustrated in Fig. 4.

Once [A] is known, the formation curve can be constructed (Fig. 5) and the two stability constants calculated.

The numerical values taken from the graph must still be corrected for the terms D and G. The stability constants obtained after all these corrections have been made are as follows:

$$K_1 = \frac{1}{[A]_{\bar{n}=0.5}} = \frac{[PdCl_2(SG)]}{[PdCl_2][SG]} = 2.6 \times 10^5$$

$$K_2 = \frac{1}{[A]_{\bar{n}=1.5}} = \frac{[PdCl_2(SG)_2]}{[PdCl_2(SG)][SG]} = 2.4 \times 10^4.$$

The value of K_1 obtained by the Bjerrum method agrees well with that already obtained, so it was thought justifiable to proceed with the computation of K_2 from Fig. 5.

CONCLUSION

The finding of relatively low stability constants for the palladium chloride–SG complexes leads us to the assumption that SG reacts as a monodentate ligand rather than by forming a chelate, although structurally this reagent could possibly also act as a bidentate ligand. Since two chloride ions are definitely bound to the palladium, chelate formation would require 6-co-ordinated palladium, which is very improbable; most palladium complexes are of the square planar type $PdCl_2X_2$.

Zusammenfassung—Die Bildungskonstanten von Palladium-Chloro-komplexen wurden mit einem neuen Ansatz für die Deutung der Ultraviolettspektren ermittelt. Die Reaktion von $PdCl_4{}^{2-}$ mit Sulfa-guanidin (SG) wurde interpretiert und quantitativ ausgewertet. Die Bildungskonstanten des gemischten Komplexes $Pd(SG)_2Cl_2$ wurden spektrophotometrisch bestimmt. Die Stabilitätskonstanten für die stufenweise Bildung der Palladium-Chlorokomplexe sind log $k_1 = 3,48$; log $k_2 = 2,79$; log $k_3 = 2,35$; log $k_4 = 1,1$ und für die Reaktion von $PdCl_4{}^{2-}$ mit SG log $k_1 = 5,42$; log $k_2 = 4,38$.

Résumé—On a déterminé les constantes de formation du palladium avec les ions chlorure par une nouvelle approche de l'interprétation des spectres dans l'ultra-violet. On a interprété et évalué quantitativement l'interaction de $PdCl_4{}^{2-}$ avec la sulfaguanidine (SG). Les constantes de formation du complexe ligand mixte $Pd(SG)_2Cl_2$ ont été déterminées spectrophotométriquement. Les constantes de stabilité pour la formation par degrés des complexes palladium chlorure sont: $\log k_1 = 3,48$; $\log k_2 = 2,79$; $\log k_3 = 2,35$; $\log k_4 = 1,1$ et, pour l'interaction de $PdCl_4{}^{2-}$ avec SG, $\log k_1 = 5,42$; $\log k_2 = 4,38$.

REFERENCES

1. G. Koster and G. Schmuckler, *Anal. Chim. Acta*, 1967, **38**, 179.
2. J. R. Durig, R. Layton, D. W. Sink and B. R. Mitchell, *Spectrochim. Acta*, 1964, **21**, 1367.
3. D. H. Templeton, G. W. Wath and C. S. Gomer, *J. Am. Chem. Soc.*, 1943, **65**, 1608.
4. A. K. Sundram and E. B. Sandell, *ibid.*, 1955, **77**, 855.
5. H. A. Droll, B. P. Block and W. C. Fernelus, *J. Phys. Chem.*, 1957, **61**, 1000.
6. K. Burger and D. Dyrssen, *Acta Chem. Scand.*, 1963, **17**, 1489.
7. K. G. Jörgensen, *Final Tech. Rep.*, DA-91, 508-EUC-247 (1958).
8. A. A. Grinberg and N. V. Kiseleva, *Zh. Neorgan. Khim.*, 1959, **3**, 1804.
9. S. A. Shchukarer, O. A. Lobaneva, M. A. Ivanova and M. A. Kononova, *Vestn. Leningrad Univ.*, 16, No. 10, *Ser. Fiz. i Khim.*, 1961, **2**, 152; *Chem. Abstr.*, 1961, **55**, 24362.
10. C. M. Harris and S. E. Livingston, *Rev. Pure. Appl. Chem.*, 1961, **12**, 16.
11. F. J. C. Rossotti and H. S. Rossotti, *The Determination of Stability Constants*, p. 282. McGraw-Hill, New York, 1961.
12. C. M. Harris, S. E. Livingstone and I. H. Reece, *J. Chem. Soc.*, 1959, 1505.
13. I. R. Wyatt, *Chem. Weekbl.*, 1966, **24**, 62.
14. L. Newman and N. Hume, *J. Am. Chem. Soc.*, 1957, **79**, 4571.
15. *Idem, ibid.*, 1957, **79**, 4576.
16. J. Bjerrum, *Metal Ammine Formation in Aqueous Solution*, p. 27. Haase and Son, Copenhagen, 1957.
17. P. H. Bell and R. O. Roblin, *J. Am. Chem. Soc.*, 1942, **64**, 2905.

COLORIMETRIC DETERMINATION OF TRACES OF SELENIUM, TELLURIUM, MANGANESE AND CERIUM

P. P. Naidu* and G. Gopala Rao

Department of Chemistry, Andhra University, Waltair, India

Summary—Methods are described for the colorimetric determination of micro- and semi-micro quantities of selenium, tellurium, cerium and manganese. The test solution in 0.35–$3M$ condensed phosphoric acid medium is oxidized with an excess of permanganate. The colour intensity of the unreacted permanganate is measured at 530 nm.

THE COLORIMETRIC determination of selenium, tellurium, manganese and cerium has generally been based on the complexation of these metals with suitable organic reagents, though manganese has also been determined by oxidizing it to manganese(III) or (VII), and cerium indirectly through the oxidative action of cerium(IV).[1–3] Although various indirect titration procedures are known, involving oxidation of a lower oxidation state of these elements, followed by back-titration of the excess of oxidant, no-one has hitherto proposed to measure the excess colorimetrically. We have now developed such a method for the rapid and accurate determination of micro to macro amounts of these elements—when they occur individually. Mixtures of them cannot be analysed by this method, of course. The method is made selective for these four elements by using a preliminary treatment which oxidizes other elements to their highest oxidation state. The method is based on oxidizing with permanganate [which is reduced to manganese(III)] in condensed phosphoric acid medium, and measuring the excess of permanganate, at 525 nm.

This method of oxidation was originally developed by Lingane and Karplus[4] for titration of manganese(II).

EXPERIMENTAL

Reagents

Potassium permanganate. A $0.01M$ solution is prepared and diluted to $0.004M$.

Manganese(II) sulphate. A $0.01M$ solution is prepared and standardized,[4] then diluted to $2.50 \times 10^{-4}M$.

Selenium(IV). A $0.01M$ solution is prepared from sodium selenite and standardized,[5] then suitably diluted.

Cerium(III). An approximately $0.05M$ solution is prepared by reducing cerium(IV) sulphate with the required quantity of oxalic acid. The solution is boiled thoroughly, and filtered if necessary. The solution is standardized by the persulphate method,[6] and then suitably diluted.

Tellurium(IV). A $0.01M$ solution is prepared from potassium tellurite and standardized,[7] then suitably diluted.

Condensed phosphoric acid. Orthophosphoric acid (100 ml) is heated in a 250-ml beaker with 3–4 ml of nitric acid (1 + 1) until fumes of nitrogen dioxide are no longer evolved. The acid is stored in a brown bottle.

Preliminary work

It is best to measure the permanganate at ~525 nm. A green filter with maximum transmission at 530 nm can be used.

The rate of oxidation was found to be dependent on the permanganate concentration. When aliquots of standard test solution were treated in 50-ml standard flasks with 1–8 ml of condensed

---

* Present address: Airborne Mineral Surveys and Exploration, Central Laboratories, N.M.D.C. Buildings, Faridabad (Haryana State), India.

phosphoric acid, then diluted to about 30 ml with conductivity water, cooled, treated with different volumes of permanganate and diluted to the mark, the absorbance at 525 nm became constant after 3 min if the permanganate was present in 50% excess or more.

Determination of manganese

Two procedures are proposed for the determination of manganese; in one a calibration curve is used, and in the other it is determined directly. By the second procedure, traces (about 2 μg) of manganese can be determined within 10 min. An exactly known strength of permanganate solution is necessary for the second procedure.

Procedure A. About 2–20 ml of test solution containing from 0·02 to 0·4 mg of manganese are taken in a 50-ml volumetric flask and treated with 2–8 ml of condensed phosphoric acid. The mixture is diluted to approximately 35 ml with water and allowed to cool to room temperature. Exactly 5·00 ml of permanganate solution are then added and the solution is made up to the mark. The reagents must be added in the order given. The absorbance is then measured (green filter or 525 nm) against water or a solution containing the phosphoric acid at the same concentration. A calibration curve is prepared. Since manganese(III) obeys Beer's law at the wavelength used, it does not affect the calibration apart from its effect on the slope.

Procedure B. Three different-sized aliquots of sample solution are taken in 50-ml volumetric flasks, treated with 2–8 ml of condensed phosphoric acid and diluted to about 40 ml with water. An accurately measured volume of permanganate (10 ml of 0·004M will usually do) is added to each flask (the same volume to each). (The normality of the permanganate must be known.) Then the three solutions are made up to the mark and their absorbances measured at 525 nm after 2 min. A graph is drawn of sample volume *vs.* absorbance and is extrapolated to the abscissa. The intercept corresponds to the volume of sample containing manganese(II) equivalent to the permanganate added, in the reduction of manganese(VII) to manganese(III). The concentration of manganese(II) can easily be calculated by simple proportion.

$$N_{Mn(II)} = \frac{N_{Mn(VII)} \times V_{Mn(VII)}}{V_{sample}},$$

where V stands for volume (ml) and N for normality. The permanganate normality is calculated on the basis of a 5-electron reduction, in order to compensate for 1/5 of the manganese(III) being derived from reduction of the permanganate. The error of the method is $\pm 0\cdot 8\%$ by procedure A and $\pm 0\cdot 3\%$ by procedure B.

Determination of selenium

Procedure A for the determination of selenium is similar to the one given for manganese.

Procedure B. Take three different volumes of sample in 25-ml volumetric flasks and add an excess of permanganate of known strength as for manganese, and measure the absorbances. In another 25-ml flask add an excess of sample to the amount of permanganate used for the other tests, in order to reduce all the manganese(VII) to manganese(III). Dilute to the mark and measure the absorbance. Plot the absorbance of the first solutions *vs.* volume of sample and read off the volume of sample corresponding to the absorbance of the manganese(III) only. Calculate the result by simple proportion as before except that the permanganate normality is calculated for a 4-electron reduction.

The error is $\pm 0\cdot 7\%$ for method A and $\pm 0\cdot 4\%$ for method B.

Determination of cerium and tellurium

Procedure A can be applied for the determination of cerium or tellurium; procedure B (for selenium) is applicable to cerium but not to tellurium.

Interferences

Copper(II), cobalt(II), nickel(II), chromium(III), iron(III), vanadium(V), tungsten(VI), uranium-(VI), arsenic(V), antimony(V) and molybdenum(VI) do not interfere provided the test solution is used instead of water as a blank. Magnesium, aluminium and calcium also do not interfere.

Applications

To test the reliability of the method under practical conditions, and compare its performance with other methods, a variety of samples was analysed.

In general, a suitable weight of sample was decomposed with an appropriate acid in a 500-ml Pyrex beaker covered with a watch-glass, and after dilution and thorough boiling to remove gaseous

reaction products, the resulting solutions were cooled and made up to volume in volumetric flasks. Whenever nitric acid was used to dissolve the samples, 1 g of urea was added before final dilution to volume, to ensure complete absence of oxides of nitrogen. (Separate experiments were made to confirm that permanganate has no action on urea under the experimental conditions.) Aliquots (5, 10, 15 and 20 ml) of these solutions were taken in 50-ml volumetric flasks and diluted to nearly 40 ml with conductivity water. Then 2–8 ml of condensed phosphoric acid were added and the samples were oxidized with a known excessive volume of permanganate of known concentration. The solutions were made up to the mark and the absorbance measured at 530 nm (green filter) against the sample solutions similarly treated but without addition of permanganate. Procedures A and B were applied for the determination of manganese and selenium, but only procedure A for cerium and tellurium. Results are presented in Tables I–III.

Manganese rail steel, chromium–molybdenum steel, chromium–vanadium steel, chromium–nickel steel, nickel–molybdenum–vanadium steel, and copper–nickel–chromium cast iron. Since all these samples contained appreciable amounts of vanadium, an oxidizing attack was used in preparing the solutions to make sure that vanadium would finally be present in the quinquevalent state: 1-g samples were dissolved in 10 ml of nitric acid (1 + 1) and 5 ml of hydrochloric acid. The solutions were then boiled down to a small volume with 20 ml of concentrated nitric acid to reoxidize any vanadium reduced by the hydrochloric acid. The solutions were finally boiled with 5 ml of concentrated sulphuric acid to expel all chloride ion. Before final dilution (to 500 ml), the chloride ion was tested for with silver nitrate.

Cobalt–molybdenum–tungsten steel and molybdenum–tungsten–chromium–vanadium steel. The samples (1 g) were decomposed by boiling with 5 ml of syrupy orthophosphoric acid and 10 ml of sulphuric acid (1 + 1). When the samples were almost completely decomposed, they were boiled with 2 ml of nitric acid and finally diluted to 250 ml.

Copper–manganese, ferrocerium, iron selenide, cerium–uranium–bismuth, uranium–chromium– cerium, tellurium–tin, tellurium–antimony–lead, tellurium–antimony–copper–bismuth alloys and refined selenium powder. Owing to non-availability of samples, synthetic mixtures were prepared by mixing the salts (as oxides and nitrates) in the correct compositions; 1-g samples were decomposed with nitric acid and sulphuric acid. The ions to be determined were added as standard solutions to the solid samples before the decomposition.

Monazite. A 1-g sample was digested in a porcelain evaporating dish with 15 ml of concentrated sulphuric acid on a sand-bath until most of the acid had evaporated. It was then cooled and leached with 1N sulphuric acid, filtered and made up to 500 ml.

*Rocks, minerals and ores.** The following general procedure was used for opening out.

A 2-g sample was fused in a silica crucible with 4–5 g of fusion mixture (potassium and sodium carbonates, 1:1). The cooled fused mass was treated with 20 ml of concentrated hydrochloric acid in a platinum dish and the resulting solution boiled down to a small volume on a water-bath. The process was repeated with another 5 ml of concentrated hydrochloric acid, but this time the solution was evaporated almost to dryness. The mass was then leached with 1M hydrochloric acid and heated strongly with sulphuric acid until fumes of sulphur trioxide were evolved. (Residual chloride was tested for with silver nitrate.) The solution was diluted to 100 ml.

Selenium dioxide, sodium selenite and sodium tellurite. A 0·5-g sample was dissolved in 1N sulphuric acid and diluted to 1 litre.

Rare earth carbonates. A 1–2-g sample was dried at 100° and decomposed with 2M sulphuric acid. The solution was boiled down to small volume, cooled, filtered and finally diluted to 500 ml.

Manganese ore. About 1 g of powdered and dried sample was digested in a platinum dish on a sand-bath with 15 ml of hydrochloride acid. Silica was removed by boiling with 5–6 ml of hydrofluoric acid. Then 10 ml of sulphuric acid (1 + 1) and 5 ml of concentrated nitric acid were added and the solution was evaporated until fumes of sulphur trioxide were evolved. The solution was cooled and diluted to 1 litre.

Ferromanganese, manganese bronze and silico-manganese spring steel. A 1-g sample was dissolved in 25 ml of nitric acid (1 + 1) and 20 ml of sulphuric acid (1 + 1). The ferromanganese sample solution was diluted to 1 litre, the other two to 250 ml.

Minerals. "Minerals" were prepared artificially by mixing the salts (sodium silicate, titanium dioxide, potassium alum, ferric alum, magnesium sulphate and calcium carbonate) in the correct composition, with standard manganous sulphate solutions added before starting the decomposition

---

* An alternative procedure, for the decomposition of rocks, minerals and ores, was also used to avoid the use of hydrochloric acid: 1 g of sample was dissolved in 10 ml of hydrofluoric acid and 2 ml of sulphuric acid. The hydrofluoric acid treatment was repeated 2 or 3 times. The solution was then boiled down to a small volume with 10 ml of sulphuric acid (1 + 1) and 2 ml of nitric acid to expel all hydrogen fluoride and finally diluted to 100 ml.

TABLE I.—STEELS AND ALLOYS

Sample and composition (%)	Found, %
Manganese rail steel Mn 1·38, C 0·617, Si 0·19, P 0·02, S 0·02, Cu 0·12, Ni 0·15, Cr 0·18, V 0·011, Mo 0·005	Mn 1·38, 1·39, 1·38
Chromium–vanadium steel Mn 0·786, V 0·19, Cr 18·49, V 0·049, Co 0·078, Si 0·283, Sn 0·012, Cu 0·168, Mo 0·038, C 0·069, S 0·012, P 0·017	Mn 0·80, 0·79, 0·78
Chromium–nickel steel Mn 0·597, Ni 8·99, Cr 18·49, V 0·049, Co 0·078, Cb 0062, Sn 0·012, Cu 0·168, C 0·069, Si 0·483, S 0·025, P 0·017	Mn 0·60, 0·61, 0·60
Chromium–molybdenum steel Mn 0·458, Cr 5·15, Mo 0·575, Cu 0·076, Ni 0·083, V 0·01, C 0·094, Si 0·383, P 0·017, S 0·01	Mn 0·46, 0·46, 0·46
Cobalt–molybdenum–tungsten steel Mn 0·22, V 2·03, Cr 4·14, CO 2·26, Ni 0·056, W 1·02, Mo 5·52, S 0·01	Mn 0·21, 0·21, 0·22
Molybdenum–tungsten–chromium–vanadium steel* Mn 0·155, V 1·68, Cr 3·34, W 2·56, Mo 4·16, Cu 0·132, P 0·076, Ni 0·102, Si 0·098, C 0·062	Mn 0·16, 0·16, 0·16
Nickel–molybdenum–vanadium steel Mn 0·302, V 1·94, Cr 4·21, Cu 0·023, Ni 1·42, Mo 6·24, C 0·094, P 0·12, Si 0·282, S 0·002	Mn 0·30, 0·30, 0·30
Ferromanganese Mn 80·07, C 6·83, Si 0·89, P 0·29, S 0·01 Fe 10·56	Mn 80·1, 80·1
Copper–nickel–chromium–cast iron Mn 1·01, Cu 6·64, Ni 15·89, Cr 2·17, V 0·009, S 0·072 Ti 0·021, Co 0·08, Si 1·60, C 2·42, P 0·113, As 0·007	Mn 1·00, 1·04, 1·00
Manganese bronze Mn 1·28, Cu 57·40, Zn 37·97, Sn 0·97, Pb 0·27, Fe 0·81, Ni 0·27, Si 0·05	Mn 1·28, 1·27
Copper–manganese alloy* Mn 4·96, Cu 95·76	Mn 4·96, 4·93, 4·96
Cerium–uranium–bismuth alloy* Ce 1·92, U 4·68, Bi 2·16	Ce 1·93, 1·92, 1·95
Uranium–chromium–cerium alloy* Ce 2·63, Cr 12·16, U 1·93	Ce 2·64, 2·63, 2·63
Monazite Ce 24·14	Ce 24·0, 24·1, 24·0
Iron selenide* Se 58·67, Fe 40·49, Te 0·47	Se 58·9, 59·0, 59·0
Tellurium–antimony–copper–bismuth* Te 24·18, Sb 22·42, Cu 6·93, Bi 2·18	Te 24·2, 24·2, 24·1
Ferrocerium alloy* Ce 24·16	Ce 24·2, 24·2
Tellurium–tin alloy* Te 26·92, Sn 32·16	Te 26·9, 26·9

* Artificial mixtures.

process, and brought into solution by the fusion method described. The compositions were taken from the *Rock-forming Minerals*, Vol. I (W. A. Deer, R. A. Howie and J. Zussman).

For the samples given in Tables I–III, the following general method was adopted for detecting and determining other reducing ions such as iron(II), arsenic(III), antimony(III), vanadium(IV) (other than these, no reducing ion will be present, as can be understood from the compositions and the mode of decomposition).

An aliquot of the sample solution was treated with a known excess of cerium(IV) sulphate solution in $1N$ sulphuric acid containing 1–2 drops of 0·01% osmium tetroxide solution and the unreacted cerium(IV) was back-titrated with standard iron(II) solution, with ferroin as indicator. The amount of cerium(IV) actually required (plus 2–4 drops excess) was added to the sample solutions

TABLE II.—ROCKS, MINERALS AND ORES

Sample and composition (as oxides, %)	Manganese found
Standard rock samples (U.S.A.)	
Granite G-2	
Si 69·20, Al 15·42, Fe 2·70, Mg 0·76, Ca 1·98, Na 4·05,	0·041, 0·041
K 4·46, Ti 0·47, P 0·13, Mn 0·04, Cl 0·01, F 0·13, S 0·01	
Granodiorite GSP-1	
Si 67·22, Al 15·35, Fe 4·20, Mg 0·99, Ca 2·07, Na 2·79,	0·050, 0·050
K 5·50, Ti 0·66, P 0·28, Mn 0·05, Cl 0·03, F 0·39, S 0·03	
Andesite AGV-1	
Si 59·00, Al 17·10, Fe 7·45, Mg 1·50, Ca 4·89, Na 4·23	0·10, 0·10
K 2·87, Ti 10·05, P 0·49, Mn 0·10, Cl 0·02, F 0·04	
Periodotite PCC-1	
Si 40·55, Al 0·31, Fe 8·11, Mg 43·35, Ca 0·40, Na 0·00,	0·12, 0·12
K 0·01, Ti 0·01, Mn 0·12, Cr 0·42, Ni 0·30, Ba 0·01	
Dunite DTS-1	
Si 40·55, Al 0·31, Fe 8·60, Mg 49·85, Ca 0·03, Na 0·05,	0·12, 0·12
K 0·01, Mn 0·12, Cr 0·65, Ni 0·30, Ba 0·02	
Basalt BCR-1	
Si 54·10, Al 13·70, Fe 13·21, Mg 3·47, Ca 6·91, Na 3·26,	0·19, 0·19
K 1·69, Ti 2·25, P 0·35, Mn 0·19, Cl 0·01, F 0·05, S 0·04	
Minerals (prepared artificially)	
Almandine garnet	
Si 37·39, Ti 0·16, Al 20·72, Fe 37·23, Mn 0·86, Mg 3·85,	0·86, 0·86
Ca 0·41	
Red garnet	
Si 36·59, Ti 1·68, Al 22·42, Fe 32·20, Mn 1·42, Mg 5·41,	1·42, 1·42
Ca 0·54	
Garnet	
Si 36·96, Al 20·65, Fe 35·15, Mn 2·45, Mg 3·17, Ca 1·85	2·44, 2·43
Pink almandine garnet	
Si 37·23, Al 20·66, Fe 39·16, Mn 7·30, Mg 2·00, Ca 1·31	7·33, 7·31
Almandine-spessartine garnet	
Si 36·38, Ti 0·27, Al 19·42, Fe 23·62, Mn 18·42,	18·4, 18·4
Mg 0·82, Ca 0·56	
Ores	
Manganese ore	
Mn 54·86, Fe 15·93	54·8, 54·8

TABLE III.—OTHER PRODUCTS

Sample and composition (%)	Found by the present method, %
Selenium dioxide, Se 76·86	Se 76·9, 76·9
Sodium selenite, Se 46·65	Se 46·5
Potassium tellurite, Te 43·68	Te 43·7
Laboratory cerium(IV) sulphate solution, Ce(III) 10·14, Ce(IV) 89·73	Ce(III) 10·2, 10·2, 10·2
Cerium(IV) sulphate solution (Commercial) Ce(III) 1·16, Ce(IV) 98·84	Ce(III) 1·17, 1·17, 1·17
Rare earth carbonates Ce(III), 24·35, Ce(IV) 3·73	Ce(III) 24·34
Selenium powder* Se 99·65, Te 0·26, SiO_2, CuO 0·0014, PbO 0·012 Fe_2O_3 0·021, HgO 0·005, Sb_2O_5 0·0033	Se 99·8 99·9, 99·9.

* Artificial mixture.

before the addition of phosphoric acid and permanganate. Since the resulting cerium(III) concentration was known, a correction for it could be applied. When vanadium was present, the unreacted cerium(IV) was titrated with arsenic(III), which has no action on vanadium(V).

Zusammenfassung—Verfahren zur kolorimetrischen Bestimmung von Mikro- und Halbmikromengen Selen, Tellur, Cer und Mangan werden beschrieben. Die Probelösung in 0.35–3M kondensierter Phosphorsäure wird mit einem Überschuß Permanganat oxidiert. Die Farbintensität des nicht verbrauchten Permanganats wird bei 530 nm gemessen.

Résumé—On a décrit des méthodes pour le dosage colorimétrique de micro- et semi- micro-quantités de sélénium, tellurium, cérium et manganése. La solution essai en milieu acide phosphorique condensé 0,35–3M est oxydée avec un excés de permanganate. On mesure l'intensité de coloration du permanganate non réagi à 530 nm.

REFERENCES

1. P. L. Sarma and L. H. Dieter, *Talanta*, 1966, **13**, 347.
2. G. Somidevamma and L. S. Sarma, *ibid.*, 1967, **14**, 861.
3. E. N. Pollock, *ibid.*, 1969, **16**, 1323.
4. J. J. Lingane and R. Karplus, *Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 191.
5. J. D. McCullough, T. W. Campbell and N. J. Krilanovich, *ibid.*, 1946, **18**, 638.
6. H. H. Willard and P. Young, *J. Am. Chem. Soc.*, 1928, **50**, 1379.
7. V. Lenher and H. F. Wakefield, *ibid.*, 1923, **45**, 1423.

SULPHOXIDES AS SOLVATING REAGENTS FOR THE SEPARATION OF METAL IONS*

David C. Kennedy† and J. S. Fritz
Institute for Atomic Research and Department of Chemistry
Iowa State University, Ames, Iowa 50010, U.S.A.

Summary—The solvent extraction properties of the following sulphoxides have been evaluated: di-n-octyl sulphoxide (DOSO), bis(n-octylsulphinyl)methane (BOSM), bis(n-octylsulphinyl)ethane (BOSE) and *p*-tolyl sulphoxide (PTSO). By use of reversed-phase paper chromatography as a qualitative surveying technique, the interactions of these sulphoxides with some fifty metal ions were investigated in several acid–ligand systems. All sulphoxides were studied in 1–10M hydrochloric and nitric acids; DOSO and BOSM were also studied in perchloric acid and ammonium thiocyanate–perchloric acid mixtures. Observations are made concerning sulphoxide–metal interactions and the existence of several useful analytical separation systems is pointed out. The synthesis and characterization of BOSM and BOSE are described.

ORGANIC sulphoxides contain the semi-polar sulphur-oxygen grouping $>S \rightarrow O$, which is very effective in solvating metal ions and metal–ligand complexes. This ability is amply demonstrated by the simplest sulphoxide, dimethyl sulphoxide, which forms a large number of metal complexes. The higher molecular-weight sulphoxides, unlike the analogous organophosphorus compounds, have received scant attention as reagents for separations. The small amount of work that has been reported, however, has verified that such sulphoxides are excellent reagents for solvent extraction of metal ions in solution. The extraction of uranium from nitric and hydrochloric acids has been studied.[1-3] Other investigations have been concerned with the extraction of thorium,[4,5] gold,[6] zirconium,[7] mineral acids[8,9] and with fundamental studies on the nature of sulphoxide–metal interactions.[3,8] Symmetrical alkyl sulphoxides have mainly been used, but there has been mention of methyl alkyl sulphoxides.[10,11]

The purpose of the present work is to survey the analytical possibilities of separations with higher molecular-weight sulphoxides, by using paper chromatography. Paper is impregnated with an appropriate sulphoxide, and approximately 50 different metal ions are studied, aqueous solutions of different acids at varying concentrations being used as eluents. Complexation by the sulphoxide (or solvation of a metal–ligand complex by the sulphoxide) is indicated when the R_f value is significantly lower than that on unimpregnated paper. For conditions where complexation is indicated, it is expected that a metal ion will be extracted from aqueous solution into an organic solvent containing a dissolved sulphoxide. Obviously, chromatographic experiments on paper impregnated with a solid sulphoxide do not exactly duplicate the situation existing in solvent extraction, where the sulphoxide is dissolved in an organic solvent. At high acid concentrations, for example, some solid complexes might exhibit some

---

† Present address: Research Laboratories, Rohm and Haas Company, Philadelphia, Pennsylvania.

solubility in the eluent, and this could be mistaken for decreased complex stability. Nevertheless, for all systems where solvent extraction was investigated extraction of metal ions does occur in approximately the same concentration range of acid ligand that gives low R_f values in paper chromatography. Paper chromatography has the advantage of permitting far more rapid survey of variables such as metal ion, acidic ligand, and acid ligand concentration, than would be feasible with solvent extraction.

EXPERIMENTAL

Apparatus

Pyrex jars, 0·3 m high, and 0·4-m diameter plate-glass covers were used for chromatographic tanks. Rectangular frames 0·23 m wide and 0·28 m high, constructed of 6-mm glass rod, were used to support the chromatographic paper.

Reagents

Di-n-octyl sulphoxide (DOSO). Prepared by oxidizing di-n-octyl sulphide at room temperature with hydrogen peroxide added slowly as a dilute solution in glacial acetic acid. After the 2-hr reaction period, a large amount of water was added and the solid sulphoxide was filtered off, washed with water, air-dried, and recrystallized from 95% ethanol. The m.p. (71·5–72·5°) and the infrared spectra ($\nu_{S-O} = 1049$ cm^{-1}) correspond to those reported in the literature.[7]

p-*Tolyl sulphoxide (PTSO)*. Commercial material used without further purification; m.p. 93–95°.

Bis(n-octylsulphinyl)methane (BOSM). The corresponding sulphide was first prepared by refluxing octyl mercaptan with an excess of di-iodomethane in the presence of ethanolic potassium hydroxide. The product was purified by extracting several times first with aqueous ethanol and then with water. After drying over anhydrous sodium sulphate, the sulphide, in glacial acetic acid, was oxidized with a slight excess of a dilute solution of hydrogen peroxide in glacial acetic acid, added slowly; the mixture was allowed to react at room temperature overnight. A large amount of water was added to precipitate the sulphoxide, which was then filtered off, washed with water, and air-dried. The crude BOSM was recrystallized several times from ethanol until the sulphone peaks in the infrared spectrum of the compound were reduced to a low, constant level.

The final product, a soft, waxy solid, melted in the range 112–114°. The mass spectra revealed a prominent peak at $m/e = 336$ which corresponds to the molecular weight of the parent ion of the bis-sulphoxide. A peak at $m/e = 338$, 10% of the intensity of the $m/e - 336$ peak, is indicative of the presence of two sulphur atoms in the parent ion. A peak was observed at $m/e = 352$ with 4% of the intensity of the parent ion. This ion, which also appears to contain two sulphur atoms, corresponds to a species containing one sulphoxide group and one sulphone group. A peak was also observed at $m/e = 378$ with an intensity of less than 1% of that of the parent ion. The position of this peak corresponds to the molecular weight of the bis-sulphone.

The infrared spectrum of BOSM in chloroform shows a very intense, broad band centred at 1033 cm^{-1}, indicative of the sulphoxide group. The existence of a small amount of sulphone impurity was indicated by the presence of two weak peaks at 1136 and 1321 cm^{-1}.

The NMR spectrum of BOSM in deuterochloroform displayed a distorted triplet at δ 0·88 and an intense singlet at δ 1·31 which are characteristic of the n-octyl methylene and methyl protons. A triplet observed at δ 2·95 is attributable to the n-octyl methylene protons adjacent to the sulphoxide group. The isolated methylene protons were manifested as a singlet at δ 3·94 and a doublet centered at 3·93 (J = 20 Hz). The singlet is believed to correspond to the *dl* configuration of the bis-sulphoxide whereas the doublet is believed to arise from the non-equivalent methylene protons of the *meso* configuration. The proton integration gives a ratio of 6·0:23·0:3·8:1·9 for $(CH_3)_2$:$[(CH_2)_6]_2$: $(CH_2SO)_2$:$SOCH_2SO$. The ratio of *meso* to *dl* appears to be approximately unity.

Analysis of the compound gave 10·0% oxygen and 17·3% sulphur (theoretical values 9·56% oxygen and 19·17% sulphur). The oxygen:sulphur ratio indicates that the sulphone impurity is considerably higher than that indicated by the mass spectrometry.

Bis(n-octylsulphinyl)ethane (BOSE). The corresponding sulphide was first prepared by refluxing n-octyl bromide with a 10% excess of 1,2-dimercaptoethane in the presence of ethanolic potassium hydroxide. The product was purified by extracting several times with aqueous sodium hydroxide solution followed by extractions with water. The sulphide was dried over anhydrous sodium sulphate and then oxidized with hydrogen peroxide by the procedure described for BOSM. A large amount of water was added to the acetic acid solution and the solid product which formed was filtered off, washed with water and air-dried. The crude bis-sulphoxide was purified by two fractional crystallizations from ethanol. The final product, a white solid in the form of light, platelike crystals, melted in the range 132·5–133·5°.

The mass spectra revealed only a small peak at $m/e = 350$ corresponding to the molecular weight of the parent ion of the bis-sulphoxide. In the fragmentation pattern, however, several strong peaks were observed at m/e values corresponding to logical fragmentation ions of the bis-sulphoxide.

The infrared spectrum of BOSE in chloroform displayed a strong absorption peak centred at 1021 cm^{-1} indicative of the presence of the sulphoxide group. Two weak absorption peaks were observed at 1132 and 1318 cm^{-1} suggesting the presence of a small amount of sulphone impurity.

The NMR spectrum of BOSE in deuterochloroform showed essentially the same pattern for the n-octyl methylene and methyl protons as that described for BOSM. A distorted triplet, centred at δ 2.79 was interpreted as arising from the n-octyl methylene proton adjacent to the sulphoxide group. A complex pattern centred at δ 3.11 was attributed to the isolated methylene groups. This is compatible with the complicated splitting expected from the AA'BB' system present in the expected mixture of diastereoisomers. The proton integration gives a ratio of $3.0{:}12.6{:}2.0{:}1.9$ for CH_3: $(CH_2)_5$:CH_2SO:—CH_2.

Analysis of BOSE gave 18.3% sulphur and 9.9% oxygen (theoretical values of 18.40% sulphur and 9.18% oxygen), indicating some sulphone impurity.

Di-n-octyl sulphone. Di-n-octyl sulphone was oxidized with a large excess of hydrogen peroxide in glacial acetic acid. The product was precipitated by adding water and was filtered off, washed, and air-dried. The infrared spectrum of the compound in chloroform revealed intense sulphone absorption peaks at 1130 and 1318 cm^{-1}. No sulphoxide absorption could be observed. The m.p., 76–$77°$, corresponds to that reported in the literature.[1]

Several metals were chromatographed on paper impregnated with di-n-octyl sulphone to determine whether, as assumed, sulphones posses little co-ordinating ability. The metals studied were chosen on the basis of being the ones most likely to be extracted by a neutral donor from the particular acids used as eluents. Impregnation of the paper with di-n-octyl sulphone had very little effect on the R_f values, indicating that the presence of small amounts of sulphone impurities (such as in BOSE) should not effect the solvent extraction behaviour of sulphoxides other than to act as inert diluents.

Chromatography

For chromatographic work $0.05M$ solutions of the sulphoxides in isopropanol or 80% isopropanol–20% chloroform were used. Metal ions were used as 0.01–$0.05M$ solutions of the perchlorates, where possible, or as the nitrates or chlorides. For studies involving thiocyanate, the eluting solution consisted of ammonium thiocyanate in $1M$ perchloric acid.

Whatman No. 1 chromatographic paper (0.23×0.285 m sheets) was used for all chromatographic work.

Procedure. The chromatographic paper was fastened to the glass frames with either rubber cement or with Teflon clamps. The frames were then dipped in the $0.05M$ solutions of sulphoxide to impregnate the paper with the compound under investigation. The excess of solution was allowed to drain off and the frames were suspended in a fume-chamber to permit all solvent to evaporate. Metals were then applied to the impregnated paper with 2-mm disposable wooden applicator sticks. For most metals, comparison chromatograms were also run on untreated paper.

After elution of the papers with the appropriate acid, they were sprayed with one of two colour-forming reagents to determine the location of the metal ions. Metals of the hydrogen sulphide group were detected by spraying with a 50% solution of ammonium polysulphide in methanol. The remaining metals were detected by spraying with a 0.1% solution of Arsenazo I in 90% methanol–water, followed by exposure to ammonia gas.

R_f values were calculated for the geometrical centre of the spot as the point of reference.

RESULTS

Hydrochloric acid systems

Papers impregnated with various sulphoxides were used to chromatograph 46 different metal ions at hydrochloric acid concentrations ranging from 1 to $10M$. Results are summarized in Figs. 1–4. A low R_f indicates that the metal ion or its chloride complex is complexed by the sulphoxide, which is held stationary by the paper. (A probable exception is barium, which has a low R_f because of the low solubility of barium chloride in concentrated hydrochloric acid).

Comparison of Figs. 1 and 2 shows generally lower R_f values for DOSO than for PTSO, indicating stronger complexation by DOSO. Apparently the electron-withdrawing tendencies of the aromatic rings weaken the polarity of the S—O group, through which co-ordination to the metal atom occurs.

FIG. 1.—The chromatographic behaviour of metal ions on paper impregnated with di-n-octyl sulphoxide, eluted with hydrochloric acid.

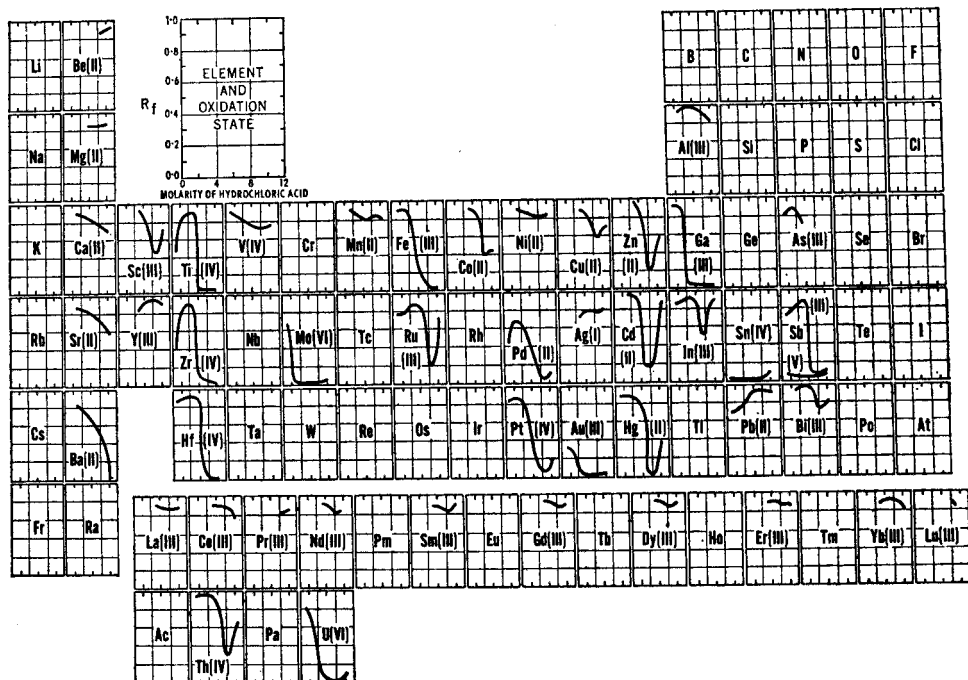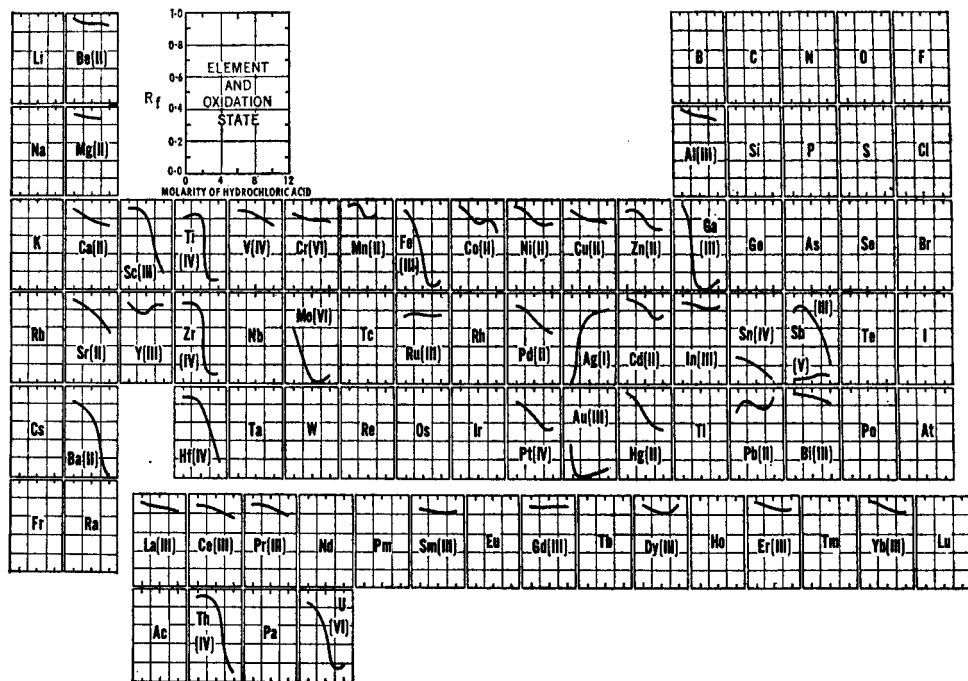FIG. 2.—The chromatographic behaviour of metal ions on paper impregnated with p-tolyl sulphide, eluted with hydrochloric acid.
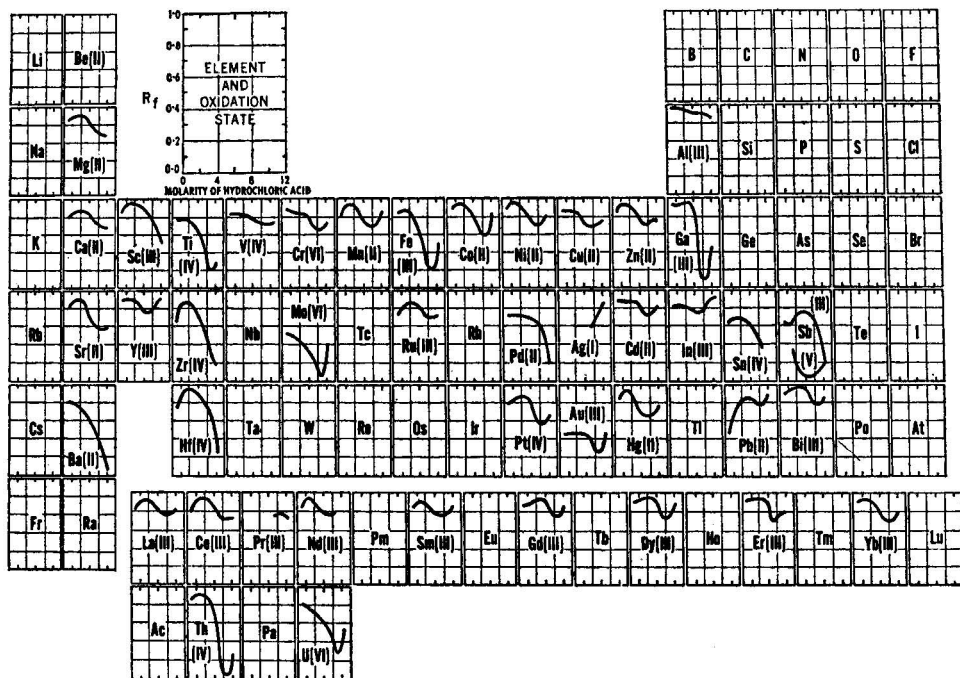
FIG. 3.—The chromatographic behaviour of metal ions on paper impregnated with bis(n-octylsulphinyl)methane, eluted with hydrochloric acid.
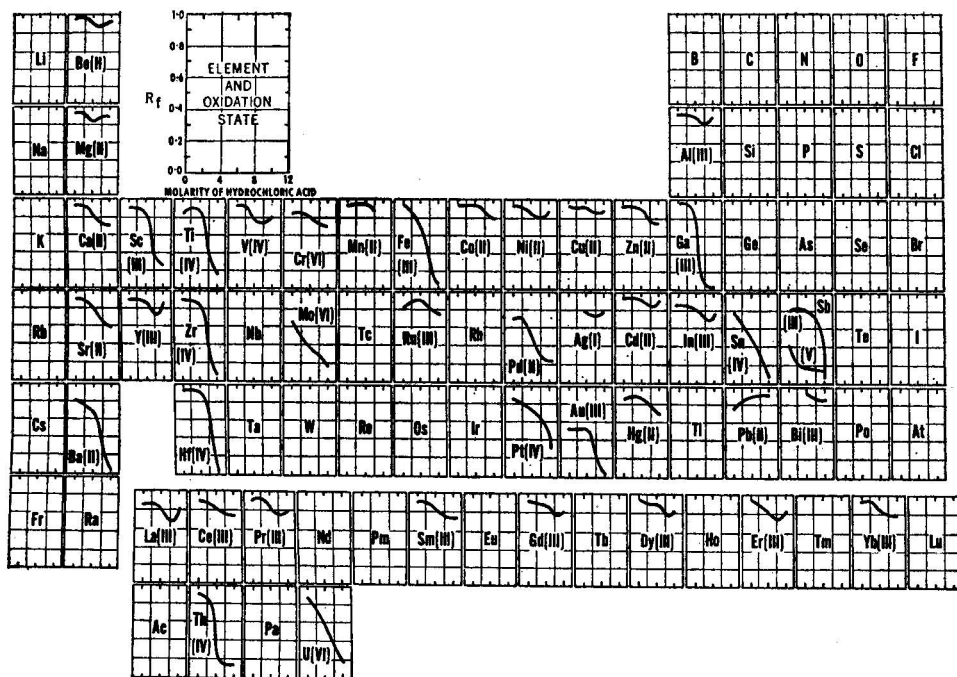

FIG. 4.—The chromatographic behaviour of metal ions on paper impregnated with bis(n-octylsulphinyl)ethane, eluted with hydrochloric acid.

It was thought that both S—O groups in BOSM might co-ordinate with the metal ion, forming a 6-membered ring that would be a stronger complex than would be possible with DOSO. However, the R_t values for both BOSM and BOSE are in general higher than for DOSO at comparable acidities, indicating that chelation probably does not occur. It is possible that steric effects make it impossible for a metal to co-ordinate several chloride ions and at the same time co-ordinate both S—O groups.
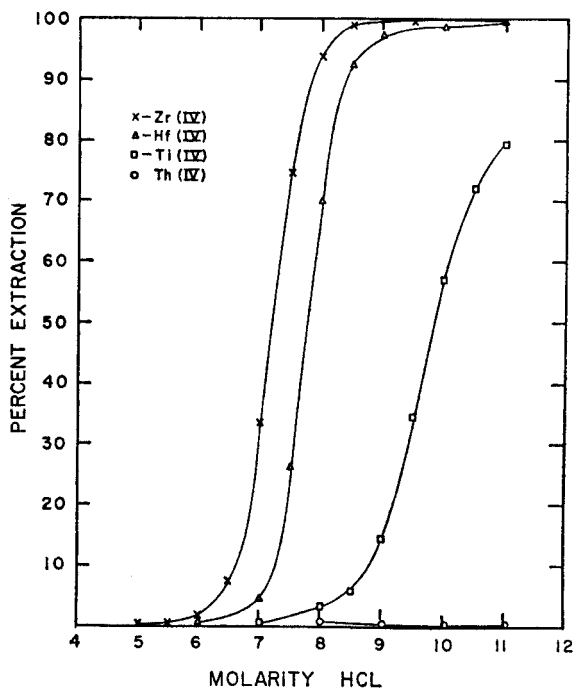

FIG. 5.—The degree of extraction of titanium(IV), zirconium, hafnium, and thorium into 0·1M DOSO in chloroform as a function of hydrochloric acid concentration.

Figures 1–4 and especially Fig. 1 suggest many separation possibilities. For example, the low R_t values for titanium(IV), zirconium and hafnium with 6–11M hydrochloric acid indicate that these elements might be extracted by solutions of DOSO in an organic solvent. Actual curves for extraction of these elements and of thorium by 0·1M DOSO in chloroform confirm this (Fig. 5). The data in this figure indicate that in 8–11M hydrochloric acid zirconium and hafnium can easily be separated from thorium by batch extraction. The intermediate extraction of titanium(IV) will prevent its separation from the other metals by batch extraction. However, it was found that the addition of a drop of 30% hydrogen peroxide to the aqueous phase completely suppresses the extraction of titanium(IV), apparently owing to the formation of a peroxy complex. The extraction of zirconium and hafnium is not affected by the hydrogen peroxide.

Before attempting actual separations it was first determined that zirconium and hafnium could be quantitatively back-extracted by 5M hydrochloric acid. Binary

mixtures of $0.01M$ metal ions in $10.5M$ hydrochloric acid were separated by extraction with $0.1M$ DOSO in chloroform. Hydrogen peroxide was added to prevent extraction of titanium(IV). After back-extraction with $5M$ hydrochloric acid, the metal ions in the original and back-extracted aqueous phases were determined by titration with $0.01M$ EDTA. Table I summarizes the results of these separations.

TABLE I.—LIQUID–LIQUID BATCH EXTRACTION SEPARATIONS

Experiment	Metal	Amount added, mmole	Amount found, mmole	Recovery, %
1	Zr(IV)	0·136	0·136	100·0
	Th(IV)	0·140	0·139	99·4
2	Hf(IV)	0·125	0·123	98·7
	Th(IV)	0·140	0·140	100·0
3	Zr(IV)	0·136	0·137	100·7
	Ti(IV)	0·173	0·165	95·4
4*	Zr(IV)	0·136	0·134	98·6
	Ti(IV)	0·173	0·173	100·0

* Separation performed in $9.5M$ hydrochloric acid.

Figure 1 indicates that in approximately $1M$ hydrochloric acid only tin(IV) and antimony(V) have low R_f values on DOSO-impregnated paper. In $\sim 3M$ hydrochloric acid molybdenum(VI) also has a low R_f. Thus it may be possible to separate these elements from all other elements studied. Still another possibility suggested by Fig. 1 is the separation of gallium from aluminum, indium, iron(III) and other metal ions in 4–$5M$ hydrochloric acid.

Nitric acid systems

Paper impregnated with various sulphoxides was used to chromatograph metal ions in nitric acid solutions ranging from 1 to $11M$. Results are given in Figs. 6–9. Fewer metal ions have low R_f values than in hydrochloric acid, but complex formation by DOSO is indicated for some metal ions including Ti(IV), Zr, Hf, Pd(II), Au(III), Sb(V), Bi, Th and U(VI).

For most metal ions the R_f values indicate weaker complexation for PTSO, BOSM and BOSE than for DOSO. An interesting exception is the behavior of Fe(III) and Ru(III) which are complexed by PTSO, but not by DOSO. This phenomenon has been confirmed by solvent extraction and is being studied further. The rare earths are another exception. Little complexation is indicated for DOSO; there is some complexation for BOSM and rather strong complexation for BOSE in 6–$8M$ nitric acid. Yttrium and scandium are also complexed by BOSE.

When the rare earths were chromatographed on papers containing various loadings of BOSE, a plot of $\log 1/R_f$ vs. log of relative BOSE loading gave a straight line of slope $= 1$, indicating a 1:1 combining ratio of BOSE:rare earth. The plot in Fig. 10 shows that retention of rare earths by BOSE on paper reaches a maximum near the middle of the rare earth series. The decrease in retention in the latter half of the series is surprising because the formation constants of the rare earth–nitrate complexes, which are assumed to be extracted, increase regularly from lanthanum

830 D. C. KENNEDY and J. S. FRITZ

FIG. 6.—The chromatographic behaviour of metal ions on paper impregnated with di-n-octyl sulphoxide, eluted with nitric acid.
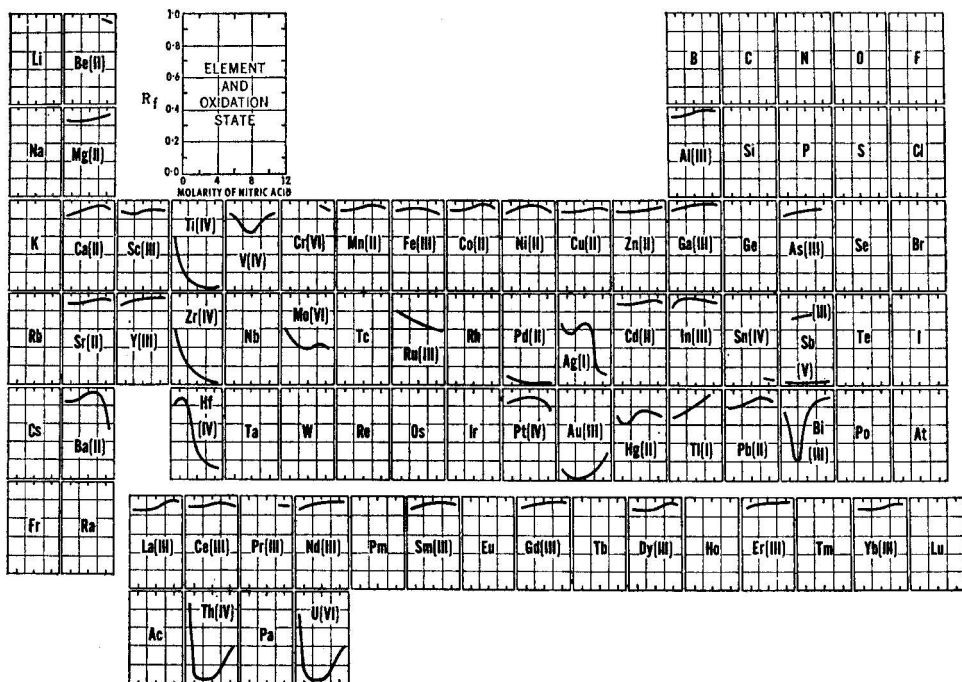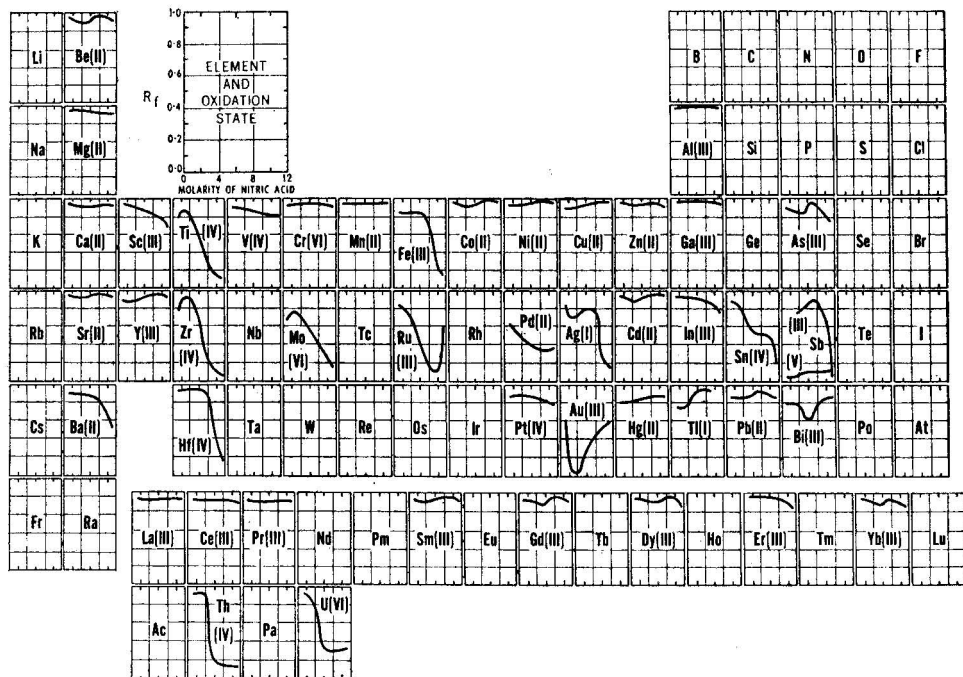

FIG. 7.—The chromatographic behaviour of metal ions on paper impregnated with p-tolyl sulphoxide, eluted with nitric acid.
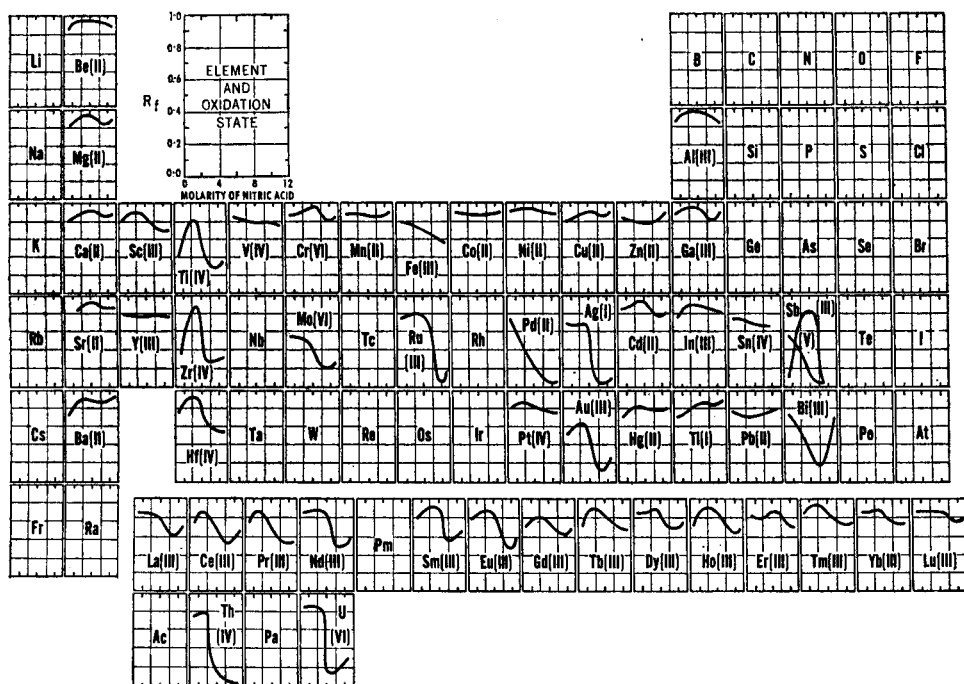
FIG. 8.—The chromatographic behaviour of metal ions on paper impregnated with bis(n-octylsulphinyl)methane, eluted with nitric acid.
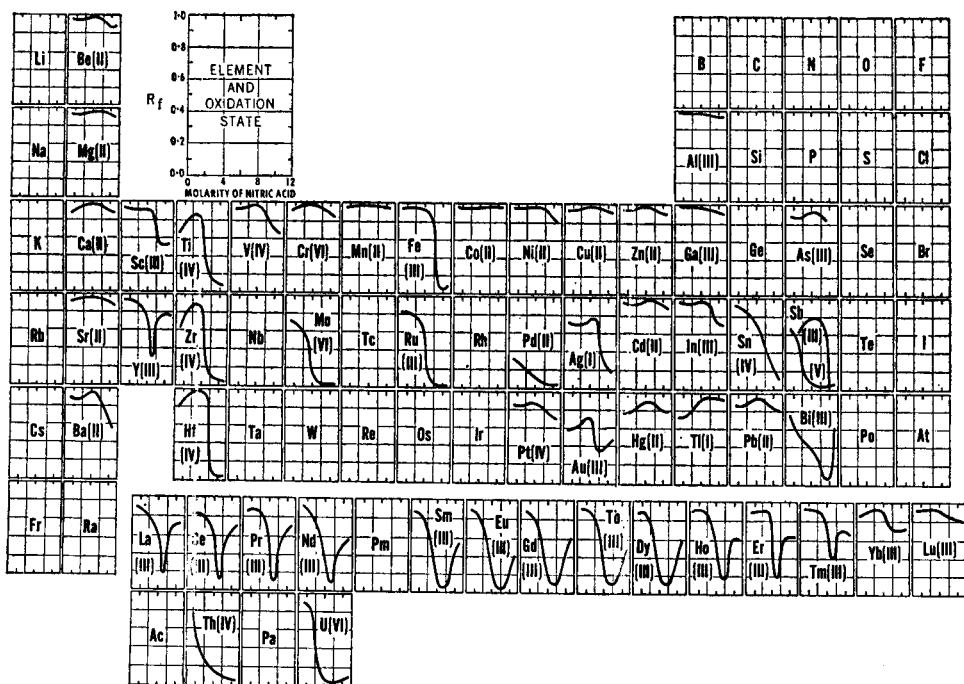

FIG. 9.—The chromatographic behaviour of metal ions on paper impregnated with bis(n-octylsulphinyl)ethane, eluted with nitric acid.
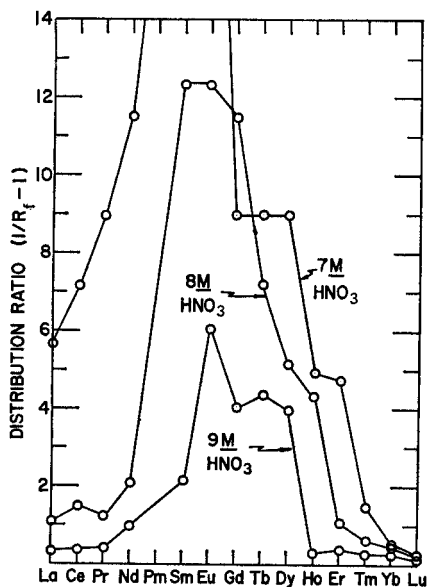
4

FIG. 10.—The chromatographic behaviour of the lanthanides on paper impregnated with
bis(n-octylsulphinyl)ethane, eluted with nitric acid.

to lutetium. Apparently, the steadily decreasing ionic radii of the lanthanides, coupled with the aforementioned steric effects, weaken the co-ordinating ability of the bis-sulphoxides towards the higher rare earths.

Thiocyanate systems

Behaviour of metal ions on paper impregnated with DOSO and BOSM, with aqueous perchloric acid–ammonium thiocyanate solutions, is summarized in Figs. 11 and 12. Again DOSO retains most metal ions more strongly than BOSM. The following metal ions are strongly retained by DOSO on paper over the entire range of thiocyanate concentrations studied: Ti(IV), Zr, Hf, Mo(VI), Sn(IV), Th and U(VI). The behaviour of zinc and cadmium is unusual. The possibility of separating them was confirmed by solvent extraction studies using $0.5M$ DOSO in 1,2-dichloroethane. From $1M$ perchloric acid–$0.5M$ ammonium thiocyanate, zinc was 98.5% extracted while cadmium was only 2.2% extracted.

Perchloric acid systems

Finally, the chromatographic behaviour of metal ions on DOSO-impregnated paper was studied as a function of aqueous perchloric acid concentration (Fig. 13). Very few metal ions show evidence of any co-ordination. The outstanding exception is uranium(VI) which shows quite low R_f values over a broad range of perchloric acid concentrations. More detailed studies on the extraction of uranium will be the subject of a forthcoming paper.

Low R_f values are also observed for Pd(II) and Au(III). For Au(III) this behaviour is probably due to the chloride used to prepare the aqueous solution. In the case of
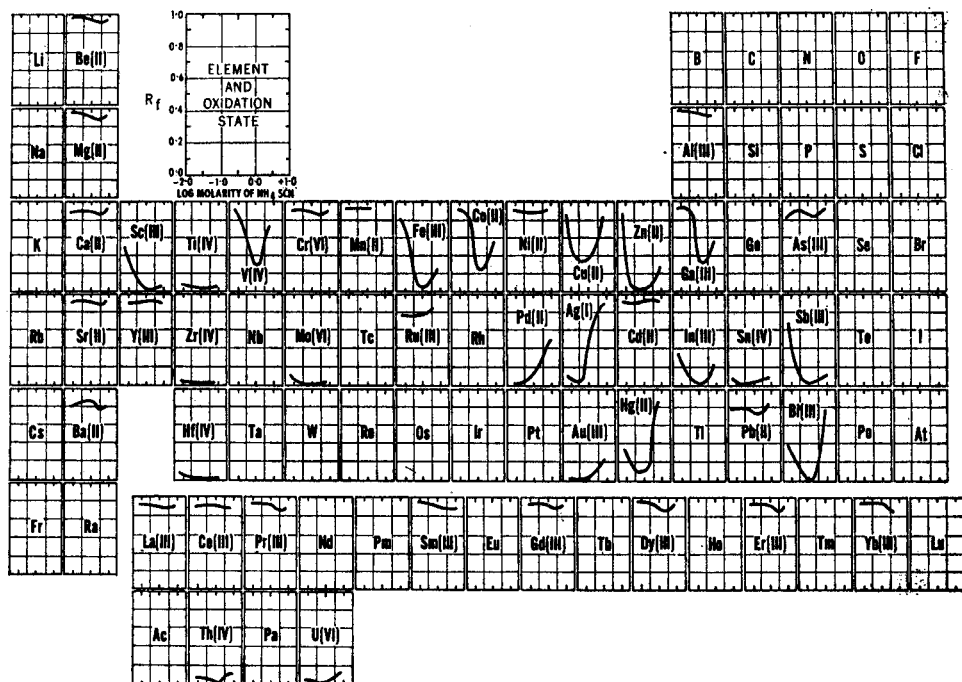
FIG. 11.—The chromatographic behaviour of metal ions on paper impregnated with di-n-octylsulphoxide, eluted with $1M$ $HClO_4$-NH_4SCN.
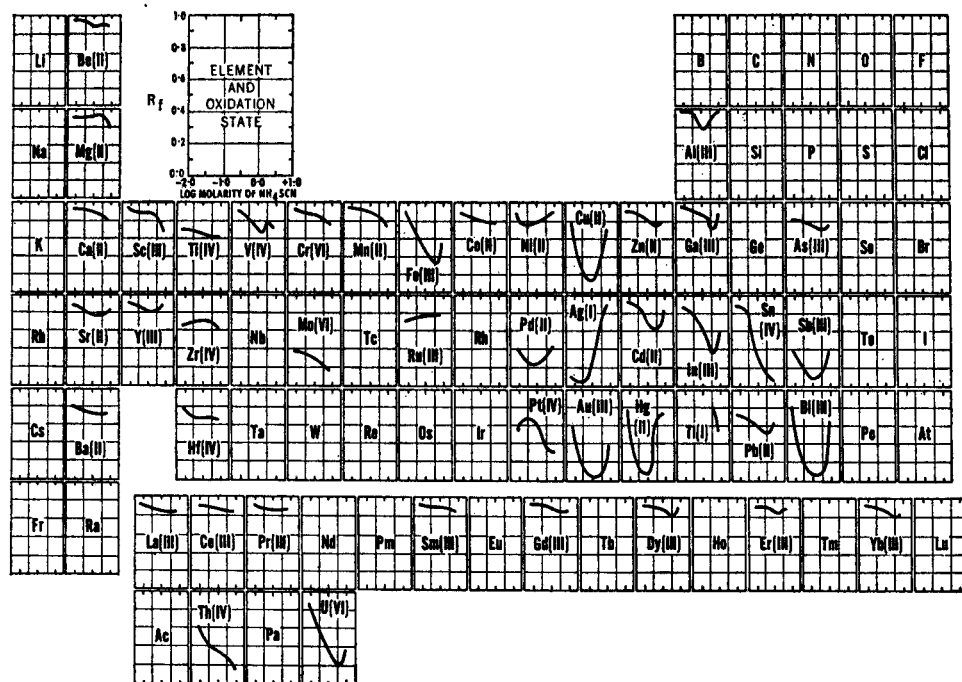
FIG. 12.—The chromatographic behaviour of metal ions on paper impregnated with bis(n-octylsulphinyl)methane, eluted with $1M$ $HClO_4$-NH_4SCN.
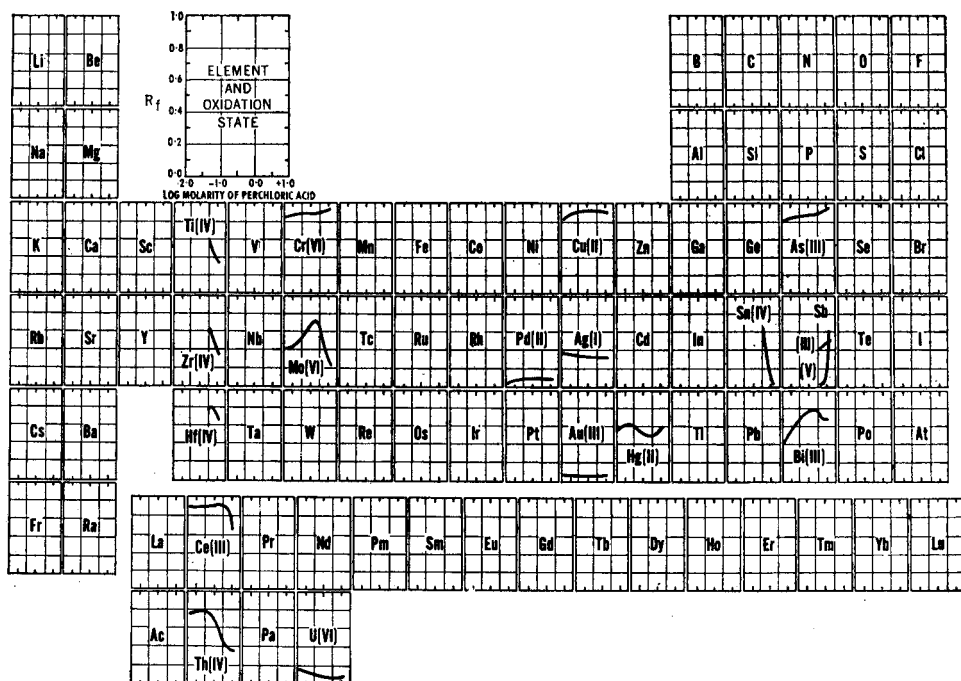
FIG. 13.—The chromatographic behaviour of metals ions on paper impregnated with di-n-octyl sulphoxide, eluted with perchloric acid.

Pd(II), there is a possibility that the low R_f value may be due to Pd ← S co-ordination with DOSO. This type of interaction is well documented for the analogous DMSO complex; $PdCl_2 \cdot 2DMSO$.[12]

Zusammenfassung—Die Extraktionseigenschaften folgender Sulfoxide wurden ermittelt: Di-n-oktylsulfoxid (DOSO), Bis(n-oktyl-sulfinyl)-methan (BOSM), Bis(n-oktylsulfinyl)äthan (BOSE) und p-Tolylsulfoxid (PTSO). Mit Hilfe der Papierchromatographie mit umgekehrten Phasen zur qualitativen Übersicht wurden die Wechselwirkungen dieser Sulfoxide mit etwa 50 Metallionen in mehreren Säure-Ligand-Systemen untersucht. Alle Sulfoxide wurden in 1–10M Salzsäure und Salpetersäure untersucht; DOSO und BOSM auch in Überchlorsäure und Mischungen aus Ammoniumthiocyanat und Überchlorsäure. Es werden Beobachtungen über Wechselwirkungen zwischen Sulfoxid und Metall mitgeteilt und auf verschiedene nützliche Trennsysteme hinge-wiesen. Synthese und Charakterisierung von BOSM und BOSE werden angegeben.

Résumé—On a évalué les propriétés de solvant d'extraction des sulfoxydes suivants: di-n-octyl sulfoxyde (DOSO), bis(n-octylsulfinyl) méthane (BOSM), bis(n-octylsulfinyl)éthane (BOSE) et p-tolyl sulfoxyde (PTSO). Par l'emploi de la chromatographie sur papier à phases inversées comme technique qualitative d'étude, on a étudié les inter-actions de ces sulfoxydes avec quelques cinquante ions métalliques dans plusieurs systèmes acide-ligand. Tous les sulfoxydes ont été étudiés en acides chlorhydrique et nitrique 1–10M; DOSO et BOSM ont aussi été étudiés en acide perchlorique et dans des mélanges

thiocyanate d'ammonium acide perchlorique. On effectue des observations concernant les interactions sulfoxyde métal et l'on fait ressortir l'existence de plusieurs systèmes de séparation analytique utiles On décrit la synthèse et la caractérisation de BOSM et BOSE.

REFERENCES

1. C. B. Herrin, *M.S. Thesis*, University of Oklahoma, Norman, Oklahoma, 1960.
2. W. Korpak, *Nukleonika*, 1964, **9**, 1.
3. V. G. Torgov, A. V. Nikolaev, V. A. Mikhailov, L. G. Stadnikova and I. L. Kotlyarevskii, *Zh. Neorgan. Khim.*, 1968, **13**, 228.
4. P. K. Gaur and S. R. Mohanty, *Naturwissenschaften*, 1963, **50**, 614.
5. P. E. Gaur, S. R. Mohanty and A. S. Reddy, *Proc. Nucl. Radiat. Chem. Symp.*, *Waltair, India*, 1966, pp. 56–64.
6. J. R. Webb, *M.S. Thesis*, University of Oklahoma, Norman, Oklahoma, 1964.
7. S. R. Mohanty and P. Nalini, *Curr. Sci. Calcutta*, 1967, **36**, 175.
8. W. Korpak, *Nukleonika*, 1962, **7**, 715.
9. *Idem, ibid.*, 1963, **8**, 747.
10. *Ibid., U.S. At. Energy Comm. Rept.*, **ORNL–3945**, p. 177 (1966).
11. *Ibid., ibid.*, **ORNL–4145**, p. 211 (1967).
12. R. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, 1960, **82**, 2986.

EXTRACTION CHROMATOGRAPHY OF URANIUM WITH DIOCTYL SULPHOXIDE*

James S. Fritz and David C. Kennedy†

Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.

Summary—Uranium(VI) is quantitatively extracted from aqueous perchlorate media into dioctyl sulphoxide in 1,2-dichloroethane. The extracted species contains four sulphoxides for each uranium. Most other metal ions are not appreciably extracted. On columns containing a solid support impregnated with dioctyl sulphoxide in 1,2-dichloroethane, uranium(VI) may be separated quantitatively from metal ions such as thorium(IV), zirconium(IV) and rare earths(III).

In a recent report[1] the evaluation of sulphoxides as solvent extraction reagents was described; reversed-phase paper chromatography was used as a qualitative technique to investigate the interaction of several sulphoxides with a large number of metals in several acid systems. It was observed that uranium(VI) was strongly retained on paper impregnated with di-n-octyl sulphoxide (DOSO) and eluted with perchloric acid. The weak extraction of the 50 other metals studied [except of gold(III) and palladium(II)] indicated that a nearly specific analytical separation of uranium(VI) might be possible in this system. It was decided, therefore, to study the extraction of uranium(VI) and other metals from perchloric acid solutions into DOSO dissolved in an organic diluent. From the results of this study, it was hoped that an extraction system could be developed which would permit the analytical separation of uranium from most other metals.

EXPERIMENTAL

Reagents

Dioctyl sulphoxide (DOSO) was prepared as described earlier.[1]

Chromatographic column

The support used was XAD-2, a macroreticular polystyrene resin obtained from Rohm and Haas. It was ground and sieved to 60–80 mesh. Conventional glass chromatographic columns were filled with XAD-2 slurry in methanol. When the methanol level had dropped just to the top of the resin bed, 0·5M DOSO in 1,2-dichloroethane was passed slowly through the column and sorbed by the XAD-2 support. The interstitial DOSO solution was then displaced by aqueous 0·9M lithium perchlorate–0·1M perchloric acid.

Column separations

Samples added to the column contained approximately the same concentrations of perchlorate as the eluents. Eluents were pre-equilibrated with the organic phase. Flow-rates varied from 1 to 3 ml/min.

Analytical methods

Metal ions were determined by standard analytical procedures, mostly involving titration with EDTA. Uranium was determined spectrophotometrically with Arsenazo I.[2]

FUNDAMENTAL STUDIES

First a number of organic solvents were evaluated as diluents for DOSO; $0.01M$ solutions of uranium(VI) in $1M$ perchloric acid were extracted with $0.1M$ DOSO in various diluents. The results of these extractions are summarized in Table I.

TABLE I.—EXTRACTION OF U(VI) FROM $1M$ HClO$_4$ INTO $0.2M$ DOSO (IN ORGANIC SOLVENT)

2-Phase Systems		3-Phase Systems	
Diluent	Extraction, %	Diluent	Extraction, %
Chlorobenzene	50	Butyl acetate	70
Chloroform	50	Diethyl ether	88
n-Octanol	50	Benzene	95
n-Butanol	55	Toluene	95
IBMK	65	Carbon tetrachloride	97
n-Butyronitrile	70	Xylene	99
2-Octanone	75	Cyclohexane	99·5
1,2-Dichloroethane	75	Methyl laurate	99·8
Tributyl phosphate	89		
Nitrobenzene	95		

The diluents in Table I are divided into two categories; two-phase systems and three-phase systems. In the three-phase systems, a viscous yellow liquid or flaky yellow solid (which apparently contained all the uranium) was formed between the aqueous phase and the diluent phase. Although the three-phase systems are characterized by generally high extraction, they were considered to be unsuitable analytically. Of the two-phase systems, n-butyronitrile and 1,2-dichloroethane behaved well, and the latter was selected as the most satisfactory. Tributyl phosphate was not studied further because of its limited ability to dissolve DOSO.

The effect of the concentration of DOSO on the extraction of uranium(VI) was the subject of the next experiment; $0.01M$ solutions of uranium(VI) in $1M$ perchloric acid were extracted with 0.1–$0.5M$ DOSO in 1,2-dichloroethane. The results of this study gave a linear log–log plot of distribution coefficient vs. DOSO concentration, with a slope of 3.97, confirming that the combining ratio of DOSO with uranium(VI) in perchlorate media is 4:1, indicating the formation of the species $UO_2(DOSO)_4^{2+}$ in which DOSO ligands have completely filled the inner co-ordination sphere of the uranyl ion. A practical consequence of the composition of the complex is that the distribution coefficient is a function of the fourth power of the DOSO concentration. Thus if the latter is changed from 0.1 to $0.5M$, the distribution ratio increases nearly 500-fold. The concentration of DOSO was fixed at $0.5M$ for further extraction studies.

A few brief experiments were performed to determine how the uranium(VI), once extracted, could best be recovered from the organic phase. Back-extraction with dilute sulphuric acid was found to be best. It was found that uranium(VI) which had been extracted into $0.5M$ DOSO in 1,2-dichloroethane could be quantitatively recovered by back-extracting three times with $0.1M$ sulphuric acid or twice with $1M$ acid.

The effect of perchlorate concentration on the extraction of uranium(VI) was next studied. The perchloric acid solutions used ranged in concentration from 0.05 to $6.0M$. The lithium perchlorate solutions used were $0.025M$ in perchloric acid and varied in perchlorate concentration from 0.05 to $4.22M$, the concentration of a
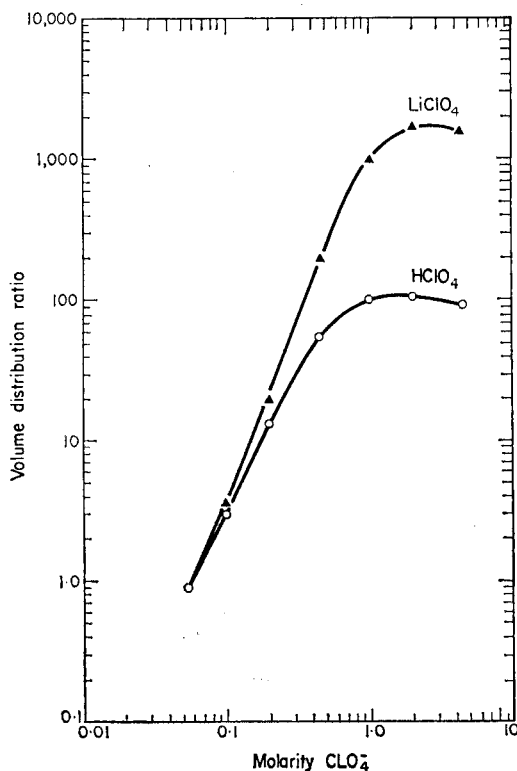
FIG. 1.—The distribution ratio of uranium(VI) extracted into $0.5M$ DOSO in 1,2-dichloroethane as a function of the concentration of perchloric acid or lithium perchlorate in the aqueous phase.

saturated solution of lithium perchlorate at 27°. The results of this study are presented in Fig. 1.

The distribution ratios for the perchloric acid solutions, after an initially linear increase reach a limiting value of 100 for 1–2M acid and then decrease slightly. This behaviour at high perchloric acid concentrations is probably due to competitive extraction of the acid by DOSO. The linear portion of the curve has a slope of 2·0, confirming that the formula of the extractable complex is $\{[UO_2(DOSO)_4^{2+}][ClO_4^-]_2\}$.

The curve for the extraction of uranium(VI) from lithium perchlorate at constant hydrogen ion concentration has a longer linear portion than the perchloric acid curve and also a higher slope, 2·6. This curve also deviates from linearity and decreases at higher concentrations of perchlorate, possibly owing to partitioning of lithium perchlorate. At all concentrations above 1M lithium perchlorate, however, the distribution ratio is greater than 1000, the magnitude necessary for quantitative (99·9%) extraction of uranium(VI).

A series of extractions was next performed to determine the effect of hydrogen ion concentration on the extraction of uranium(VI) from 1M perchlorate solutions. The solutions [0·01M in uranium(VI)] contained lithium perchlorate and perchloric acid. The pH of each was measured before extraction. A plot of distribution ratio as a function of pH is presented in Fig. 2.
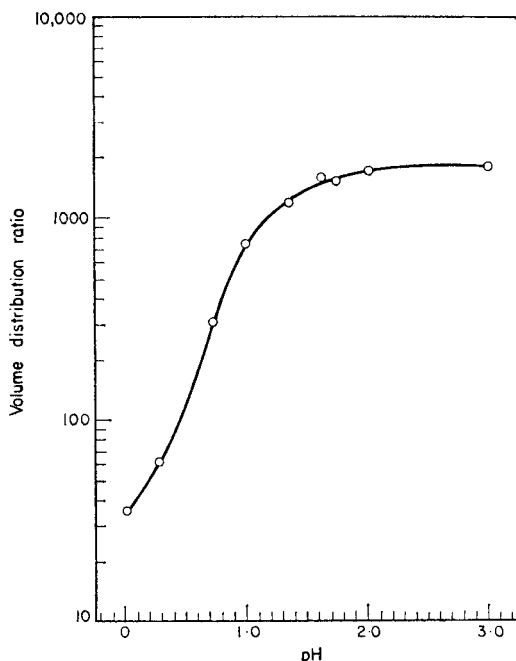
FIG. 2.—The distribution ratio of uranium(VI) extracted into 0·5M DOSO in 1,2-dichloroethane from 1·0M aqueous perchlorate mixtures, as a function of the pH of the aqueous phase.

The distribution ratios for the extraction of uranium(VI) from 1M perchlorate approach a limiting value of about 1900 with decreasing hydrogen ion concentration. The decrease in extraction at low pH is again apparently the result of competitive extraction of perchloric acid. These data show that a quantitative extraction of uranium(VI) is possible from 1M perchlorate solutions at pH 1 or higher. On this basis, it was decided to limit further extraction studies to a 1M lithium perchlorate medium that was 0·025M in perchloric acid (pH 1·65).

A study was next made of the extraction of other metals (0·01M solutions) under the conditions established for quantitative extraction of uranium(VI). The metal perchlorates were used when possible. Nitrates or chlorides were used only when it was known that the metals would not form complexes with these anions. For other metals, such as iron(III), palladium(II), gallium(III), where strong complexation by the chloride ion was expected, the chlorides were fumed to near dryness with concentrated perchloric acid and taken up in a solution of 1M lithium perchlorate. An exception to this procedure was tin(IV); a considerable amount of hydrochloric acid was required to keep it in solution.

The metal solutions were extracted for 5 min with 0·5M DOSO in 1,2-dichloroethane and the extent of extraction was quantitatively determined. Table II lists the metals studied, in order of decreasing extraction. An examination of the data in Table II reveals very few metals, in addition to uranium(VI), which are strongly extracted. Palladium(II) and gold(III) are two notable exceptions. These two metals are also strongly extracted by DOSO on paper.[1] The behaviour of palladium(II) and gold(III) is an indication of strong sulphur-metal interaction in their complexes.

TABLE II.—THE EXTRACTION OF METALS FROM 1·0M LITHIUM PERCHLORATE–0·025M PERCHLORIC ACID INTO 0·5M DOSO IN 1,2-DICHLOROETHANE

Metal	Extraction, %	Volume distribution ratio	Metal	Extraction, %	Volume distribution ratio
Pd(II)*	~100·0	>5 × 10^5	Ti(IV)	2·9	0·030
U(VI)	99·9	1·63 × 10^3	Lu(III)	2·0	0·020
Au(III)	98·7	75·9	Al(III)	0·61	0·006
Hg(II)	94·4	16·9	Cd(II)	0·55	0·0056
Ce(IV)†	72·5	2·63	Hf(IV)	0·39	0·0039
Sc(III)	42·7	0·744	Cs(I)	0·28	0·0028
Sn(IV)§	31·7	0·464	As(III)	0·24	0·0024
Ag(I)	28·9	0·406	Cr(III)	0·19	0·0019
V(IV)	15·6	0·185	Zn(II)	0·13	0·0013
Fe(III)‡	12·7	0·145	Ce(III)	0·12	0·0012
Pb(II)	9·9	0·110	Zr(IV), Ba(II)		
Mo(VI)	9·3	0·103	Co(II), Sr(II)		
Th(IV)	8·0	0·087	Cu(II), Ni(II)	<0·10	<0·0010
In(III)	5·7	0·060	Mn(II), Gd(III)		
Ga(III)	5·7	0·059	Y(III), Pt(IV)		
Bi(III)	5·5	0·058	Ru(III)		

* In the presence of 0·1M HCl kinetics are slow and $D_v = 530$.
† Reduced slowly to Ce(III).
§ Hydrochloric acid required to keep Sn(IV) in solution.
‡ In the presence of 0·1M HCl extraction = 35·6%.

The decrease in the rate and magnitude of extraction of palladium(II) in the presence of dilute hydrochloric acid (footnote 1) shows that DOSO must compete with chloride ions for co-ordination sites to form the extractable complex. This indicates that the composition of this complex is probably similar to that of uranium(VI), i.e., [Pd(DOSO)$_4^{2+}$][ClO$_4^-$]$_2$.

It should be pointed out that the strong extraction of uranium(VI) from perchlorate solution is not a phenomenon unique to this system. The important step is the formation of the cation UO$_2$(DOSO)$_4^{2+}$. Once this is accomplished, an anion is needed merely to give charge equivalence and yield an ion-pair that is readily solvated in the organic phase. The perchlorate ion is a fairly good counter-ion, but other anions could serve the purpose equally well or better. It might be expected that an organic anion, such as an aromatic sulphonate, would be a better counter-ion than perchlorate. This was demonstrated for the case of 2-naphthalene sulphonic acid. Qualitative experiments showed that the extraction by DOSO of uranium(VI) in the presence of this anion was nearly quantitative. Gillette[3] studied the extraction of a number of aromatic sulphonic acids by an analogous organic cation, tricaprylammonium chloride.

Separations

Examination of the data in Table II reveals the potential for separating uranium(VI) from a large number of other metal ions. Simple solvent extraction should separate uranium(VI) quantitatively from the last dozen or so metal ions listed in Table II. However, if a column packed with a solid support impregnated with DOSO in 1,2-dichloroethane is used, uranium(VI) should be retained quantitatively from an aqueous perchlorate solution while all other metals listed [except palladium(II), gold(III) and probably mercury(II)] should pass through the column.

The sorption (and subsequent elution) of uranium on a 90×20 mm column containing $0.5M$ DOSO (in 1,2-dichloroethane) on 60–80 mesh XAD-2 was first studied. When 0·05 mmole of uranium(VI) was sorbed on the column, no metal could be detected in the effluent during elution with 250 ml of $1M$ perchloric acid. Elution with 100 ml of $1M$ sulphuric acid gave 99·8% recovery of the added uranium. Similarly, 1·87 μmole (0·445 mg) of uranium(VI) sorbed on a 100×6 mm column were not eluted with 60 ml of $1M$ perchloric acid, but elution with 10 ml of $1M$ sulphuric acid gave 100·5% recovery of the added uranium. The uranium may also be desorbed by elution with 10 ml of methanol.

TABLE III.—SEPARATION OF URANIUM(VI) FROM THORIUM(IV) AND ZIRCONIUM(IV)

Metal	Added, *mmole*	Found, *mmole*	Recovery, %
U(VI)	0·0510	0·0508	99·5
Th(IV)	0·234	0·233	99·8
U(VI)	0·0510	0·0510	100·8
Zr(IV)	0·266	0·265	99·6

Two experiments were performed in which moderate amounts of uranium(VI) were separated from thorium and zirconium. Mixtures containing 0·05 mmole of uranium(VI) and 0·25 mmole of the other metal in $1M$ perchloric acid were sorbed on the large column. Zirconium and thorium were both eluted with 30 ml of $1M$ perchloric acid, and uranium(VI) was eluted as previously described. Table III gives the results of these analyses.

The separation and recovery of small amounts of uranium(VI) from large amounts of other metal ions was next attempted. Samples of rare earth oxides weighing from 3 to 5 g were dissolved in perchloric acid. The acid concentration was adjusted to $1M$ and the solution passed through a 90×20 mm column containing $0.5M$ DOSO (in 1,2-dichloroethane) on XAD-2. Known quantities of uranium(VI) were added to some samples. The uranium(VI) was then eluted from the column with 100 ml of $1M$ sulphuric acid and determined spectrophotometrically with Arsenazo. The results are reasonably good (see Table IV). The "uranium" found in the blanks appears to stem at least partly from Arsenazo absorbance resulting from metal impurities in the sulphuric acid eluent.

TABLE IV.—DETERMINATION OF TRACES OF URANIUM IN SALTS

Salt	U added, *ppm*	U found, *ppm*
3·5 g Sm_2O_3	0	37
3·5 g Sm_2O_3	686	646
3·5 g Eu_2O_3	0	6
3·5 g Eu_2O_3	137	134
5·0 g $ThCl_4$	0	4·2
5·0 g $ThCl_4$	0	4·0

Separation of possible traces of uranium from specially purified thorium chloride was next attempted. A $1M$ perchlorate solution containing a total of 5 g of thorium chloride was passed through a smaller (100×6 mm) column of $0.5M$ DOSO (in 1,2-dichloroethane) on XAD-2, and the uranium was eluted from the column with methanol. Analysis of this effluent by the Arsenazo spectrophotometric method gave

an average uranium content of 4·1 ppm in the solid thorium chloride sample, after subtraction of a column blank (no ThCl$_4$ present) of 1·2 ppm. That the substance measured in the thorium sample was actually uranium was proved by extracting a thorium sample 5 times with fresh DOSO in 1,2-dichloroethane, evaporating the solvent and analysing the solid DOSO by neutron activation. Uranium was definitely identified from the gamma-ray energies of the fission products, and the uranium content of the thorium chloride was found to be 3·6 ± 1·8 ppm, which is in good agreement with the values reported in Table IV.

Zusammenfassung—Uran(VI) wird aus wäßrigen Perchloratmedien quantitativ in Dioktylsulfoxid in 1,2-Dichloräthan extrahiert; die extrahierte Spezies enthält 4 Sulfoxidmoleküle pro Uran. Die meisten anderen Metallionen werden nicht in merklichem Umfang mit extrahiert. Auf Säulen, die einen mit Dioktylsulfoxid in 1,2-Dichloräthan imprägnierten festen Träger enthalten, kann man Uran(IV) quantitativ von Metallionen wie Thorium(IV), Zirkonium(IV) und dreiwertigen seltenen Erden trennen.

Résumé—On extrait quantitativement l'uranium(VI) de milieux perchlorate aqueux en dioctyl sulfoxyde dans le 1,2 dichloréthane. L'espèce extraite contient quatre sulfoxydes par uranium. La plupart des autres métaux ne sont pas extraits de manière appréciable. Sur des colonnes contenant un support solide imprégné de dioctyl sulfoxyde en 1,2 dichloréthane, on peut séparer quantitativement l'uranium(VI) d'ions métalliques tels que thorium(IV), zirconium(IV) et terres rares(III).

REFERENCES

1. D. C. Kennedy and J. S. Fritz, *Talanta*, 1970, **17**, 823.
2. J. S. Fritz and M. Richard, *Anal. Chim. Acta*, 1959, **20**, 164.
3. J. S. Fritz and R. K. Gillette, *Anal. Chem.*, 1968, **40**, 1777.

DETERMINATION OF SILVER, GOLD AND PALLADIUM BY A COMBINED FIRE-ASSAY ATOMIC-ABSORPTION PROCEDURE

SILVE KALLMANN and EVERETT W. HOBART
Ledoux & Co., Teaneck, N.J. 07666, U.S.A.

Summary—A method is described which combines the best features of the fire-assay procedure with an atomic-absorption technique. The precious-metal bead resulting from the fire-assay concentration step is dissolved in acids, the solution evaporated to dryness and the residue dissolved in a measured quantity of cyanide solution. The atomic-absorption measurement of this solution allows the determination of as little as 0·017 ppm of silver, 0·08 ppm of gold, and/or 0·08 ppm of palladium in various precious-metal-bearing materials with a precision of ±1%.

THE CLASSICAL fire-assay method provides an excellent way to extract and concentrate traces of precious metals from large samples of inhomogeneous materials. Its chief limitations are related to transferring quantitatively small amounts of precious metal (often <0·05 mg) to an analytical balance and to separating the various components by chemical methods.

A number of workers have reported methods for determining silver and gold in specific ores by a direct chemical attack followed by atomic-absorption measurements.[1–7] Such procedures may be suitable for routine analyses of relatively rich ores taken from particular mines, but both the sensitivity and accuracy of these direct methods suffer from the use of relatively small samples and from potentially incomplete extraction of silver and gold. Nonetheless, the sensitivities of the atomic-absorption technique for gold, silver, and palladium are sufficiently great to suggest that atomic absorption may be ideally suited to the analysis of the final bead of precious metals resulting from the fire-assay procedure.

A typical fire-assay bead results from a complete decomposition of an assay ton (29·1666 g), or a fraction thereof, of sample and consists only of the silver, gold, and platinum metals. As will be shown below, such a bead can be decomposed in acids and concentrated into 5 ml of solution for atomic-absorption measurements. It was found that 0·1 ppm of silver, 0·3 ppm of gold or 0·3 ppm of palladium can be measured by atomic absorption with a precision of ±1%. Thus, 0·5 μg of silver, from a 30-g sample (0·017 ppm or 0·0005 oz/ton) can be determined with good precision by combining atomic-absorption with fire assay. To achieve such remarkable sensitive and precise results, it is necessary to establish suitable means for dissolving the beads and for maintaining the noble metals in stable solution for atomic-absorption measurement.

Various media have been recommended for the atomic-absorption measurement of gold, silver and palladium. These include 25% hydrochloric acid,[3–7] dilute nitric acid,[8] potassium cyanide solution[1] and organic extracts.[7] Concentrated hydrochloric acid is unsatisfactory because of its significant attack on the steel aspirator.

Preliminary experimentation revealed that hydrochloric acid solutions must be avoided when analysing samples containing significant quantities of gold, because of possible reduction of the gold in the steel capillary of the aspirator, resulting in clogging of the capillary and loss of a significant fraction of the gold. In addition, the solubility of silver chloride in moderately concentrated hydrochloric acid is quite limited. Nitric acid solutions are deemed inadvisable, because of the probability of losing traces of silver by chloride contamination. Potassium or sodium cyanide solutions, in contrast, form extremely stable complex ions with all the metals of interest and, in addition, provide a high concentration of readily ionized alkali metal atoms in the flame to minimize ionization of gold, silver, and palladium atoms. Five ml of 2% potassium cyanide solution will hold over 50 mg of silver or palladium and even larger amounts of gold as stable complexes. Thus relatively large quantities of silver, gold, or palladium can be concentrated into a small volume, permitting the determination of traces of the other individual precious metals.

EXPERIMENTAL

Decomposition of the sample

Gold, silver, and/or palladium in ores and concentrates. A fire-assay fusion and, if necessary, a scorification are carried out, producing a lead button which should contain a minimum of 0·5 μg of silver, 1·5 μg of gold or 1·5 μg of palladium. In the case of concentrates, the final bead resulting from the cupellation step will usually contain more than 2 mg and sometimes in excess of 100 mg of combined silver and gold. Silver is usually the preponderant element.

If the sample charge contains less than 1 mg of combined silver and gold, a few mg of silver are added to the fusion flux for the quantitative collection of gold and/or palladium. Similarly, for the determination of silver, a few mg of gold are added to the flux, when the expected combined weight of silver plus gold is less than 1 mg.

The bead is weighed, if one of the elements is determined "by difference", transferred to a 50-ml beaker, and treated with 15 ml of hot $4M$ nitric acid. When there is no further reaction 5 ml of concentrated hydrochloric acid are added and the solution is heated until decomposition is complete. (If gold was added to collect the silver, the bead is attacked with 20 ml of hot *aqua regia*.) After dissolution, the cover is washed and removed and the solution evaporated to dryness at low temperature, preferably on a steam-bath.

Gold and/or silver in copper. The sample is decomposed by heating strongly with concentrated sulphuric acid, with a mercury salt as catalyst. When decomposition is complete, the cold solution is diluted with water. A few drops of dilute hydrochloric acid or sodium chloride solution are added to precipitate the silver. After standing overnight, the solution is filtered and the residue is washed with cold water and ignited in a scorifier. Following scorification and cupellation, the bead is treated with nitric, then hydrochloric acid, as described above.

Gold and silver in drill cores and other survey samples. Since such material is usually low in silver and gold, it is advisable to add silver to a portion of the sample for the collection of the gold, and gold to another portion for the collection of the silver. In the case of extremely low-grade material, the purity of the gold or silver collector should be examined by running portions of it through the entire fusion, scorification, cupellation and atomic-absorption steps.

Gold, silver and/or palladium in jeweller's sweeps. The material may be nickel, chromium or copper-base containing varying amounts of gold, silver, palladium, and/or platinum. Decomposition can be achieved by assay fusion, scorification and acid decomposition or by a combination of these. The final bead, depending on its composition, is first attacked with nitric acid, followed by hydrochloric acid (if silver is the preponderant element), or by *aqua regia* (if gold, palladium and platinum are the preponderant elements). In the case of samples with a silver to gold ratio of less than 3:1, it may be necessary to decant the solution, saturated with silver chloride, and attack the remaining metal by heating with fresh hydrochloric acid, with intermittent addition of nitric acid.

If the silver content exceeds 25 mg, the silver chloride, after evaporation of the excess of acid and dilution, may be filtered off and weighed. If the silver chloride is discoloured by co-precipitated gold, palladium or platinum, it should be reprecipitated. This, it was found, can be done most expeditiously by treating the silver chloride in 1–5% v/v sulphuric acid with zinc metal,[9] followed by filtration and dissolution of the silver sponge in nitric acid and precipitation of silver chloride with hydrochloric acid.

The filtrate from the silver chloride, or the solution containing silver, gold, and palladium, is evaporated to dryness.

Gold, palladium, and silver in electronic scrap. Some samples can be dissolved directly in acids. However, the sample frequently is not homogeneous and may contain a large quantity of base metals which would complicate a direct determination of small amounts of precious metals. It is therefore advantageous to use preliminary fire-assay procedures until a bead is obtained which contains the three metals under discussion and possibly also platinum. In cases of extreme inhomogeneity, it may be desirable to melt all of the material either directly or by matting, in order to obtain a satisfactory analytical sample.

The final bead resulting from the cupellation step is dissolved by heating with concentrated hydrochloric acid, with occasional addition of concentrated nitric acid. As the attack slows down, more nitric acid is added from time to time. If dissolution of the bead is incomplete, additional hydrochloric acid is added. In extreme cases, the solution is decanted off and the undissolved sample is treated with fresh acids. All solutions are finally combined.

Silver alloys for palladium, and palladium sweeps with silver added as collector. The bead is dissolved in nitric acid, without addition of hydrochloric acid, thus avoiding the handling of large quantities of silver chloride. The solution may contain undissolved gold, which can be disregarded.

Atomic-absorption measurements of the solutions

The solution resulting from one of the decomposition steps is evaporated to dryness in a 50-ml beaker on a steam-bath. An exactly measured volume of 2% w/v potassium cyanide solution is added to the cold dry salts and stirred until a clear solution is obtained. If dilution to more than 25 ml is contemplated, about 30 ml of cyanide solution are used to dissolve the salts, with a little heat if needed, and then the solution is washed into an appropriate volumetric flask with additional cyanide solution.

Using the three-slot Boling burner with the Perkin–Elmer 303 Atomic Absorption Spectrophotometer, we find the wavelengths and concentration ranges indicated in the following table to be suitable.

Element	Concentration range, $\mu g/ml$	Wavelength, nm
Au	0·3–50	242·8
	10–100	267·6
Ag	0·1–10	328·1
	2–20	338·3
Pd	0·3–30	247·6
	5–60	340·4

In some cases, a single volume can be chosen to place the concentrations of all three elements in their optimum ranges for measurement. In other cases, it will be necessary to prepare a more concentrated solution for determining the minor constituents, followed by dilution of aliquots with cyanide solution for determining the major constituents.

Standard solutions are prepared by dissolving weighed quantities of silver, gold or palladium in nitric and/or hydrochloric acids, evaporating to dryness, dissolving in 2% w/v potassium cyanide solution and diluting to definite volumes with cyanide solution. Between 10 and 12 standard solutions are required to cover the useful concentration range of each element. These solutions have been found to be stable for periods of up to 6 months, when stored in polyethylene bottles.

Each absorbance measurement of a sample is immediately followed by measurement of the closest standard. By running samples in duplicate and reading each portion twice, results are precise to within about 1% of the amount present. A recording attachment has proven to be extremely useful for evaluation of the measurements. A digital read-out accessory lessens the opportunities for human error and minimizes the time required to calculate results.

DISCUSSION

To avoid mechanical losses during fire-assay steps, it is necessary that for the determination of gold the sample charge contain at least five times as much silver as gold. Similarly, for the determination of trace amounts of silver, it is necessary that the sample charge contain an excess of gold to avoid silver losses during fire-assaying. When required, the addition of 10 mg of silver or gold respectively is recommended

TABLE I.—EFFECT OF COLLECTOR IN FIRE ASSAY PROCEDURE

Test No.	Element determined	Taken, μg	Found, μg	Collector
1	Ag	10	none	—
2	Ag	—	1·8	10 mg Au
3	Ag	10	10·6	10 mg Au
4	Ag	100	85	—
5	Ag	100	104	10 mg Au
6	Ag	200	182	—
7	Ag	200	203	10 mg Au
8	Ag	500	482	—
9	Ag	500	504	10 mg Au
10	Ag	1000	953	—
11	Ag	1000	1009	10 mg Au
12	Ag	5000	4670	—
13	Ag	5000	4985	50 mg Au
14	Au	10	none	—
15	Au	—	0·5	10 mg Ag
16	Au	10	10·5	10 mg Ag
17	Au	100	93	—
18	Au	100	101	10 mg Ag
19	Au	500	481	—
20	Au	500	496	10 mg Ag
21	Au	1000	990	—
22	Au	1000	1007	10 mg Ag
23	Au	3000	2985	20 mg Ag
24	Au	5000	5060	50 mg Ag
25	Pd	10	none	—
26	Pd	—	0·3	10 mg Ag
27	Pd	10	10·4	10 mg Ag
28	Pd	100	98	10 mg Ag
29	Pd	200	205	10 mg Ag
30	Pd	500	493	10 mg Au
31	Pd	1000	1009	10 mg Ag
32	Pd	3000	2965	10 mg Au
33	Pd	5000	5021	10 mg Ag

for quantitative collection. Silver and gold serve equally well as collector for palladium. The necessity of adding a collector is demonstrated in Table I. The absence of a collector yields distinctly low silver values (Tests 1, 4, 6, 8, 10, 12), gold values (Tests 14, 17, 19, 21) and palladium values (Test 25). The presence of 10 mg of collector ensures the quantitative recovery of silver (Tests 3, 5, 7, 9, 11, 13), gold (Tests 16, 18, 20, 22, 23, 24), and palladium (Tests 27 to 33). In these tests, the desired element was added in the form of a standard solution to the assay crucible containing an appropriate flux. The collector (silver or gold) was added to the assay crucible as metal. The final beads were dissolved in an appropriate acid, as described in the procedure, prior to atomic-absorption measurements in a cyanide medium. The standard solutions were examined by atomic absorption in the same cyanide medium, and the results indicated that the precision of the measurements were $\pm 1\%$. Although only high-purity reagents were used which gave no positive silver tests by pure fire-assay methods, the high silver results in Tests 2 and 3 indicate that the flux contains parts per milliard amounts of silver which are collected by the gold.

Table II indicates that atomic-absorption measurements of gold, silver or palladium are not dependent on the relative proportions of the metals, nor are they significantly affected by the presence of other platinum metals.

TABLE II.—DETERMINATION OF GOLD, SILVER, AND PALLADIUM IN THE PRESENCE
OF EACH OTHER AND OF OTHER PLATINUM METALS

Element determined	Amount taken, μg	Amount found, μg	Other elements present					
			Au, mg	Ag, mg	Pd, mg	Pt, mg	Ru, mg	Rh, mg
Au	3	2·5	—	10	5	2	1	1
Au	5	4·5	—	10	5	2	—	—
Au	10	10·6	—	10	5	—	—	—
Au	50	49	—	10	5	2	1	1
Au	100	101	—	10	5	5	5	5
Au	300	303	—	5	10	5	5	5
Au	600	604	—	50	2	2	—	—
Au	600	599	—	—	30	1	1	1
Ag	2	2·5	10	—	3	2	1	1
Ag	10	11·5	10	—	5	2	1	1
Ag	20	21	50	—	5	5	1	1
Ag	100	99	15	—	3	3	1	1
Ag	300	302	10	—	2	2	2	2
Ag	300	303	30	—	1	1	1	1
Ag	500	502	50	—	2	2	—	—
Ag	500	497	—	—	30	—	—	—
Pd	3	3·5	—	5	—	1	1	1
Pd	10	10·6	5	5	—	1	1	1
Pd	20	18	5	5	—	1	1	1
Pd	50	52	10	10	—	2	2	2
Pd	100	103	10	10	—	1	1	1
Pd	300	298	5	5	—	1	1	1
Pd	500	496	10	10	—	—	—	—

Table III gives some comparison of gold results obtained in our laboratory by
(a) fire assay, followed by parting and weighing of gold bead and (b) fire assay,
followed by acid dissolution and atomic absorption.

TABLE III.—DETERMINATION OF GOLD: COMPARISON OF CONVENTIONAL FIRE-ASSAY/PARTING
AND WEIGHING PROCEDURE WITH FIRE-ASSAY/ATOMIC-ABSORPTION PROCEDURE

Material	Weight of sample, assay ton (29·16 g)	Au found by weighing, mg	Au found by atomic absorption, mg
Copper Conc. 1	0·5	trace	0·011
2	0·5	trace	0·005
3	0·5	0·27	0·285
4	0·5	0·14	0·147
5	0·5	0·34	0·352
6	0·5	0·84	0·83
7	0·5	1·04	1·048
Blister Copper 1	1	0·15	0·152
2	1	1·23	1·21
Zinc Conc. 1	0·5	0·06	0·073
2	1	0·22	0·233
Lead Conc. 1	1	0·10	0·098
2	1	0·82	0·83
Silicate 1	1	0·09	0·092
2	1	0·94	0·93

SILVE KALLMANN and EVERETT W. HOBART

Zusammenfassung—Ein Verfahren wird beschrieben, das die besten Eigenschaften der Schmelzanreicherung mit einer Atomabsorptionsmessung verbindet. Die Edelmetall-Perle aus dem Schmelzanreicherungs-Schritt wird in Säuren gelöst, die Lösung zur Trockne eingedampft und der Rückstand in einer gemessenen Menge von Cyanidlösung aufgenommen. Die Atomabsorptionsmessung dieser Lösung erlaubt die Bestimmung von immerhin 0,017 ppm Silber, 0,08 ppm Gold und/oder 0,08 ppm Palladium in verschiedenen edelmetallführenden Materialien mit einer Genauigkeit von ±1%.

Résumé—On décrit une méthode qui combine les meilleurs caractères de la technique par voie sèche avec une technique d'absorption atomique. La bille de métal précieux résultant du stade de concentration par voie sèche est dissoute dans des acides, la solution évaporée à sec et le résidu dissous dans une quantité mesurée de solution de cyanure. La mesure d'absorption atomique de cette solution permet la détermination de quantités aussi faibles que 0,017 p.p.m. d'argent, 0,08 p.p.m. d'or, et/ou 0,08 p.p.m. de palladium dans divers produits contenant des métaux précieux, avec une précision de ±1%.

REFERENCES

1. A. M. Olson, *At. Absorption Newsletter*, 1965, **4**, 279.
2. E. C. Simmons, *ibid.*, 1965, **4**, 281.
3. B. S. Rawling, M. D. Amos and M. C. Greaves, *Proc. Australian Inst. Min. Metall.*, 1961, 199; *Nature*, 1960, **188**, 137.
4. A. Strosheim and G. J. Wessels, *Appl. Spectry.*, 1963, **17**, 65.
5. R. Lockyer and G. E. Hames, *Analyst*, 1959, **84**, 385.
6. L. R. P. Strasheim, E. Butler and C. Maskew, *J. S. Afr. Inst. Min. Metall.*, 1962, **62**, 796.
7. F. M. Tindall, *At. Absorption Newsletter*, 1965, **4**, 339.
8. M. Fixman, *ibid.*, 1965, **4**, 243.
9. G. H. Walden, L. P. Hammett and S. M. Edmonds, *J. Am. Chem. Soc.*, 1934, **56**, 350.

ABSORPTIOMETRIC DETERMINATION
OF SULPHIDE ION

S. A. RAHIM* and T. S. WEST
Department of Chemistry, Imperial College of Science and Technology,
London, S.W.7

Summary—An absorptiometric method is described for sulphide ion, based on the green colour which is formed when sulphide ions are treated in ammoniacal solution with iron(III) and an excess of nitrilotriacetic acid. The recommended procedure can be applied from 1200 down to 8 ppm of sulphide and is interfered with seriously only by selenite from amongst seventeen other anions examined. The colour system is stabilized by an excess of sulphite. Suggestions are made about the nature of the colour body and its mechanism of production.

ALTHOUGH the inorganic reactions of sulphide ions are probably better known than those of most ions, there are few methods available for the determination of small amounts of sulphide. The best known is probably the colorimetric method based on the reaction product formed between sulphide ions and p-amino-N,N-dimethylaniline in the presence of iron(III) chloride.[1] According to Mecklenburg and Rosenkränzer[2] as much as 3 hr development time is required for the complete formation of the blue colour with sulphide concentrations as low as 0·02 ppm. The temperature must also be controlled within 2° for precise results to be obtained. Generally this method has been applied to gas analysis. Several other anions, *e.g.*, sulphite and hyposulphite, interfere. Numerous empirical recipes for this colour reaction have been described, but need not be detailed here.

Measurement of the absorbance of suspensions or sols of insoluble sulphides of various metals, *e.g.*, of lead,[3] has been used from time to time, but generally such methods have not found favour because of the unstable nature of the systems. In other instances the sulphide has been converted into thiocyanate which is then determined with iron(III). More recently a fluorimetric method has been described in which the sulphide ion is caused to react with the non-fluorescent palladium complex of 8-hydroxyquinoline-5-sulphonic acid at pH 9·2, thus liberating the free ligand which fluoresces quite strongly at this pH.[4] In this way, as little as 0·2 ppm has been detected, but several ions interfere.

In this contribution we describe a colour reaction between sulphide ion, iron(III) and various complexing agents such as nitrilotriacetic acid and apply it to the determination of small amounts of sulphide in aqueous solution.

In the course of investigations several years ago,[5] of the masking action of derivatives of iminodiacetic acid on various colour formation and precipitation reactions of inorganic ions it was found that very intense green colours were formed upon mixing solutions of iron(III) with iminodiacetic acid, methyliminodiacetic acid or nitrilotriacetic acid, *etc*, and sulphide ions in the presence of ammonia. Other reagents of the same group, such as EDTA, *trans*-1,2-diaminocyclopentane-$N,N,N'N'$-tetra-acetic acid and *trans*-1,2-diaminocyclohexane-$N,N,N'N'$-tetra-acetic acid yielded transient

* Present address: Chemistry Department, University of Mosul, Mosul, Iraq.

cherry red colours which rapidly faded to a light grey shade and subsequently developed a dark green colour.

It is possible to differentiate the aminopolycarboxylic acids into two groups, *viz.* those which form relatively weak iron(III) complexes and give green colours, and those which form relatively strong iron(III) complexes and give transient cherry red colours which eventually fade to green. It is also possible to devise a colorimetric method for the determination of iron(III).[5] Since absorptiometric methods for iron(III) abound, however, and since the sensitivity of the sulphide reaction for iron is not particularly high, we have not investigated this possibility further. We did, however, establish that an absorptiometric method could be devised for the determination of moderate concentrations of sulphide ion, based on this colour formation.[5] The colour was not very stable at low sulphide concentrations, however, and lacked sufficient intensity to make it worthwhile as a practical procedure, so the method was not then investigated further. This paper describes a re-examination of the problem.

Evolution of analytical procedure

Preliminary absorption spectra obtained by mixing iron(III) ammonium sulphate solution with an excess of nitrilotriacetic acid (NTA), sulphide ion and ammonia and measuring quickly against a water blank showed that pronounced maxima were formed at 435 nm and 640 nm with a very slight maximum at 550 nm. In the absence of sulphide, some absorption was shown at 435 nm, but very little at 640 nm. The sensitivity of detection was considerably greater at 640 nm than at 435 nm. Attempts were then made to find the optimal time for development of maximum absorbance. These experiments revealed that colour formation was instantaneous and that the colour of solutions not containing an excess of sulphide faded rapidly, whilst those containing an excess maintained a steady absorbance for at least 30 min. These observations provided valuable guidance subsequently, but further experiments were limited to those in which an excess of iron(III), NTA and ammonia was added with respect to sulphide.

It was found that it was best to maintain the NTA in considerable excess over the ferric iron to obtain the maximum yield of colour. A composite solution containing iron(III) and a 5-fold molar ratio of NTA was therefore added as a single reagent. The order of addition of reagents was also found to be important in that most colour was generated when the test (sulphide) solution was treated first of all with ammonia and then with the composite solution. Maximum colour formation occurred when the mixture of all the reagents was diluted immediately to the mark and measured, rather than allowed to stand for a few minutes before dilution. This evidence and the obvious stability of the colour suggested that aerial oxidation of the coloured compound was responsible for the fading. The incorporation of hydroxyammonium chloride or ascorbic acid in the mixture to prevent such oxidation had a deleterious effect, however, owing to the reduction of iron(III) to iron(II). At this point, the causes of colour instability were also thought to be due to coagulation of the green colour body, and it appeared that the system was behaving as a sol rather than as a true solution. Various surface-active agents and protective colloids were, therefore, incorporated in the colour system to try to stabilize it, *e.g.*, Cetavlon, Triton X 100, Lissapol NX, polyethylene glycol, glycerine and gelatin. Only gelatin showed any

sensitization and stabilization effect, and that was only slight. The addition of various inorganic electrolytes was finally examined in an effort to provide some stabilization, *viz.* potassium chloride, potassium aluminium sulphate, disodium hydrogen ortho-phosphate, sodium selenite, sodium selenate and sodium sulphate. With the exception of potassium chloride which was without any effect, and of sodium selenite which inhibited the colour formation if added first to the sulphide solution, all showed some degree of sensitization, but it was most marked with sodium sulphate and sodium selenate. It was found that when the sodium sulphate (or selenate) was added to the ammoniacal sulphide solution before the iron(III)–NTA solution there was a gradual increase in colour for 1 min followed by a stable period of 3–4 min and a slow decrease in absorption on further standing.

The slight enhancement and stabilization effect of sulphate was attributed to a protective action on the (suspected) colloidal colour body, and the subsequent fading to gradual oxidation of the green reaction product. It is known that sulphite does not readily reduce iron(III) to iron(II) except in the presence of catalysts such as thio-cyanate,[6] yet it may be used to reduce dissolved oxygen in aqueous solutions (*e.g.*, in polarography). Consequently, further experiments were performed with sodium sulphite in place of sodium sulphate. This had the desired effect of giving considerable sensitization of the colour reaction, stabilization and prevention of short-term fading of the green colour. Stable colours could now be maintained for up to 10 min and the maximal colour formation occurred within 2 min of mixing the solutions. This effect is shown in Table I for the determination of 600 μg of sulphide in a final volume

TABLE I.—MAXIMAL COLOUR FORMATION IN THE Fe(III)/NTA/S^{2-} SYSTEM (600 μg OF S^{2-} + 1 ml OF NH$_3$ SOLUTION + 20 ml OF 20% Na$_2$SO$_3$ SOLUTION + 0·5 ml OF Fe(III)/ NTA DILUTED TO 50 ml)

Standing time, *min*	0	1	2	5	10	12	15
Absorbance (5-mm cell)	0·70	0·715	0·725	0·725	0·725	0·725	0·715

of 50 ml. Because of the protective action of sulphite all dilute standard sulphide test solutions were subsequently prepared in the presence of an excess of sodium sulphite (10%).

Figure 1 shows the absorption spectra obtained. The sulphide solutions used in (2) and (3) did not contain sodium sulphite. These curves were measured in 10-mm cells against distilled water between 2 and 12 min after preparation of the solutions. They show that the maximum absorption for sulphide now occurs at 635 nm in the presence of sulphide and that the blank absorption of the reagents is almost negligible at this wavelength. The difference between curves (3) and (2) shows the benefit of the pres-ence of excess of sulphate ions whilst that between curves (3) and (4) shows the superior sensitization by excess of sulphite.

The best conditions for devising a method for the absorptiometric determination of sulphide ion having thus been established, a test was made of adherence to the Lambert–Beer law. It was found that in the presence of excess of sulphite ion, by the method recommended, Beer's law was obeyed in the range 200–1200 μg of sulphide in a final volume of 50 ml. The extrapolation of the calibration curve showed a slight positive intercept on the concentration axis. The molar absorptivity at 635 nm for the sulphide ion corresponds to 540 l.mole^{-1}.mm^{-1}. When the standard sulphide
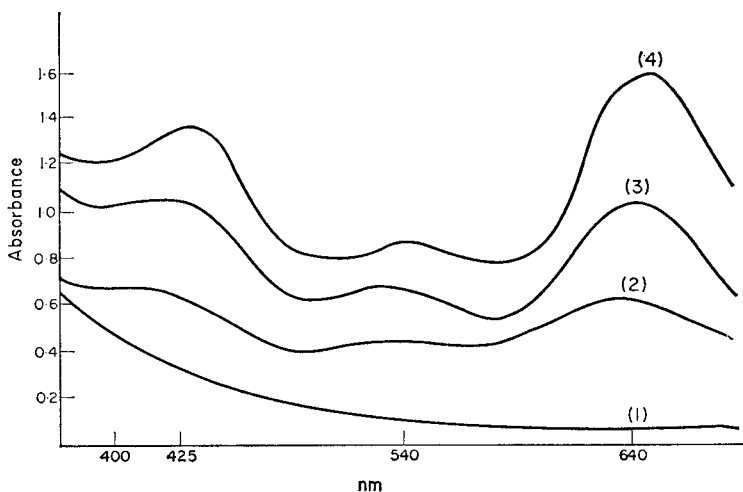
FIG. 1.—Absorption spectra of FeIII/NTA/S^{2-} system.
(1) Blank reaction: Na$_2$SO$_3$ + 1 ml of NH$_3$ solution + 0·5 ml of Fe(III)/NTA solution, diluted to 50 ml; 10-mm cuvette; reference distilled water. (2) As (1) plus 600 μg of S^{2-} and without Na$_2$SO$_3$. (3) As (2) plus 20 ml of 20% Na$_2$SO$_4$ solution. (4) As (3) but with 600 μg of S^{2-} prepared in 10% Na$_2$SO$_3$ solution and with 20 ml of 20% Na$_2$SO$_3$ solution in place of Na$_2$SO$_4$. All spectra were measured on a scanning spectrometer within 5 minutes of preparation.

test solution was prepared in the absence of sodium sulphite, but 20% sodium sulphite solution was still added in the procedure, the molar absorptivity fell to 420 l.mole^{-1}.mm^{-1}. This difference is attributed to loss of sulphide ion by attack from dissolved oxygen when the test solution is not protected in this way. In the absence of excess of sulphite either in the standard solution or in the procedure [Curve (2)], the molar absorptivity was 210 l.mole^{-1}.mm^{-1}.

Effect of other ions on the analytical method

The effect of cations was not examined in detail since it is known that many are not compatible in solution with sulphide ion.

Of 17 anions examined, however, the following did not interfere in 100-fold molar excess relative to sulphide: SO$_3$$^{2-}$, SO$_4$$^{2-}$, SeO$_4$$^{2-}$, NO$_3$$^-$, CO$_3$$^{2-}$, ClO$_3$$^-$, Cl$^-$, Br$^-$, I$^-$, CH$_3COO^-$, PO$_4$$^{3-}$ and OH$^-$. The following ions, which interfered at 100-fold excess, could be tolerated at <10-fold excess: oxalate, citrate, tartrate and chromate (negative error). Selenite completely inhibited the colour formation.

The precision of the method was tested by replicate analyses of 0·4 ml of a 3 × 10^{-2}M sulphide solution by the recommended procedure. This yielded a mean absorbance of 0·97, standard deviation 0·027.

EXPERIMENTAL

Reagents

Standard sulphide solution, 1000 ppm. Dissolve and dilute to 100 ml 0·7490 g of analytical-reagent grade Na$_2$S.9H$_2$O with freshly prepared 10% w/v sodium sulphite solution. This solution should be prepared fresh daily.

$$1 \text{ ml} \equiv 1000 \text{ } \mu\text{g S}^{2-}.$$

Sodium sulphite solution, 20% w/v.

Iron(III)/NTA composite solution. Dissolve 1·91 g of nitrilotriacetic acid in 25 ml of 1M sodium hydroxide with warming. Dissolve 1·92 g of iron(III) ammonium sulphate in water containing 1 drop of 1M sulphuric acid. Mix the two solutions and dilute to 100 ml in a volumetric flask.

Calibration curve and procedure

Transfer 0·2–1·2-ml aliquots of the 1000-ppm sulphide test solution (*i.e.*, 200–1200 μg) to 50-ml standard flasks. Add 20 ml of 20% sodium sulphite solution, 1 ml of concentrated ammonia solution and 0·5 ml of the iron(III)/NTA reagent solution. Immediately dilute the contents of the flasks to 50 ml and measure the absorbance of each solution 2–12 min from the time of preparation in 5-mm cuvettes at 635 nm against a water blank.

Use this procedure in the same way for unknown solutions containing 8–1000 ppm of sulphide, using sample volumes containing, 200–1000 μg of sulphide.

DISCUSSION

The proposed method for sulphide can be applied down to 8 ppm if 25 ml of sample are available and up to 1000 ppm in a 1-ml test sample. The sensitivity is not very high, but the selectivity is good.

We have been able to reach no definite conclusions as to the exact nature of the green absorbing species. Application of the usual Job, mole-ratio and slope-ratio plots led to meaningless numerical results. It is also known[7] that the complexones never act as direct chromogenic reagents. The action of protective colloids and, more particularly, electrolytes such as sodium sulphate, and sulphite, taken in conjunction with the non-stoichiometric reaction relationships and the obvious tendency for coagulation to occur, lead us to believe that we are dealing with a colloidal basic form of iron(III) sulphide. The action of the NTA appears to be to form a protective complex of iron(III) which hydrolyses progressively as shown in Fig. 2(*a*). An alternative mechanism is shown in Fig. 2(*b*).

The former postulate seems the more probable since the progressive hydrolysis of polyaminocarboxylate complexes of iron(III) in alkaline solution is known, whereas there appears normally to be little preferential affinity for sulphide ion relative to
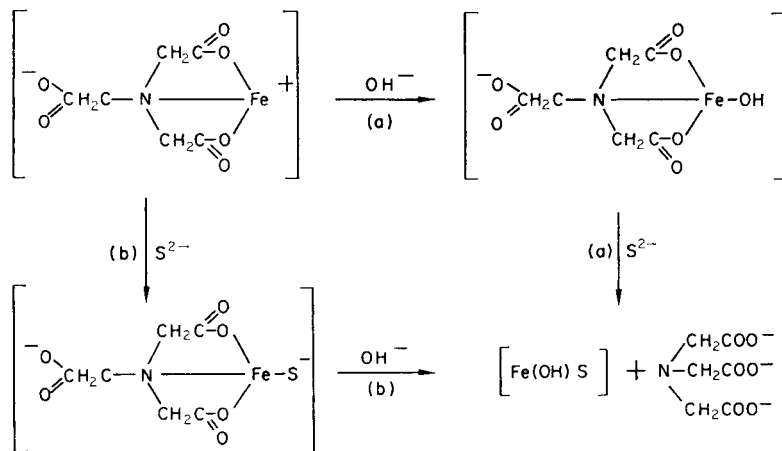

FIG. 2.—Probable mechanisms for colour production in the Fe(III)/NTA/S^{2-} system. (*a*) S^{2-} replacement of NTA in the partially hydrolysed Fe(III)/NTA complex. (*b*) OH⁻ replacement of NTA in a ternary Fe(III)/NTA/S^{2-} complex.

hydroxyl ion in the absence of NTA. A nearly neutral colloid is suggested by the protective action of the electrolytes.

Other derivatives of iminodiacetic acid[7] also yield green colours, e.g., iminodiacetic acid, methyliminodiacetic acid, UDA, DHEG, as do other complexing agents for iron, e.g., citrate, tartrate, but the most intense colour is obtained with NTA. This probably arises because of the speed of release of $[Fe(III)OH]^{2+}$ from the NTA-complex being best suited to the formation of colloidal particles of basic ferric sulphide of the shape and size appropriate to maximum absorbance.

The system approximates to the NTA complex of iron(III) acting as a hydrolytic reagent for the precipitation of a basic ferric sulphide from homogeneous solution.

Zusammenfassung—Ein absorptiometrisches Analysenverfahren für Sulfidionen wird beschrieben. Es beruht auf der grünen Farbe, die entsteht, wenn man Sulfidionen in ammoniakalischer Lösung mit Eisen(III) und einem Überschuß Nitrilotriessigsäure behandelt. Das empfohlene Verfahren kann von 1200 bis herab zu 8 ppm Sulfid verwendet werden. Es wird unter 17 untersuchten anderen Ionen nur durch Selenit ernstlich gestört. Das Farbsystem wird durch einen Überschuß von Sulfit stabilisiert. Über die Natur des Farbkörpers und über seine Entstehungsweise werden Vermutungen angestellt.

Résumé—On décrit une méthode absorptiométrique pour l'ion sulfure, basée sur la coloration verte qui se forme lorsque les ions sulfure sont traités en solution ammoniacale par le fer (III) et un excès d'acide nitrilotriacétique. On peut appliquer la technique recommandée de 1200 à 8 p.p.m. de sulfure et elle n'est sérieusement gênée que par le sélénite parmi dix sept autres anions examinés. Le système coloré est stabilisé par un excès de sulfite. On présente des suggestions sur la nature du corps coloré et son mécanisme de production.

REFERENCES

1. E. Fischer, *Berichte*, 1883, **16**, 2234.
2. W. Mecklenburg and F. Rosenkränzer, *Z. anorg. allgem. Chem.*, 1914, **86**, 143.
3. R. H. Vallance, D. F. Twiss and A. R. Russell, *Text-book of Inorganic Chemistry, Vol. VII, Part II, Sulphur, Selenium and Tellurium*, (ed. J. Newton Friend), Griffin, London, 1931.
4. J. S. Hanker, A. Gelberg and B. Witten, *Anal. Chem.*, 1958, **30**, 93.
5. I. P. Sanderson and J. S. West, *M. Sc. Thesis*, Birmingham University, 1960.
6. F. Burriel-Martí and F. Lucena Conde, *Anal. Chim. Acta*, 1949, **3**, 547.
7. T. S. West, *Complexometry with EDTA and Related Reagents*, 3rd Ed., B.D.H., Poole, U.K., 1969.

COLUMN CHROMATOGRAPHIC SEPARATION OF GALLIUM, INDIUM AND THALLIUM*

JAMES S. FRITZ, R. THOMAS FRAZEE and GARY L. LATWESEN†

Institute for Atomic Research and Department of Chemistry, Iowa State University,
Ames, Iowa 50010, U.S.A.

Summary—Distribution ratios are given for the extraction of gallium-(III), indium(III) and thallium(III) from aqueous solutions of hydrobromic acid into di-isopropyl ether and isobutyl methyl ketone. Based on the results obtained, a scheme is presented for the quantitative separation of these elements from each other by liquid–liquid partition chromatography. The effect of a number of other metal ions upon the separation is also studied. The separation method has been applied to the analysis of a series of lead–indium alloys.

METHODS for separation of gallium(III), indium(III) and thallium(III) have been reviewed in a book by Korkisch.[1] Solvent extraction methods for these elements are predominately based on extraction from different concentrations of hydrochloric or hydrobromic acid. Irving and Rossotti[2] have reviewed the extraction of these elements by diethyl ether. Gallium is nearly quantitatively extracted from 5–7M hydrochloric acid into diethyl ether and is partially extracted from 4–5M hydrobromic acid. Indium is only slightly extracted from hydrochloric acid but is strongly extracted from 4M hydrobromic acid. Thallium is nearly quantitatively extracted into diethyl ether from >1M hydrochloric or >1M hydrobromic acid.

A practical difficulty with solvent extraction is that quantitative separations are obtained only when conditions are such that one element is completely extracted while the elements from which it is separated are not extracted at all. Greater flexibility is obtained through the use of column extraction chromatography, where only a significant *difference* in extractibility is needed for quantitative separation.

In the present work conditions have been worked out for quantitative column chromatographic separation of tervalent gallium, indium and thallium. Aqueous solutions of these metal ions in hydrobromic acid are passed through a column containing isobutyl methyl ketone (IBMK) or di-isopropyl ether (IPE) on a solid granular support. Gallium comes through first; indium and thallium are then eluted successively with lower concentrations of hydrobromic acid. This separation method has also been used for the analysis of lead–indium alloys.

EXPERIMENTAL

Reagents

Aldrich "purissimum" grade IBMK and Fisher certified grade IPE were used, and equilibrated with the appropriate aqueous solvent before use.

All metal salts and inorganic acids were reagent grade and were used without further purification.

Inert support

Amberlyst XAD-2, an inert cross-linked polystyrene polymer, was obtained from Rohm and Haas as 20–50-mesh beads. The beads were ground and sieved and 80–100-mesh fraction was used. The inert support was washed with 6M hydrochloric acid and methanol, and air-dried before use.

Sample solution

Solutions of metal ions were prepared by mixing 5-ml portions of the appropriate metal ion solutions and evaporating the sample solutions to near dryness. Then 2 ml of concentrated hydrobromic acid were added and the samples again taken to near dryness. The residue was then taken up in 5 ml of the appropriate eluent for transfer to the chromatographic column.

Column preparation

The column support was slurried in a portion of equilibrated organic solvent and allowed to remain in contact with the organic solvent for an hour to ensure complete saturation. The slurry was then transferred to the chromatographic column (a 150 × 10 mm column fitted with a coarse frit and a stop-cock), and a small plug of glass wool was used to prevent the top of the column from being disturbed during addition of the sample or eluent. Approximately 3 column-volumes of equilibrated acid were passed through the column to displace the interstitial organic solvent on the column. The organic phase was run down to the level of the column before the equilibrated acid was added.

Distribution ratios

Distribution ratios were obtained by shaking 20 ml of equilibrated organic phase with 20 ml of the equilibrated aqueous phase containing a known amount of solute. After equilibration in a separatory funnel, the phases were separated and the aqueous phase was analysed for metal ion content.

Methods of analysis

Most metal ions were determined by titration with EDTA by standard methods. Thallium(III) cannot be titrated in a hydrobromic acid solution because of the stability of the thallium bromide complex. Therefore, 10 ml of nitric acid were added to the thallium fraction from the column. The sample was heated very mildly to accelerate the formation of bromine, which was carefully expelled by alternately heating and cooling. After expulsion of the bromine, the sample was evaporated to a volume of 3–5 ml, 10 ml of *aqua regia* were added, and the sample was again evaporated to 3–5 ml. The *aqua regia* oxidation was repeated. A known volume of EDTA in excess was added and the solution diluted to 150 ml with water. The excess of EDTA was then titrated with thorium at pH 2·0–2·2, Xylenol Orange being used as indicator.

Antimony(III) and arsenic(III) were determined by titration with standard potassium bromate (Methyl Orange indicator). Antimony and arsenic were not evaporated with hydrobromic acid before extraction because of their tendency to volatilize.

Mercury(II) was determined by titration with thioglycerol, with the thio analogue of Michler's ketone as indicator.

Selenium(IV) was determined in a sulphuric acid solution by adding a 10-ml excess of 0·05N potassium permanganate; 5 ml of phosphoric acid were added to prevent the formation of manganese dioxide. After 30 min the residual potassium permanganate was determined by adding a slight excess of iron(II) ammonium sulphate followed by a back-titration with potassium permanganate.

RESULTS

Two organic solvents, IPE and IBMK, were investigated as extractants. IPE is less soluble in the aqueous hydrobromic acid phase and is very easily volatilized prior to analysis of the aqueous phase. IBMK, however, is a more powerful extractant and is also sufficiently volatile.

Distribution coefficients for gallium, indium and thallium at various concentrations of hydrobromic acid are given in Table I for IPE and in Table II for IBMK. These data reveal that gallium is only very slightly extracted by IPE over the entire concentration range of hydrobromic acid studied. Indium is not extracted appreciably at hydrobromic acid concentration below 4M but is over 90% extracted from 5M hydrobromic acid. Thallium is essentially completely extracted from 1–5M hydrobromic acid by IPE.

TABLE I.—DISTRIBUTION RATIOS AND DEGREE OF EXTRACTION OF Ga(III), In(III) AND Tl(III) FROM AQUEOUS HYDROBROMIC ACID INTO IPE

	Molar concentration HBr									
	1·0		2·0		3·0		4·0		5·0	
	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %
Ga	~0	~0	~0	~0	~0	~0	<0·01	<1·0	0·40	29
In	<0·01	<1·0	0·025	2·4	0·27	21	3·84	79	14·6	94
Tl	267	99·6	—	—	535	99·8	—	—	267	99·6

TABLE II.—DISTRIBUTION RATIOS AND PERCENTAGE EXTRACTION OF Ga(III), In(III) AND Tl(III) FROM AQUEOUS HYDROBROMIC ACID INTO IBMK

	Molar concentration HBr									
	0·25		0·5		1·0		2·0		3·0	
	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %	Distribution ratio	Extracted, %
Ga	—	—	—	—	—	—	<0·1	<1	0·32	19
In	0·13	12	—	—	4·2	81	49	98	124	99·2
Tl	—	—	150	99·3	178	99·4	—	—	58	98·3

Column separations were performed on a column packed with 80–100 mesh Amberlyst XAD-2 impregnated with IPE. The elution curve in Fig. 1 shows excellent results for sequential elution of gallium with 5M hydrobromic acid, indium with 1M hydrobromic acid, and thallium with 3M nitric acid followed by IPE.

The data in Table II show significant differences in the extractability into MIBK of the elements studied. Accordingly, for separation on a column of XAD-2 impregnated with IBMK, 3M hydrobromic acid was selected for elution of gallium, 0·25M hydrobromic acid for elution of indium, and thallium was eluted with 3M
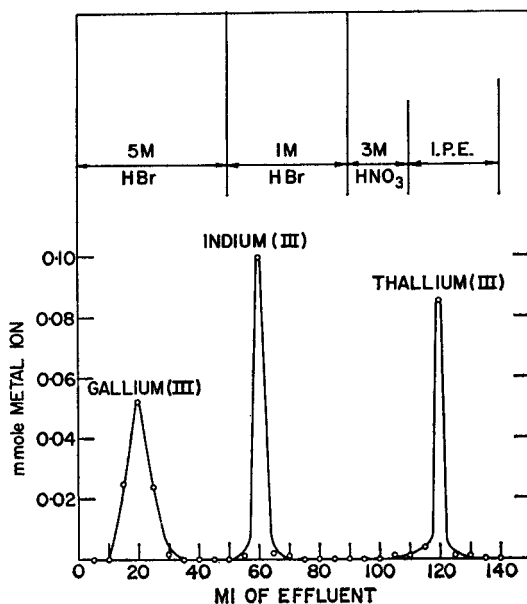
FIG. 1.—Elution of 100 μmole each of gallium(III), indium(III) and thallium(III) from a 120 × 10 mm column of 80–100 mesh Amberlyst XAD-2 impregnated with IPE. Amberlyst XAD-2 support equilibrated with di-isopropyl ether; flow-rate 1·0–1·5 ml/min.

nitric acid and IPE as before. A typical elution curve is given in Fig. 2. Quantitative results for separations on both IPE and IBMK columns are summarized in Table III.

The separation of gallium from indium on the IBMK column is also possible with 2M hydrobromic acid (instead of 3M) provided the amount of indium is small. The effect of loading on indium elution is given in Table IV.

Distribution ratios of a number of other metal ions were determined (Table V) in order to ascertain which might interfere in the column separations just described. Only selenium(IV) and iron(III) are strongly extracted by IPE from 5M hydrobromic acid. In the 3M hydrobromic acid–IBMK system, tin(IV) and mercury(II) are strongly extracted in addition to selenium(IV) and iron(III). Copper(II) and iron(III) are reduced at least partially to their lower oxidation states.

The elements most likely to interfere with the analytical separation scheme are tin(IV), iron(III), copper(II) and mercury(II). The behaviour of these elements on the column was studied by determining the break-through volume and elution volume
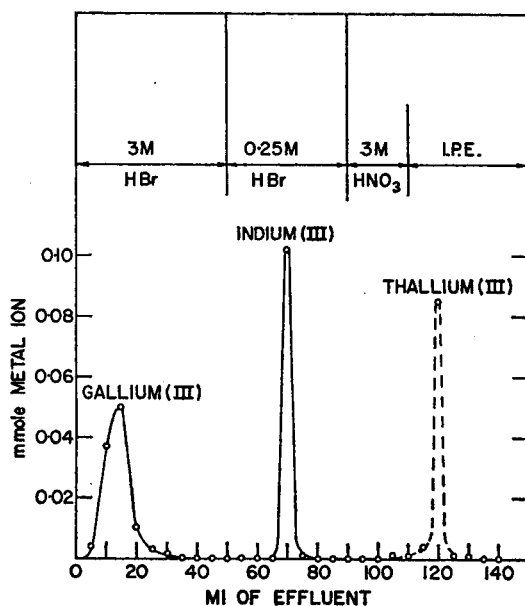
FIG. 2.—Elution of 100 μmole each of gallium(III), indium(III), and thallium(III) from a 120 × 10 mm column of 80–100 mesh Amberlyst XAD-2 impregnated with MIBK.
Amberlyst XAD-2 support equilibrated with isobutyl methyl ketone; flow-rate 1·0–1·5 ml/min.

TABLE III.—SEPARATION OF GALLIUM(III), INDIUM(III) AND THALLIUM(III). ELUTION CONDITIONS ARE AS STATED IN FIG. 1 FOR IPE COLUMN AND IN FIG. 2 FOR IBMK COLUMN

Column	Sample composition, mmole of each element	Recovery, %*		
		Ga	In	Tl
IPE	0·10	100·1	99·5	99·9
IPE	0·25	100·2	99·5	98·9
IBMK	0·10	100·0	99·7	99·4
IBMK	0·25	99·8	100·3	99·9

* Average of 2 or 3 individual results.

TABLE IV.—EFFECT OF COLUMN LOADING ON THE ELUTION OF 0·25 MMOLE OF INDIUM(III) FROM AMBERLYST XAD-2 IMPREGNATED WITH IBMK. COLUMN: 100 × 10 MM; FLOW RATE: 1–1·5 ML/MIN

Column loading, mmole	Eluent, [HBr]	Indium breakthrough, ml	Indium elution, ml
~0·25	3M	>120	—
~0·25	2M	20–30	>120
~0·025	2M	>120	—
~0·025	1M	10–20	60–70

Table V.—Distribution ratios for batch extraction of various elements from hydrobromic acid

Element	Distribution ratio			
	5M HBr–IPE	3M HBr–IBMK	2M HBr–IBMK	1M HBr–IBMK
Al(III)	0·08	0·09	—	—
Sn(IV)	0·45	25	4·2	0·59
Pb(II)	0·06	0·13	—	—
As(III)	0·27	0·04	—	—
Sb(III)	0·03	0·32	—	—
Bi(III)	~0	0·05	—	—
Se(IV)	2·5	2·1	—	—
Y(III)	0·01	0·01	—	—
VO(II)	<0·01	<0·01	—	—
Cr(III)	0·19	<0·01	—	—
Mn(II)	0·33	0·30	—	—
Fe(III)	17·5	12·1	0·70	0·03
Co(II)	<0·01	<0·01	—	—
Ni(II)	<0·01	<0·01	—	—
Cu(II)	<0·01	0·37	—	—
Zn(II)	<0·01	1·0	—	—
Cd(II)	0·05	1·0	—	—
Hg(II)	0·04	4·4	3·2	2·7
Mo(VI)	0·09	0·09	—	—
Ca(II)	~0	~0	—	—
Mg(II)	~0	0·02	—	—
Dy(III)	~0	<0·01	—	—
Yb(III)	0·02	0·04	—	—
Th(III)	0·01	0·01	—	—

(Table VI). Only iron(III) would cause difficulty on the IPE column. Both iron(III) and tin(IV) are held up on the IBMK column from 3M hydrobromic acid, although elution is more rapid with 2M hydrobromic acid.

Table VI.—The breakthrough volume and elution volume for various metal ions in hydrobromic acid. Column: 120 × 10 mm; flow-rate: 1–1·5 ml/min

	5M HBr–IPE		3M HBr–IBMK		2M HBr–IBMK	
Element	Breakthrough, ml	Elution, ml	Breakthrough, ml	Elution, ml	Breakthrough, ml	Elution, ml
Sn(IV)	0–5	25–30	30–35	80–90	15–20	60–70
Fe(III)	0–5	>100	5–10	>100	0–10	20–25
Cu(II)	0–5	20–25	0–5	35–40	—	—
Hg(II)	0–5	20–25	5–10	25–30	5–10	20–25

If iron(III) may be present in samples to be analysed for indium(III), a preliminary separation from hydrochloric acid on an IPE-impregnated XAD-2 column might be advantageous. Iron(III), gallium and antimony(V) have been shown previously[3] to be strongly held by such a column from 6 to 8M hydrochloric acid. Thallium(III) is strongly extracted by IPE from hydrochloric acid at these concentrations ($D = 100$ in 6M and 55 in 8M hydrochloric acid) and should also be strongly held. However, indium has a distribution coefficient less than 0·01 in both 6 and 8M hydrochloric acid and passes readily through a column. In presence of 5M hydrobromic acid, indium is retained by the IPE column. This sequence should result in an extremely selective separation method for indium.

ANALYSIS OF LEAD–INDIUM ALLOYS

The general method described earlier was applied to the separation of indium from lead–indium alloys. For this separation a rather high concentration of hydrobromic acid is advantageous in order to complex lead and prevent precipitation of lead bromide. In $4.4M$ hydrobromic acid the distribution ratio for indium into IBMK is approximately 200 and that for lead is only 0·06, which gives a separation factor of over 3000. A sample containing 0·1 mmole each of lead and indium in 4 ml of $4.4M$ hydrobromic acid was added to a 90 × 12 mm column of 60–80-mesh Amberlyst XAD-2 impregnated with IBMK and conditioned with $4.4M$ hydrobromic acid. Lead was eluted from the column with 15 ml of $4.4M$ hydrobromic acid at a flow-rate of 2 ml/min, and indium was then eluted with 15 ml of $0.1M$ hydrochloric acid. Titration of the separated lead and indium with EDTA gave quantitative recoveries within normal titration error.

The method was then applied to the analysis of lead-indium alloys (5–20 mole % indium). The samples (600–800 mg) were dissolved in 15 ml of hydrobromic acid, and most of the acid was evaporated after dissolution. The residue was taken up in $4.4M$ hydrobromic acid, transferred to a 25-ml volumetric flask, and diluted to volume with the same solvent. Aliquots (5 ml) were then transferred to the 90 × 12 mm IBMK column for separation. Lead and indium were eluted with $4.4M$ hydrobromic acid and $0.1M$ hydrochloric acid respectively as before, and titrated. Results for analysis of different sections of an alloy containing approximately 10 mole % of indium are given in Table VII. Although the samples were not homogeneous, the precision and material balance in each case are good enough to indicate that the analyses are correct.

TABLE VII.—ANALYTICAL RESULTS FOR LEAD–INDIUM ALLOYS

Sample number	In(III) present, mmole	Pb(II) present, mmole	Indium, mole %	Material balance, % of total recovered
I, aliquot a	0·0731	0·628	10.4_3	100·2
I, aliquot b	0·0729	0·628	10.4_0	
II, aliquot a	0·0862	0·724	10.6_4	100·2
II, aliquot b	0·0860	0·723	10.6_3	
III, aliquot a	0·0941	0·747	11.1_8	100·4
III, aliquot b	0·0945	0·748	11.2_2	

Zusammenfassung—Verteilungsverhältnisse für die Extraktion von Gallium(III), Indium(III) und Thallium(III) aus wäßrigen bromwasserstoffsauren Lösungen in Diisopropyläther und Isobutylmethylketon werden angegeben. Auf Grund der erhaltenen Ergebnisse wird ein Schema für die quantitiv Trennung dieser Elemente voneinander durch flüssig-flüssig-Verteilungschromatographie angegeben. Der Einfluß einer Anzahl anderer Metallionen auf die Trennung wird ebenfalls untersucht. Das Trennverfahren wurde auf die Analyse einer Reihe von Blei-Indium-Legierungen angewandt.

Résumé—On donne les rapports de partage pour l'extraction de gallium-(III), indium(III) et thallium(III) de solutions aqueuses d'acide bromhydrique en diisopropyléther et isobutylméthylcétone. On présente

un schéma, basé sur les résultats obtenus, pour la séparation quanti-tative de ces éléments l'un de l'autre par chromatographie de partage liquide–liquide. On étudie aussi l'influence d'un certain nombre d'autres ions métalliques sur la séparation. La méthode de séparation a été appliquée à l'analyse d'une série d'alliages plomb–indium.

REFERENCES

1. J. Korkisch, *Modern Methods for the Separation of Rarer Metal Ions*, Pergamon, Oxford, 1969.
2. H. M. Irving and F. J. C. Rossotti, *Analyst*, 1952, **77**, 801.
3. J. S. Fritz and G. L. Latwesen, *Talanta*, 1970, **17**, 81.

SPECTROPHOTOMETRIC DETERMINATION OF NICKEL(II) WITH MOLYBDOPHOSPHORIC ACID

R. L. HELLER* and J. C. GUYON®

Department of Chemistry, University of Missouri, Columbia,
Missouri 65201, U.S.A.

Summary—A sensitive spectrophotometric method for the determination of nickel, based on the reduction of a complex formed between molybdophosphoric acid and Ni(II) at pH 4·3 has been developed. Excess of molybdophosphoric acid is eliminated by complexation with sodium citrate. The method is rapid and the system obeys Beer's law up to 5 ppm of Ni(II). The molar absorptivity is $1·30 \times 10^3$ l.mole^{-1}.mm^{-1}. The technique compares favourably with existing photometric methods for nickel in sensitivity and is reasonably selective.

A SENSITIVE colorimetric technique for the determination of traces of nickel has been developed. The method is rapid and the system obeys Beer's law up to 5 ppm of nickel. The molar absorptivity is $1·30 \times 10^3$ l.mole^{-1}.mm^{-1} at a wavelength of 695 nm. The limit of detection in 10-mm cells is approximately 0·1 ppm.

The method is based upon reduction of a complex formed between nickel(II) and excess of molybdophosphoric acid at pH 4·3. Since the excess of molybdophosphoric acid is also reducible under the conditions of analysis, it is rendered unreducible by complexation with citrate before reduction of the nickel-molybdophosphate by tin(II) chloride. The reduced solutions are an intense blue with maximum absorbance at 695 nm.

EXPERIMENTAL

Reagents

Demineralized distilled water was used throughout.

Sodium molybdate dihydrate solution, 0·1000M.

Potassium dihydrogen phosphate solution, 0·0500M.

Molybdophosphate reagent mixture. Prepared by mixing 600 ml of the 0·1000M sodium molybdate with 100 ml of the 0·0500M phosphate and diluting to 1 litre, to yield a solution containing molybdenum and phosphate in molar ratio 12:1.

Sodium citrate dihydrate solution, 5% w/v.

Stock nickel solution, 1000 *ppm.* Dissolve 4·95 g of reagent grade Ni(NO₃)₂·6H₂O in a 1-litre volumetric flask and dilute to the mark. Prepare a 100-ppm solution by appropriate dilution.

Tin(II) chloride solution. Prepare fresh daily by addition of 1·01 g of reagent grade SnCl₂·H₂O and 1·00 ml of concentrated hydrochloric to a 100-ml volumetric flask and dilution to the mark.

Keep all reagents in polyethylene bottles to avoid contamination with silicate.

Calibration curve

Add 0·00, 0·25, 0·75, 1·25, 2·00, 3·00, 4·00, and 5·00 ml of a standard 100-ppm nickel solution to a series of 150-ml beakers. To each beaker add 5·0 ml of the molybdate–phosphate reagent and 50 ml of demineralized water and adjust the pH to 4·3 by dropwise addition of 1M hydrochloric acid. Start a timer and simultaneously deliver rapidly 2·0 ml of 5% sodium citrate solution from a 2-ml hypodermic syringe. Exactly 5 sec later add 1·0 ml of a 1% tin(II) chloride solution by means of a 1-ml syringe. Quantitatively transfer the solutions to 100-ml volumetric flasks, dilute to the mark, and mix well. After 10–30 min, measure the absorbance at 695 nm *vs.* water. Plot absorbance *vs.* ppm of nickel.

* Current address: Shell Oil Co., P.O. Box 100, Houston, Texas 77536.

General procedure

Dissolve the sample and treat the solution to remove any interfering ions. Nickel may be separated from most interfering substances by ion-exchange. The sample should be neutral and diluted to about 50 ml before addition of the reagents as outlined above.

RESULTS

Preliminary studies consisted of varying the concentrations of molybdate–phosphate reagent, sodium citrate, tin(II) chloride and hydrochloric acid until the blue hue of reduced molybdophosphoric acid was more enhanced in the presence of nickel than in its absence.

The results were used in a systematic study and optimization of variables. Figure 1 shows the absorption spectrum resulting from reduction of the molybdophosphoric
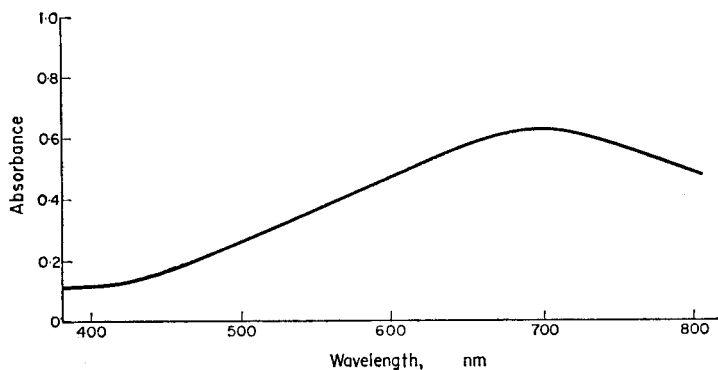
FIG. 1.—Absorption spectrum of molybdophosphoric acid—nickel complex.

acid nickel complex after elimination of the excess of molybdophosphoric acid with sodium citrate. There is a broad absorption peak with its centre at 695 nm. All subsequent measurements were made at this wavelength.

Effect of pH

The effect of varying pH on the system was studied by mixing 3·00 ml of the molybdate–phosphate reagent and 2·00 ml of 100-ppm nickel solution in a 150-ml beaker, adding 50 ml of water and varying amounts of $1M$ hydrochloric acid, mixing and reading the pH; a stopwatch was then started and simultaneously 2·00 ml of 5% sodium citrate solution were delivered from a 2-ml syringe; 5 sec after addition of the citrate, 1·00 ml of the tin(II) chloride solution was added from a 2·ml hypodermic syringe. The mixture was quantitatively transferred to a 100-ml volumetric flask, diluted to the mark and mixed. After 30·0 min the absorbance at 695 nm was read. Figure 2 shows the typical pH-dependence of a heteropoly acid system. A pH of 4·3 was chosen as optimum for maximum sensitivity and minimum pH-dependence.

Choice of acid

Sulphuric, acetic and nitric acids were also tried. Sulphuric acid resulted in a lower absorbance than that obtained with hydrochloric acid, probably because a molybdophosphoric acid–sulphate complex is formed under the experimental conditions.[1–4] Acetic acid also gave lower absorbance. Though nitric acid gave slightly
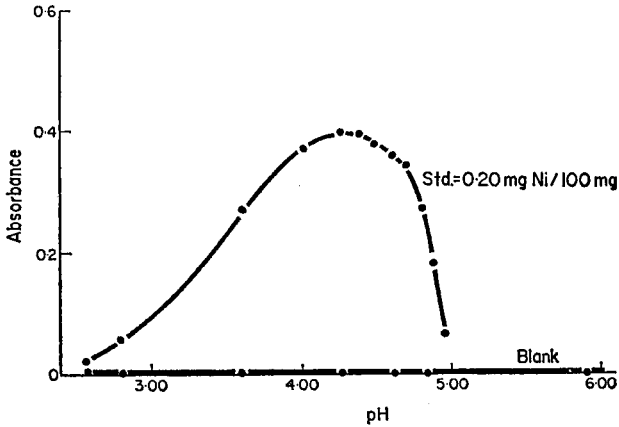
FIG. 2.—Effect of pH.

greater colour enhancement, hydrochloric acid was chosen because of its non-oxidizing nature.

Effect of molybdate–phosphate concentration

The procedure outlined under *Effect of pH* was used except that the amount of molybdate–phosphate reagent was varied, 3 ml of nickel solution were used and the pH was adjusted to 4·3. A blank was run with each sample. Figure 3 shows the results. A volume of 5 ml of molybdate–phosphate mixture was chosen as optimum. Volumes greater than 6·0 ml gave an increased absorbance in both sample and blank; this was attributed to lack of sufficient citrate to eliminate the excess of molybdophosphoric acid.
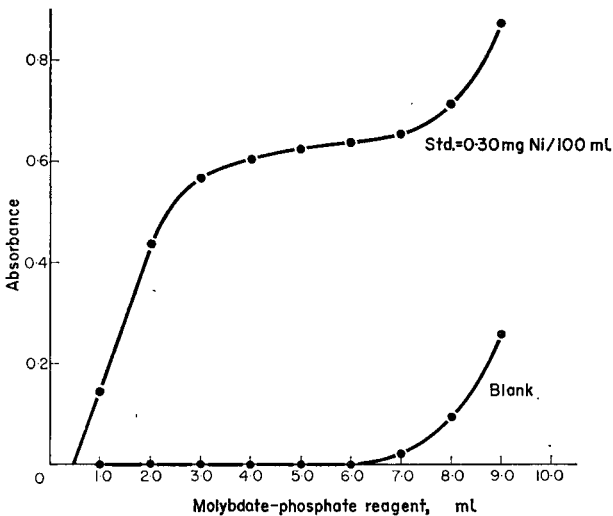
FIG. 3.—Effect of molybdate–phosphate concentration.

Choice of reductant and effect of reductant concentration

Citrate rapidly destroys the molybdate–phosphate–Ni(II) complex so a fast reductant is necessary to complete the reduction before the reducible species is destroyed. Only tin(II) chloride was found to meet this requirement. Figure 4 shows the effect of varying the reductant concentration. A volume of 2·0 ml of the 1% tin(II) chloride reductant was chosen as the most satisfactory.
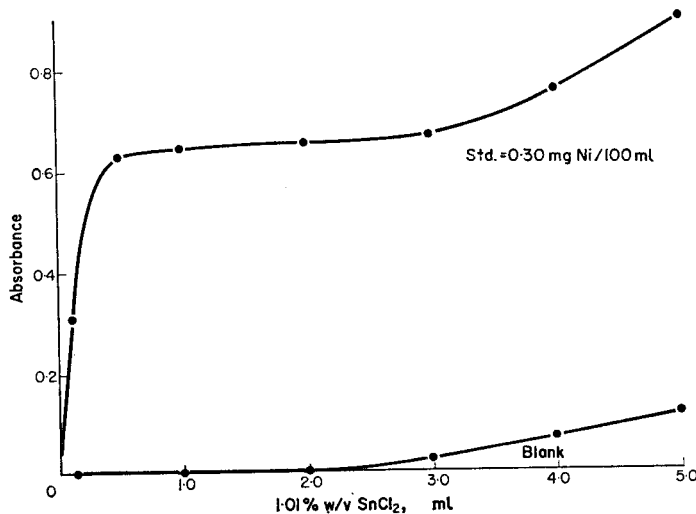
FIG. 4.—Effect of concentration of tin(II) chloride.

Effect of citrate concentration

Figure 5 shows the results of varying the citrate concentration. At low citrate concentrations, the blanks and samples show high absorbance, the difference reflecting the lack of sufficient citrate to complex the excess of molybdophosphoric acid. A volume of 2·0 ml of citrate was chosen as optimum.

Effect of varying time between addition of citrate and tin(II) chloride

The time between addition of citrate and tin(II) was varied from 5 to 100 sec. Figure 6 shows the results. Apparently, citrate almost instantaneously destroys the excess of molybdophosphoric acid but destroys the molybdate–phosphate–Ni(II) complex at a much slower rate. A time interval of 5 sec was chosen as convenient.

Effect of colour development time

Immediately following reduction, the solution exhibits its greatest absorbance. The absorbance decreases slightly for a period of 5 min, than remains constant until 30 min after the reductant has been added; after this time it decreases slowly. All studies were made with a development time of 10–30 min; 20 min is optimum, being in the middle of the absorbance *vs.* plateau, but 30 min gives greater flexibility when a series of samples is run.

Effect of diverse ions

Varying amounts of the diverse ions from 0 to 100 ppm were added to 3-ml portions of the 100-ppm nickel standard and the effect on the absorbance was noted.
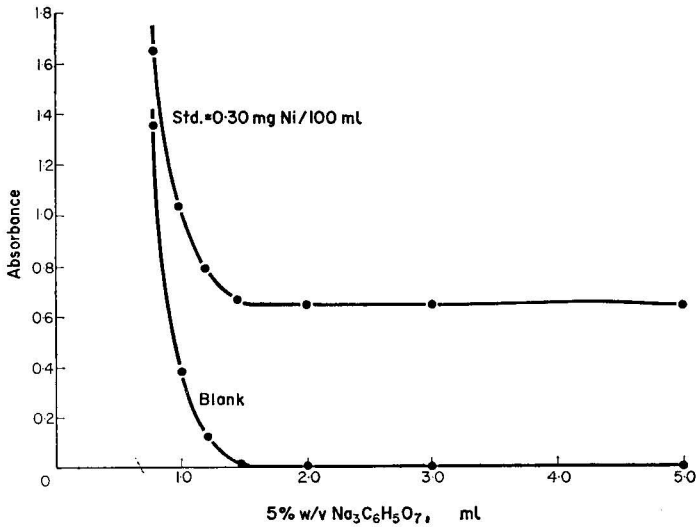
Fig. 5.—Effect of citrate concentration.

Table I shows the permitted concentrations of the diverse ions studied. A 2·0% error in the determination of nickel was considered tolerable. Besides those ions listed in the table, vanadium, titanium, silicon, germanium and tungsten interfere seriously.

Effect of temperature

The temperature of the water-bath used for storage of the samples during colour development was varied. As expected, higher temperatures result in diminished absorbance because of increased dissociation of the reducible complex. Unless the room temperature can be controlled, a thermostat controlled to $\pm 1°$ should be used.

Chemistry of the system

Visible evidence for an interaction between nickel(II) and molybdophosphoric acid is manifested by a yellow colour produced on mixing the reagents, the intensity of
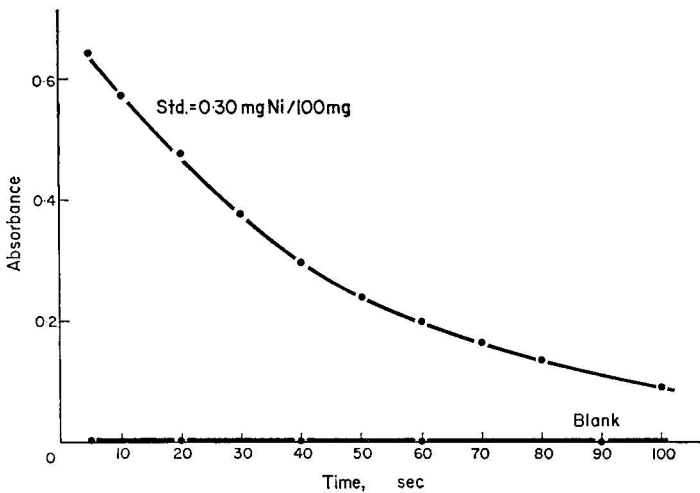
Fig. 6.—Effect of varying time between addition of citrate and tin(II) chloride.

Table I.—Effect of diverse ions

Ion	Added as	Amount permitted, *ppm*
Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	5
Cl^-	$NaCl$	100
SO_4^{2-}	Na_2SO_4	100
Fe^{3+}	$FeCl_3 \cdot 6H_2O$	ppte.
Cd^{2+}	$Cd(NO_3)_2 \cdot 4H_2O$	ppte.
Zn^{2+}	$ZnCl_2$	6
Mg^{2+}	$MgCl_2$	13
Al^{3+}	$Al(NO_3)_3$	ppte.
Mn^{2+}	$MnCl_2$	16
Cu^{2+}	$Cu(NO_3)_2 \cdot 3H_2O$	*
Cr^{3+}	$Cr(NO_3)_3 \cdot 9H_2O$	†
ClO_4^-	$KClO_4$	100
$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	100
IO_3^-	KIO_3	100
SCN^-	$KSCN$	100
Br^-	KBr	100
NO_3^-	$NaNO_3$	100
SO_3^{2-}	Na_2SO_3	100

* Forms citrate complex.
† Complete interference.

which is proportional to the nickel concentration. Further indication of interaction is given by a bathochromic shift in the ultraviolet spectral region, proportional to the nickel concentration.

Mole-ratio studies gave contradictory results and failed to reveal the stoichiometry of the system. However, studies on the mole ratio of nickel phosphate indicated that more than one complex may exist, depending on the nickel concentration.

This behaviour leads to the conclusion that a mixed heteropoly acid of molybdo-phosphoric acid and nickel(II) is formed in the system.

Zusammenfassung—Ein empfindliches spektrophotometrisches Ver-fahren zur Bestimmung von Nickel wurde entwickelt; es beruht auf der Reduktion eines Komplexes aus Molybdophosphorsäure und Ni(II) bei pH 4,3. Ein Überschuß von Molybdophosphorsäure wird durch Komplexbildung mit Natriumcitrat entfernt. Das Verfahren geht schnell und das System erfüllt das Beersche Besetz bis zur einer oberen Grenze von 5 ppm Ni(II). Cer molare Extinktionskoeffizient betragt $1,30 \times 10^3 1\ mol^{-1}\ mm^{-1}$. Das Verfahren schneidet im Vergleich mit bekannten photometrischen Bestimmungsmethoden für Nikkel gut ab; es ist empfindlich und hinreichend selektiv.

Résumé—On a élaboré une méthode spectrophotométrique sensible pour le dosage du nickel, basée sur la réduction d'un complexe formé entre l'acide molybdophosphorique et Ni(II) à pH 4,3. L'excès d'acide molybdophosphorique est éliminé par complexation avec le citrate de sodium. La méthode est rapide et le système obéit à la loi de Beer jusqu' à 5 p.p.m. de Ni(II). Le coefficient d'absorption molaire est de $1,30 \times 10^3\ 1.mole^{-1}.mm^{-1}$. La technique est favorablement comp-arable, en sensibilité, aux méthodes photométriques existant pour le nickel, et elle est raisonnablement sélective.

REFERENCES

1. J. C. Guyon and L. J. Cline, *Anal. Chem.*, 1965, **37**, 1391.
2. R. L. Heller, *Ph.D. Thesis*, University of Missouri, Columbia, Mo., 1969.
3. R. M. Matulis, *Ph.D. Thesis*, University of Missouri, Columbia, Mo., 1966.
4. K. Schriever and R. Toussaint, *Ber.*, 1958, **91**, 2639.

SHORT COMMUNICATIONS

Pyridine-2-aldoxime and 6-methylpyridine-2-aldoxime as gravimetric reagents for estimation of palladium(II) and uranium(VI)

PYRIDINE-2-ALDOXIME (I) has already been used as a spectrophotometric reagent for the estimation of iron(II),[1] cobalt(II),[2] gold(III)[3] and palladium(II),[4] and as a gravimetric reagent for cadmium(II),[5] while its 6-methyl derivative (II) has been used as a spectrophotometric reagent for iron(II).[6] With palladium(II), (I) has been reported to form a precipitate,[4] and complexes having the composition
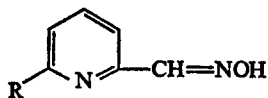
(I) R = H
(II) R = CH$_3$

PdL$_2$,[7] PdL$_2$·HCl,[7] PdL$_2$·2H$_2$O,[8] PdHL$_2$·NO$_3$[8] and PdHL$_2$·PdCl$_4$.[8] We have confirmed that on the addition of aqueous pyridine-2-aldoxime to palladium(II) chloride solution, a shining yellow precipitate (PdL$_2$) is formed instantaneously and the precipitation is quantitative over the pH range 3·0–11·0, whereas from nitrate solutions (I) quantitatively precipitates a yellow complex PdL$_2$·HNO$_3$ over the pH range 0·5–6·0. Both complexes can be used for the gravimetric estimation of palladium(II) in presence of large quantities of Fe^{3+}, Co^{2+}, Ni^{2+} and the noble metals except Au^{3+} and Os^{4+}. With uranium(VI), (I) and (II) form yellow precipitates having the compositions UO$_2$(C$_6$H$_5$N$_2$O)$_2$ and UO$_2$(C$_7$H$_7$N$_2$O)$_2$ respectively, which can be used for the gravimetric estimation of uranium(VI) in presence of large quantities of thorium, lanthanum and cerium, even when these are present together. Pd(II) does not form any insoluble compounds with (II) under the experimental conditions used.

EXPERIMENTAL

Reagents

Pyridine-2-aldoxime. Recrystallized from water and used as 1% aqueous solution.
6-Methylpyridine-2-aldoxime. Used as 1% acetone solution.
Palladium(II) solution. The chloride or nitrate was dissolved in 1M hydrochloric or nitric acid respectively, and standardized gravimetrically with dimethylglyoxime.
Uranium(VI) solution. UO$_2$(NO$_3$)$_2$·6H$_2$O dissolved in water, and standardized with oxine. Analytical grade reagents were used where possible.

Determination of palladium(II)

From palladium(II) chloride solution. To 50 ml of aqueous palladium(II) chloride solution containing 1–20 mg of Pd, add 1% pyridine-2-aldoxime solution gradually with constant stirring till 5 ml per 10 mg of Pd have been added. Adjust the pH to ∼4, keep the solution at room temperature (20–30°) for 15 min and filter off on a tared sintered-glass crucible, porosity-3. Wash the precipitate free from chloride with cold water, dry it at 120–130° and weigh as Pd(C$_6$H$_5$N$_2$O)$_2$.
From palladium(II) nitrate solution. Add reagent as before, to the 1M nitric acid solution of palladium, then digest at 50–60° for ∼15 min, cool to room temperature, and filter off as before. Transfer the precipitate from the beaker and wash it with 0·5M nitric acid till free from all ions except nitrate. Dry the precipitate at 130–140° and weigh as Pd(C$_6$H$_5$N$_2$O)$_2$·HNO$_3$.

Determination of uranium(VI)

With pyridine-2-aldoxime. To 25 ml of uranyl nitrate solution containing 6–50 mg of U, add 1% reagent solution gradually with stirring till 4 ml per 10 mg of U have been added. Adjust the pH to 4, digest the yellow precipitate at 50–60° for ∼15 min, then keep it at room temperature for ∼30 min to settle. Filter off on a porosity-3 sintered-glass crucible, and wash free from nitrate with cold water, dry at 120–130°, and weigh as UO$_2$(C$_6$H$_5$N$_2$O)$_2$.

With 6-methylpyridine-2-aldoxime. Add 1% acetone solution of the reagent gradually with stirring till 4 ml per 10 mg of U have been added. Leave for ~30 min for the precipitate to settle. Filter off on a porosity-3 sintered-glass crucible, and wash with hot water till free from nitrate ions and the reagent [tested with iron(II) solution]. Dry at 120–130°, and weigh as $UO_2(C_7H_7N_2O)_2$.

RESULTS AND DISCUSSION

The errors were ±0·4% for 3–20 mg of Pd(II) and ±0·2% for 12–50 mg of U. Errors up to 1% were observed for smaller amounts.

Palladium(II) is completely precipitated from chloride medium at pH 3–11 and from nitrate media between $1N$ HNO_3 and pH 6. Pyridine-2-aldoxime precipitates uranium(VI) completely at pH 3·5–10·0, and 6-methylpyridine-2-aldoxime does so at pH 3·0–10·5.

Palladium(II)

Tenfold amounts of acetate, oxalate, sulphate, tartrate, phosphate, fluoride, perchlorate, nickel, copper(II), cobalt(II), cadmium, zinc, bismuth, lead, antimony(III), iron(III), mercury(II), and four-fold quantities of platinum(IV), iridium(IV), ruthenium(III) and rhodium(III) do not interfere. Since palladium(II) can be readily separated from other platinum metals higher amounts of other platinum metals were not tested. Gold(III) and silver(I) even in minute quantities cause interference as they are reduced to the elemental state by the reagent. Osmium(IV), in more than twice the amount of palladium(II), and traces of iron(II), interfere as their complexes with pyridine-2-aldoxime are strongly adsorbed on the palladium precipitate, and cannot be washed out. Interference due to iron(II), however, can be eliminated by oxidizing it to iron(III); interference due to the platinum metals can be overcome by boiling with excess of the reagent for ~30 min to complex the platinum metals, cooling and then raising the pH to 4 (Methyl Red); the palladium(II) complex is then precipitated. If antimony is present, palladium should be precipitated from nitric acid medium in presence of tartaric acid.

Uranium(VI)

With both reagents uranium can be successfully estimated in presence of 10-fold quantities of thorium(IV), cerium(III) and lanthanum(III), even when these are present together (maximum error + %1 for 10-fold amounts of all three), as well as in the presence of 20-fold quantities of acetate, oxalate and borate. Cerium(IV), when present in amount thrice that of uranium(VI) does not interfere; the interference due to larger quantities can be removed by reduction to cerium(III). Tartrate and citrate interfere by complexing the uranium(VI), phosphate precipitates uranium(VI) at the pH used, and titanium(IV) and zirconium(IV) salts are hydrolysed under the conditions of the estimation and hence interfere.

Properties of the complexes

The complex obtained from palladium(II) chloride is extractable into organic solvents such as chloroform. It does not give a positive test for chlorine after fusion with sodium and is not exchanged by either IRA 410(OH) or IRC 50(H), indicating that the complex is neutral. The complex from palladium(II) nitrate is insoluble in nitric acid and in water in presence of excess of nitrate ions, but is soluble in water, not extracted by chloroform or benzene, is exchanged by IRC 50(H) and gives a positive test for nitrate ions, indicating an ionic complex. The uranium(VI) complexes with pyridine-2-aldoxime and 6-methylpyridine-2-aldoxime, are not extracted by chloroform or benzene, but are partially extracted into higher alcohols, e.g. butanol, isopentanol, cyclohexanol. The uranium(VI) complexes are not exchanged by either the IRA 401(OH) or IRC 50(H) resins, do not give a positive test for nitrate ions, and thus are neutral.

On the basis of these observations and by analogy with the copper(II) complexes with pyridine-2-aldoxime,[9] the following structures are suggested:

$$\begin{pmatrix} M = Pd; & R = H \\ M = UO_2; & R = H \text{ or } CH_3 \end{pmatrix}$$
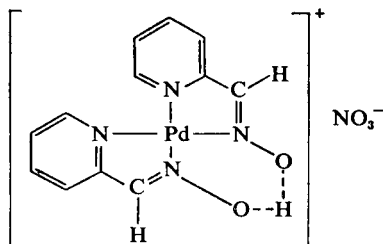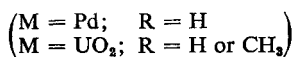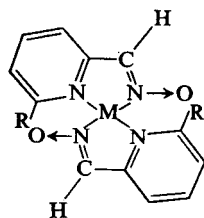
The nitrate content of the Pd(II)–(I) complex precipitated from nitrate solutions was found to be 17·1%; Pd(C$_6$H$_5$N$_2$O)$_2$·HNO$_3$ requires NO$_3^-$ = 15·1%, supporting these conclusions.

Department of Chemistry   NARAYAN KUMAR
University of Delhi   G. S. MANKU
Delhi-7, India   A. N. BHAT
                                                                       B. D. JAIN

Summary—Pyridine-2-aldoxime (I) has been found to be a sensitive reagent for the gravimetric determination of palladium(II). From chloride medium, precipitation is complete at pH 3·0–11·0, and in solution containing 1N HNO$_3$ to pH 6·0. The compositions of the precipitates (dried at 130°) correspond to PdL$_2$ and PdL$_2$·HNO$_3$ (HL representing the reagent) respectively. Pd(II) can be estimated gravimetrically in presence of acetate, oxalate, tartrate, phosphate, fluoride borate, perchlorate, Cu(II), Cd, Co(II), Fe(III), Ni, Zn, Pb, Bi, Sb(III), Pt(IV), Ir(IV), Ru(III), Rh(III); Os(IV) in quantities more than twice that of Pd(II), and Ag(I), Au(III) and Fe(II) even in traces cause serious interference. The yellow uranium(VI) complex with (I) is precipitated quantitatively over the pH range 3·5–10·0 and, after washing and drying corresponds to the composition (C$_6$H$_5$N$_2$O)$_2$UO$_2$ The uranium(VI) complex with 6-methylpyridine-2-aldoxime (II) is precipitated quantitatively over the pH range 3·0–10·5, and after washing and drying at 120–130° corresponds to UO$_2$(C$_7$H$_7$N$_2$O)$_2$. Both (I) and (II) are suitable for the estimation of 1–50 mg of uranium(VI) in the presence of up to 10-fold quantities of Th(IV), La(III) and Ce(III) even when present together. Ce(IV) in quantities more than three times that of U must be reduced to Ce(III). Tartrate, citrate, phosphate, Ti(IV) and Zr interfere, but acetate, oxalate, and borate do not.

Zusammenfassung—Pyridin-2-aldoxim (I) hat sich als empfindliches Reagens zur gravimetrischen Bestimmung von Palladium(II) herausgestellt. Aus Chloridmedium ist die Fällung bei pH 3,0–11,0 quantitativ, aus Salpetersäure bei 1N HNO$_3$–pH 6,0. Die Zusammensetzung der (bei 130° getrockneten) Niederschläge entspricht PdL$_2$ bzw. PdL$_2$·HNO$_3$ (HL bedeutet den Liganden). Pd(II) kann in Gegenwart von Acetat, Oxalat, Tartrat, Phosphat, Fluorid, Borat, Perchlorat, Cu(II), Cd, Co(II), Fe(III), Ni, Zn, Pb, Bi, Sb(III), Pt(IV), Ir(IV), Ru(III) und Rh(III) gravimetrisch bestimmt werden; Os(IV) in mehr als doppelter Menge neben Pd(II) sowie, auch in Spuren, Ag(I), Au(III) und Fe(II) stören wesentlich. Der gelbe Uran(VI)-Komplex mit (I) fällt quantitativ im pH-Bereich 3,5–10,0 aus und hat nach Waschen und Trocknen die Zusammensetzung (C$_6$H$_5$N$_2$O)$_2$UO$_2$. Der Uran(VI)-Komplex mit 6-Methylpyridin-2-aldoxim (II) fällt im pH-Bereich 3,0–10,5 quantitativ aus und entspricht nach waschen und Trocknen bei 120–130° UO$_2$(C$_7$H$_7$N$_2$O)$_2$. (I) und (II) eignen sich zur Bestimmung von 1–50 mg Uran(VI) in Gegenwart bis zu 10-facher Mengen Th(IV), La(III) und Ce(III), auch wenn sie gemeinsam auftretsen. Ist Ce(IV) in mehr als dreifacher Menge neben U vorhanden, so muß es zu Ce(III) reduziert werden. Tartrat, Citrat, Phosphat, Ti(IV) und Zr stören, Acetat, Oxalat und Borat dagegen nicht.

Résumé—On a trouvé que la pyridine 2-aldoxime (I) est un réactif sensible pour le dosage gravimétrique du palladium (II). A partir d'un milieu chlorure, la précipitation est complète à pH 3,0–11,0 et en acide nitrique à 1N HNO$_3$–pH 6,0. Les compositions des précipités (séchés à 130°) correspondent à PdL$_2$ et PdL$_2$, NO$_3$H (HL représentant le réactif) respectivement. On peut doser Pd(II) gravimétriquement en présence d'acétate, oxalate, tartrate, phosphate, fluorure, borate, perchlorate, Cu(II), Cd, Co(II), Fe(III), Ni, Zn, Pb, Bi, Sb(III), Pt(IV), Ir(IV), Ru(III), Rh(III); Os(IV) en quantités supérieures à deux fois celle de Pd(II), et Ag(I), Au(III) et Fe(II) même à l'état de traces apportent une

gêne sérieuse. Le complexe jaune d'uranium(VI) avec (I) est précipité quantitativement dans le domaine de pH 3,5-10,0 et, après lavage et séchage, correspond à la composition $UO_2(C_6H_5N_2O)_2$. Le complexe d'uranium(VI) avec la 6-méthylpyridine 2-aldoxime (II) est précipité quantitativement dans le domaine de pH 3,0-10,5 et, après lavage et séchage à 120°-130°, correspond à $UO_2(C_7H_7N_2O)_2$. (I) et (II) conviennent tous deux au dosage de 1-50 mg d'uranium (VI) en la présence de quantités de Th(IV), La(III) et Ce(III) pouvant être jusqu'à 10 fois supérieures, même lorsque ces éléments sont présents ensemble. Ce(IV) en quantités supérieures à trois celle de U doit être réduit en Ce(III). Les tartrate, citrate, phosphate, Ti(IV) et Zr interfèrent, mais non les acétate, oxalate et borate.

REFERENCES

1. A. N. Bhat and B. D. Jain, *J. Sci. Ind. Res., India*, 1962, **21B**, 576.
2. E. Gagliardi and P. Presinger, *Mikrochim. Ichnoanal. Acta*, 1965, **4**, 791.
3. A. Daodrio and C. B. Marone, *Anales Real. Soc. Espan. Fis. Quim. (Madrid)*, 1967, **63**, 553.
4. R. T. Pflaum, M. W. Wehking and R. E. Jensen, *Talanta*, 1964, **8**, 1193.
5. A. Daodrio and M. Arroyo, *Anales Real Soc. Espan. Fis. Quim. (Madrid)*, 1964, **60**, 397, 403.
6. A. N. Bhat and B. D. Jain, *Proc. Indian Acad. Sci.*, 1962, **56A**, 285.
7. R. A. Krause and D. H. Busch, *J. Am. Chem. Soc.*, 1960, **82**, 4830.
8. C. F. Liu and C. H. Liu, *Inorg. Chem.*, 1963, **2**, 706.
9. *Idem, J. Am. Chem. Soc.*, 1961, **83**, 4169.

Separation and determination of mixtures containing *p*-aminosalicylic acid and *m*-aminophenol

p-AMINOSALICYLIC ACID (PAS) decarboxylates to form *m*-aminophenol (MAP) as its major breakdown product. In order to study the stability of PAS and its salts in aqueous medium, a procedure has been developed for determining both components, which is based on chromatographic separation on an ion-exchange resin, followed by non-aqueous titration of the individual components.

The U.S.P. XVII method of analysis[1] is based on the diazotization reaction, which does not distinguish between PAS and MAP. The MAP content is determined separately by colorimetric analysis. Several procedures have been proposed for determining PAS alone, as salts and as pharmaceutical preparations. These have been noted earlier.[2-4] Non-aqueous titration procedures have been reviewed by Kucharsky and Safarík.[5] In our previous paper[4] a specific method was reported for PAS, its salts and preparations, and a non-aqueous differentiating titration was suggested for PAS and MAP.

EXPERIMENTAL

Reagents

p-Aminosalicylic acid and *m*-aminophenol were the best quality available from commercial sources. The *m*-aminophenol was further purified by recrystallization from hot water.

Sodium methoxide (0·1*M*) in benzene–methanol and 0·1*M* perchloric acid in glacial acetic acid were prepared and standardized as directed in U.S.P. XVII.[1]

Hydrochloric acid (2*M*) in 50% ethanol.

Mercuric acetate solution, 6%, in glacial acetic acid.

All chemicals and solvents were reagent grade.

Chromatography column

A 50-ml burette (10 mm bore) was used as a chromatographic column. It was plugged at the base with glass-wool to support the Dowex 50W-X8 (200–400 mesh) resin column, which was 30 mm in length and prepared as described earlier.[6] The column was conditioned with dimethylformamide for 24 hr before use.

Procedure

A series of mixtures containing varying proportions of PAS and MAP, as listed in Table I, was prepared by weight from the finely powdered compounds. The PAS was added first to a 250-ml amber, wide-mouth, screw-cap powder jar. The MAP was then added, and the bottle capped and rotated end over end until a homogeneous mixture resulted (about 5 min).

Each mixture was analysed for MAP and PAS content, the sample used containing 1 mequiv of MAP. The sample was dissolved in 20 ml of dimethylformamide and the solution was transferred quantitatively to the resin column with the aid of an additional 10 ml of dimethylformamide. The rate of flow through the column was controlled at 0·2 ml/min. The column was washed with three 10-ml portions of dimethylformamide. The eluate and washings were collected in a 50-ml volumetric flask and diluted to volume with dimethylformamide. An aliquot containing about 1 mequiv of PAS was transferred to a 150-ml beaker, dimethylformamide was added to bring the volume to about 50 ml, 1 drop of Thymol Blue indicator solution (1% in dimethylformamide) was added, and the solution, stirred magnetically and protected from carbon dioxide *etc*,[7] was titrated with 0·1M sodium methoxide to the first permanent blue colour. The PAS content of the mixture was determined. Results are recorded in Table I.

TABLE 1.—ANALYSIS OF MIXTURES CONTAINING VARYING PROPORTIONS OF PAS AND MAP

Composition of mixture		Found	
PAS, %	MAP, %	PAS, %	MAP, %
98·99	1·01	$98·8 \pm 0·0_2$	$1·1_6 \pm 0·0_3$
94·08	5·92	$94·4 \pm 0·1_4$	$5·6_3 \pm 0·1_7$
89·04	10·96	$88·5 \pm 0·2_3$	$11·5 \pm 0·2_3$
79·16	20·84	$77·0 \pm 0·1_3$	$23·0 \pm 0·1_0$
49·92	50·08	$49·6 \pm 0·8_5$	$50·4 \pm 0·8_5$

The resin column was washed with three 20-ml portions of ethanol and the washings were discarded. A total of 30 ml of 2M in 50% hydrochloric and aqueous ethanol was passed through the column at a flow-rate of 0·2 ml/min. The eluate, containing *m*-aminophenol hydrochloride, was evaporated to dryness at room temperature by passing a stream of clean air over the solution. Then 5 ml of 50% aqueous ethanol were added and the solution was again evaporated to dryness; this step was repeated. Finally, the residue was dissolved in 20 ml of glacial acetic acid, 10 ml of 6% mercuric acetate in glacial acetic acid were added,[8] followed by one drop of Methyl Violet indicator solution (1% in glacial acetic acid), and the mixture, stirred magnetically, was titrated with 0·1M perchloric acid to the first permanent emerald green colour. The MAP content was determined. Results are shown in Table I.

After each run the ion-exchange resin was regenerated by washing with water until the eluate pH was 7. Three 10-ml portions of ethanol were passed through the column, which was then washed with dimethylformamide and left filled with this solvent for 24 hr before re-use. Immediately before use the column was washed with a fresh 10-ml portion of dimethylformamide. The resin was used 5 times before being discarded.

DISCUSSION

Separation of PAS from MAP is readily achieved because of the stronger basic properties of MAP. Dowex 50W-X8, a sulphonic acid type resin, is a sufficiently strong acid to extract the MAP from the mixture. The PAS (pK_a = 3·25) is not retained by the column because of its strongly acidic nature. It appears in the eluate and is readily titrated in non-aqueous medium with sodium methoxide. The MAP is displaced from the resin with hydrochloric acid in 50% aqueous ethanol. Ethanol is used as the solvent to solubilize the MAP hydrochloride and to facilitate the evaporation of the solvent at room temperature. The MAP hydrochloride decomposed somewhat when heated for prolonged periods. By the proposed procedure no decomposition occurred; the MAP hydrochloride was recovered as a white crystalline powder. It was readily titratable in glacial acetic acid with perchloric acid. The presence of mercury(II) acetate in the titration mixture was necessary for successful titration [undissociated mercury(II) chloride is formed and the liberated acetate acts as a base].

Department of Pharmacy   MARTIN I. BLAKE
University of Illinois   JAMES HUNT
*   at the Medical Center*
Chicago, Illinois 60612, *U.S.A.*

Summary—A procedure is described for separating and determining *p*-aminosalicylic acid and *m*-aminophenol in mixtures. Separation is effected by passing a solution of the mixture in dimethylformamide through a column of strong cation-exchange resin. The eluate containing the *p*-aminosalicylic acid is titrated with sodium methoxide. The *m*-aminophenol is eluted from the column with ethanolic HCl. The eluate is evaporated to dryness, the residue dissolved in acetic acid, and the solution titrated with perchloric acid.

Zusammenfassung—Ein Verfahren zur Trennung und Bestimmung von *p*-Aminosalicylsäure und *m*-Aminophenol in Gemischen wird beschrieben. Die Trennung erreicht man, wenn man eine Lösung des Gemisches in Dimethylformamid durch eine Säule mit starkem Kationenaustauschharz laufen läßt. Das die *p*-Aminosalicylsäure enthaltende Eluat wird mit Natrium-methylat titriert. Das *m*-Aminophenol wird mit äthanolischer Salzsäure von der Säule eluiert. Das Eluat wird zur Trockne eingedampft, der Rückstand in Essigsäure aufgenommen und die Lösung mit Überchlorsäure titriert.

Résumé—On décrit une technique pour la séparation et le dosage de l'acide *p*-aminosalicylique et du *m*-aminophénol dans des mélanges. On effectue la séparation en passant une solution du mélange en diméthylformamide sur une colonne de résine échangeuse de cations forte. L'éluat contenant l'acide *p*-aminosalicylique est titré au méthoxyde de sodium. Le *m*-aminophénol est élué de la colonne par HCl ·éthanolique. L'éluat est évaporé à sec, le résidu dissous en acide acétique et la solution titrée à l'acide perchlorique.

REFERENCES

1. *The United States Pharmacopeia*, 17th rev., pp. 36, 1084, 1087. Mack, Easton, Pa., 1965.
2. J. L. Lach and J. Cohen, *Drug Std.*, 1960, **28**, 65.
3. E. Schulek, L. Maros, and I. Perl-Molnár, *Talanta*, 1963, **10**, 561.
4. J. Hunt and M. I. Blake, *J. Pharm. Sci.*, 1970 **59**, 683.
5. J. Kucharsky and L. Safarík, *Titrations in Non-Aqueous Solvents*, p. 182. Elsevier, New York 1965.
6. M. C. Vincent and M. I. Blake, *Drug. Std.*, 1958, **26**, 206.
7. M. I. Blake, *J. Am. Pharm. Assoc.*, 1957, **46**, 287.
8. C. W. Pifer and E. G. Woltish, *Anal. Chem.*, 1952, **24**, 300.

The complexes of bismuth(III) and nitrilotriacetic acid

NITRILOTRIACETIC ACID [NTA, H_3X, $N(CH_2COOH)_3$] is one of the simplest aminopolycarboxylic acids which form stable complexes with metal cations. There is no full study of the reaction of bismuth(III) and NTA. Iyer, Bhat and Shankar[1] have studied the complex formation of bismuth with NTA and Tiron by potentiometry, but they do not give the stability constants.

EXPERIMENTAL

Reagents

Bismuth perchlorate solution, $1.00 \times 10^{-3}M$. Dissolve an accurately weighed amount of pure metallic bismuth (99·999% purity) in the minimum quantity of nitric acid. Add perchloric acid and evaporate carefully to remove the nitric acid, and then dilute to volume with distilled water. The pH of the solution thus prepared was 1·30.

Nitrilotriacetic acid solution, $2.00 \times 10^{-2}M$. Suspend a known weight of the acid (dried at 105°) in water and add sodium hydroxide to dissolve it completely. Dilute with water to volume. The pH of the solution of NTA was 5·20. Dilute precisely to 1.00×10^{-3} and $2.00 \times 10^{-3}M$ for working solutions.

Control of pH and ionic strength ($\mu = 1$) was achieved by addition of standard solutions of perchloric acid, sodium perchlorate and sodium hydroxide.

The reagents used were *pro analysi* grade.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of solutions of bismuth perchlorate and NTA (in molar ratio 1:2) at different values of pH. Absorption maxima are observed at 190–195, 222, 243 and 271 nm and reach their maximum intensity in $2M$ perchloric acid, $2M$ perchloric acid, pH 1–3 and pH 4·5–7·5 media respectively. That at 222 nm is due to bismuth perchlorate, the others to bismuth–NTA complexes. Above pH 8 bismuth hydroxide precipitates. All further investigations used the absorption maxima at 243 and 271 nm.

The continuous variation and mole-ratio methods prove that the maxima at 243 nm and 271 nm are due to complex compounds with the composition Bi:NTA = 1:1 and 1:2 respectively (Figs. 2 and 3). It is more difficult to prove the existence and nature of the 1:2 complex because at pH 6, the
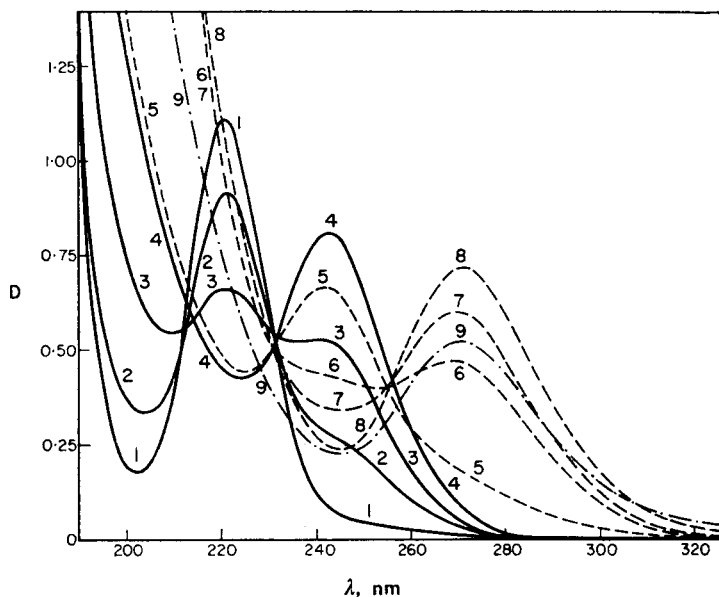
FIG. 1.—Absorption spectra.
$C_{Bi} = 1·00 \times 10^{-4}M$. $C_{NTA} = 2·00 \times 10^{-4}M$. pH: *1*——0·2; *2*—0·0; *3*—0·2; *4*—1·0; *5*—3·4; *6*—4·4; *7*—4·8; *8*—6·1; *9*—7·4; water blank.

optimum value for formation of the 1:2 complex, free bismuth hydrolyses. However, the mole ratio method (at constant concentration of NTA and pH ∼6), can be employed (curves 5 and 6, Fig. 3). An increase in the ratio Bi:NTA beyond 0·7–0·8 results in the partial hydrolysis of the 1:1 complex so the method of continuous variations is not applicable to the 1:2 complex.

The formation of the 1:1 and 1:2 complex compounds can be seen in Fig. 4, which is a plot of the absorbance at 243 nm and 271 nm as a function of pH. It is seen that formation of the 1:1 complex begins at pH about −0·2 (1·5–1·6M perchloric acid) and stops at pH 0·8–1·0. On further increase of the pH the absorbance at 243 nm begins to decrease but that at 271 nm begins to increase and reaches its maximum value at pH 5·8–6·2. Under these conditions the 1:2 complex is formed, which at equivalent ratio of the two components is partially hydrolysed. If an excess of NTA is added, the hydrolysis begins at higher pH (curve 6, Fig. 4).

The formation of the 1:1 complex can be expressed by

$$Bi^{3+} + H_4X^+ = BiH_{4-n}X^{4-n} + nH^+;$$

$$\log \frac{[Bi(H_{4-n}X)^{4-n}]}{[Bi^{3+}][H_4X^+]} = npH + \log K_1,$$
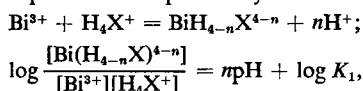
where K_1 is the equilibrium constant. The number of protons released can be established by plotting $\log [Bi(H_{4-n}X)^{4-n}]/[Bi^{3+}][H_4X^+]$ *vs.* pH. The data for the plot were taken from curve 2 of Fig. 4 and

7
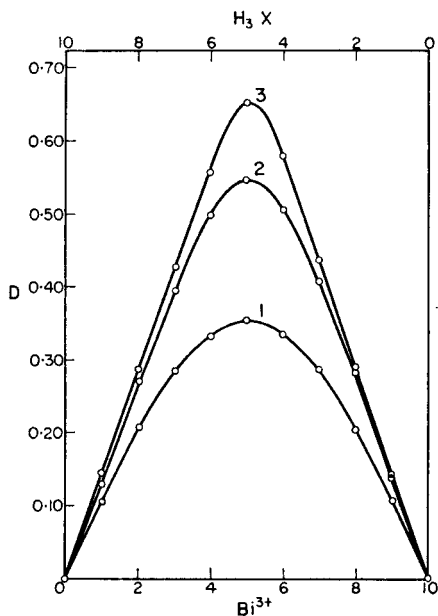
Fig. 2.—Method of continuous variation.
$C_{Bi^{3+}} + C_{NTA} = 2.00 \times 10^{-4}M$; $\lambda = 243$ nm; pH: 1—0.2; 2—0.4 and 3—0.6.
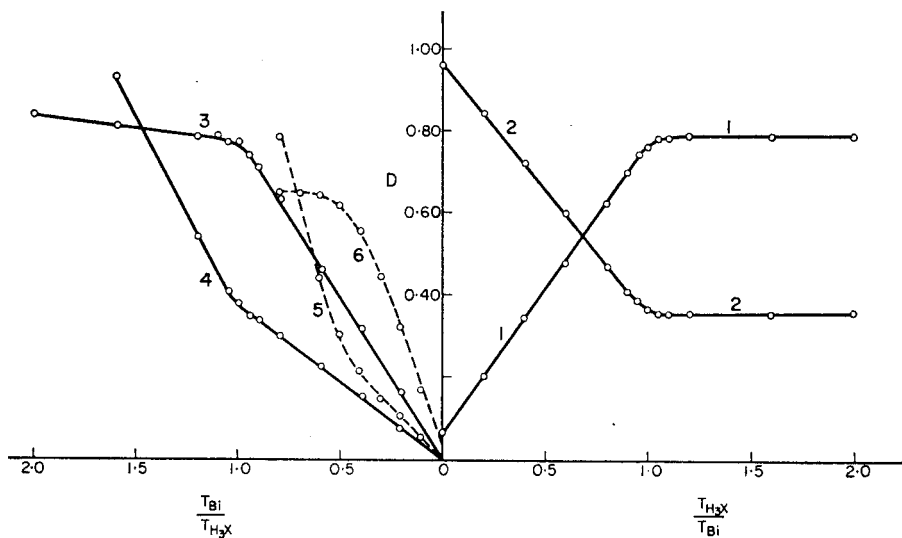
Fig. 3.—Mole-ratio method.
λ: 1, 3 and 5 at 243 nm, 2 and 4 at 222 nm and 6 at 271 nm. pH: 1, 2, 3 and 4 at 1.0,
5 and 6 at 6. $C_{Bi^{3+}}$: 1 and 2—$1.00 \times 10^{-4}M$; C_{NTA}: 3 and 4—$1.00 \times 10^{-4}M$; 5 and
6—$2.00 \times 10^{-4}M$; water blank.

from Fig. 5. The values of n obtained were 3.7 (for Bi:NTA = 2:1) and 3.5 (Bi:NTA = 1:1). The fractional value of n is explained by the fact that in the pH range used, bismuth reacts not only with H_4X^+, but also with H_3X. Therefore, the formation of the 1:1 complex can be expressed by

$$Bi^{3+} + H_4X^+ = BiX + 4H^+$$

and

$$Bi^{3+} + H_3X = BiX + 3H^+.$$
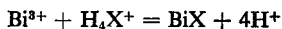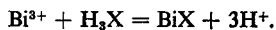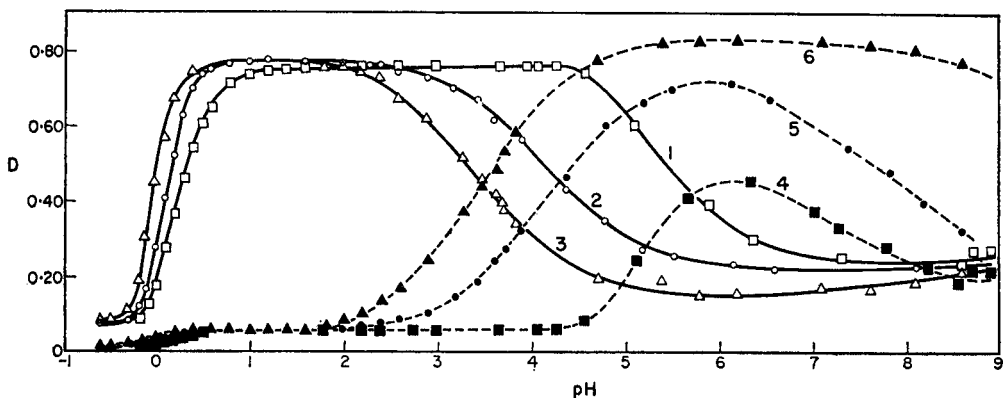
FIG. 4.—Absorbance as function of pH.
λ: *1, 2* and *3*—243 nm; *4, 5* and *6*—271 nm; $C_{Bi^{3+}} = 1.00 \times 10^{-4}M$. C_{NTA}: *1* and
4—$1.00 \times 10^{-4}M$, *2* and *5*—$2.00 \times 10^{-4}M$, *3* and *6*—$5.00 \times 10^{-4}M$; water blank.
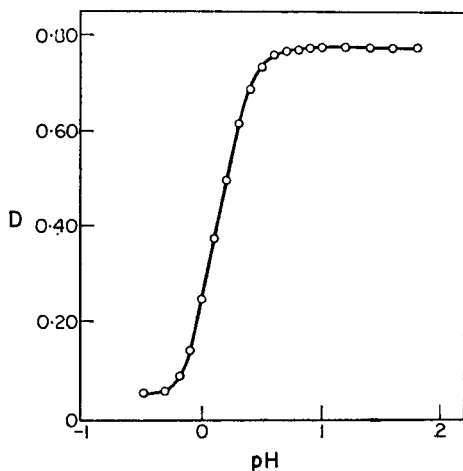
FIG. 5.—Absorbance as function of pH.
$\lambda = 243$ nm; $C_{Bi^{3+}} = 2.00 \times 10^{-4}M$; $C_{NTA} = 1.00 \times 10^{-4}M$; water blank.

The formation of the second complex can be expressed by

$$BiX + H_mX^{(m-3)} = BiX_2^{3-} + mH^+,$$
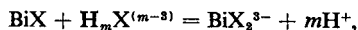
$$\log \frac{[BiX_2]}{[BiX][H_mX]} = m\text{pH} + \log K_2,$$

and the value of m obtained from the slope of a plot of log $[BiX_2]/[BiX][H_mX]$ vs. pH. Such a plot of the data of curves 5 and 6 (Fig. 4) at Bi:NTA ratios of 1:2 and 1:5 gave values for m of 1·0 and 1·1. As can be seen from curves 1 and 4 (Fig. 4) the 1:1 complex hydrolyses at pH 4·5–6 according to

$$2BiX + 3H_2O = BiX_2^{3-} + Bi(OH)_3 + 3H^+.$$
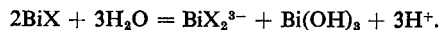
At pH values above 6 the 1:2 complex begins to hydrolyse. Since the position of the absorption maximum does not change and a precipitate of bismuth hydroxide is formed, the hydrolysis may be expressed by

$$BiX_2^{3-} + 3H_2O = Bi(OH)_3 + 2HX^{2-} + H^+.$$
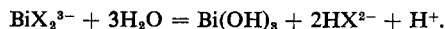
The stability constant of the 1:1 complex was calculated from the dependence of the absorbance at 243 nm on pH, for Bi:NTA ratios = 1:1, 1:2 and 2:1 at constant ionic strength $\mu = 1.0$ (curves 1

and 2 of Fig. 4 and Fig. 5). The maximum absorbance, corresponding to complete combination of all the bismuth as the 1:1 complex, was obtained by adding a large excess of NTA at pH 1, and was found to be 0·800 in a 10-mm cell for $1·00 \times 10^{-4}M$ bismuth, corresponding to a molar absorptivity of $8·00 . 10^3$ l.mole^{-1}.cm^{-1}. The stability constant for BiX was calculated at every 0·1 pH unit (for the interval from $-0·2$ to 0·8) according to the equation:

$$\beta_{\text{BiX}} = \frac{[\text{BiX}]\alpha_{\text{X}^{3-}}}{[\text{Bi}^{3+}]C_{\text{NTA}}},$$

where [BiX] and [Bi^{3+}] are the equilibrium concentrations of BiX and free bismuth, C_{NTA} is the total free NTA concentration irrespective of species and $\alpha_{\text{X}^{3-}}$ is the side-reaction coefficient for NTA:

$$\alpha_{\text{X}^{3-}} = \frac{C_{\text{NTA}}}{[\text{X}^{3-}]}.$$

The equilibrium concentration of the complex compound BiX was calculated from the absorbance and the molar absorptivity. The other equilibrium concentrations were calculated by difference from [BiX] and the initial total concentrations of reactants.

The constants used for the calculation of $\alpha_{\text{X}^{3-}}$ were $\log k_0 = 1·10$, $\log k_1 = 1·98$, $\log k_2 = 2·20$ and $\log k_3 = 8·96$ at ionic strength $\mu = 1·0$ and 20°.[2] The value of β_{BiX} was found to be $3·40 \pm 0·48 \times 10^{17}$ (30 results; 95% confidence limits).

The stepwise formation constant K_2 of BiX$_2{}^{3-}$ was calculated from

$$K_2 = \frac{[\text{BiX}_2{}^{3-}]\cdot\alpha_{\text{X}_3{}^-}}{[\text{BiX}]C_{\text{NTA}}}.$$

The values of K_2 were calculated from curves 5 and 6 of Fig. 4, and found to be $1·06 \pm 0·15 \times 10^9$ (15 results; 95% confidence limits). The overall stability constant of the 1:2 complex is therefore $3·60 \pm 0·62 \times 10^{26}$.

The molar absorptivities of BiX is $8·00 . 10^3$ l.mole^{-1}. cm^{-1} at 243 nm and of BiX$_2{}^{3-}$ $8·20 . 10^3$ l.mole^{-1}.cm^{-1} at 271 nm.

ANALYTICAL APPLICATION

The two complexes can be used for the determination of both bismuth and NTA but it is better to use BiX for photometric determination in the ultraviolet, because of the higher selectivity. The conditions for this determination are: $\lambda = 243$ nm, pH about 1, concentration of bismuth (or NTA) from 1×10^{-5} to $2 \times 10^{-4}M$. The concentration of bismuth used for determination of NTA should not be higher than 2–3 times that of the NTA, and the concentration of the NTA for the determination of bismuth should be 10^{-2}–$10^{-3}M$ (all data refer to use of a 10-mm cell).

No special study of interfering elements has been made but it is obvious that ions with a high absorbance in this region of the spectrum (e.g. NO$_3{}^-$, Fe^{3+}, to a certain degree Pb^{2+} etc.) will interfere. BiX can also form the basis of the spectrophotometric titration of bismuth and NTA.

Institute of Chemical Technology   B. P. KARADAKOV
Sofia-56, Bulgaria   D. I. VENKOVA

Summary—The reaction between bismuth(III) and nitrilotriacetic acid (NTA or H$_3$X) has been investigated by ultraviolet spectrophotometry. It has been established that bismuth(III) and NTA form two complexes with compositions bismuth(III): NTA = 1:1 and 1:2. The absorption maxima are at 243 nm (1:1) and 271 nm (1:2), the molar absorptivities being $8·00 \times 10^3$ and $8·20 \times 10^3$ l.mole^{-1}.cm^{-1} respectively. The stability constants (at $\mu = 1·0$) are: $\log \beta_{\text{BiX}} = 17·53 \pm 0·06$ and $\log \beta_{\text{BiX}_2{}^{3-}} = 26·56 \pm 0·07$. The possibility of the analytical application of BiX is briefly discussed.

Zusammenfassung—Die Reaktion zwischen Wismut(III) und Nitrilotriessigsäure (NTA oder H$_3$X) wurde ultraviolettspektrophotometrisch untersucht. Es wurde festgestellt, daß Wismut(III) und NTA zwei Komplexe mit den Zusammensetzungen Wismut(III):NTA = 1:1 und 1:2 bilden. Die Absorptionsmaxima liegen bei 243 nm (1:1) und 271 nm (1:2); die molaren Extinktionskoeffizienten betragen $8,00 . 10^3$ bzw. $8,20 . 10^3$ l mol^{-1} mm^{-1}. Die Stabilitätskonstanten (bei $\mu = 1,0$) betragen $\log \beta_{\text{BiX}} = 17,53 \pm 0,06$ und $\log \beta_{\text{BiX}_2}{}^{3-} = 26,56 \pm 0,07$. Es wird kurz diskutiert, ob BiX analytische Anwendung finden kann.

Résumé—On a étudié la réaction entre le bismuth(III) et l'acide nitrilo-triacétique (NTA ou H₃X) par spectrophotométrie ultra-violette Il a été établi que bismuth(III) et NTA forment deux complexes de compositions bismuth(III):NTA = 1:1 et 1:2. Les maximums d'absorption sont à 243 nm 1:1) et 271 nm (1:2), les coefficients d'absorption molaires étant $8,00 \times 10^3$ et $8,20 \times 10^3$ l.mole⁻¹ cm⁻¹ respectivement. Les constantes de stabilité (à $\mu = 1,0$) sont: log β_{BiX} = 17,53 ± 0,06 et log $\beta_{BiX_2{}^{3-}}$ = 26,56 ± 0,07. On discute brièvement de la possibilité de l'application analytique de Bix.

REFERENCES

1. R. K. Iyer, T. R. Bhat and J. Shankar, *Indian J. Chem.*, 1966, **4**, 452.
2. G. Anderegg, *Helv. Chim. Acta*, 1967, **50**, 2333.

Copper(I) sulphide-impregnated silicone rubber membranes as selective electrodes for copper(II) ions

THE DEVELOPMENT of precipitate-impregnated membrane electrodes has been successful for anion-selective electrodes. Pungor[1] has developed selective membrane electrodes for chloride, bromide, iodide and sulphate ions, using silicone rubber as an inert matrix. Rechnitz[2] has summarized the responses of Pungor's electrodes toward anions.

Chatterjee and Mitra[3] prepared clay membranes that responded to copper, molybdenum and cobalt ions. Morrazzani-Pelletier and Baffier[4] examined collodion and paraffin membranes, and Buchanan and Seago[5] reported on silicone rubber membranes for nickel and cobalt. However, these membrane electrodes for cations did not exhibit the desired response, stability of potentials, analytical range, or selectivity for the ions concerned. Only the silver-selective electrode (Pungor type) has been commercially developed.

The present paper describes the development of precipitate-impregnated membranes as selective electrodes for copper(II), with copper(I) sulphide and silicone rubber as the precipitate and inert matrix respectively.

EXPERIMENTAL

Preparation of copper(I) sulphide-impregnated silicone rubber membranes

A fine powder of copper(I) sulphide was obtained by heating a mixture of copper powder and sulphur in the molar ratio of 2:1 at 600° for 2 hr in an atmosphere of hydrogen sulphide and grinding the heated mixture to a particle size of less than 10 μm. The powder was mixed with about 25% w/w of silicone rubber. A copper plate ($10 \times 15 \times 1$ mm) or the end 30 mm of a platinum wire (1 mm diameter) was coated with this mixture to a thickness of about 0·5 mm, and heated at 80° to po-lymerize the rubber. The membrane was then soaked in a $10^{-2}M$ solution of copper sulphate for a week. Other resins were also used as inert matrices.

Preparation of pressed epoxy resin membranes

The copper(I) sulphide powder was mixed with up to 10% by weight of epoxy resin. The mixture was compacted under a pressure of 1·50 kg/mm³ to form a tablet with a diameter of 15 mm. After heating at 90° for 12 hr, the tablet was soaked in a $10^{-3}M$ solution of copper sulphate for a week.

Measurement of potentials

Figure 1 shows the cross-section of the membrane electrode. The end of the electrode was put into the test solution and the potentials of the membrane were measured *vs.* S.C.E. as reference electrode at 25·0 ± 0·1°. In the case of the pressed epoxy resin membrane electrodes, the measurement was made as shown in Fig. 2.

RESULTS AND DISCUSSION

The internal electrode and solution commonly used in selective membrane electrodes as shown in Fig. 2 have been eliminated by attaching the membrane to the surface of a copper plate or platinum wire which does not react with the impregnated powder (Fig. 1). This is because their use causes contamination and mechanical weakness of the membrane. The present method of preparation makes it possible to produce selective electrodes which have arbitrary size and form, and which contain the reference electrode within themselves. They can even contain various membranes which respond toward different ions.

The potential response of copper(I) sulphide-impregnated silicone rubber membranes in a solution of copper sulphate is shown in Fig. 3. The activity was derived from the concentration by means of the ion activity coefficients tabulated by Kielland.[6] The slope was Nernstian in the concentration
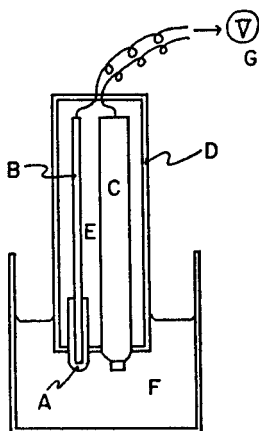
FIG. 1.—Cross-section of copper(I) sulphide-impregnated silicone rubber membrane electrode.
A. Copper(I) sulphide-impregnated silicone rubber membrane. B. Platinum wire. C. Reference electrode (S.C.E.). D. Plastic cover. E. Insulator. F. Test solution. G. pH meter.
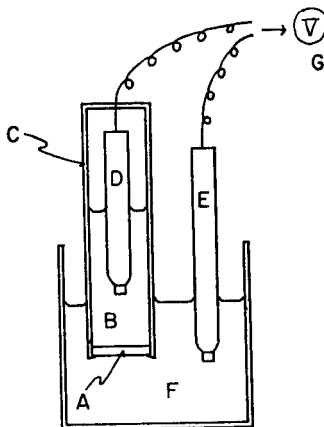
FIG. 2.—Cross-section of pressed epoxy resin membrane electrode.
A. Pressed epoxy resin membrane. B. Internal solution ($10^{-3}M$ copper sulphate). C. Plastic holder. D. Internal electrode (S.C.E.). E. Reference electrode (S.C.E.). F. Test solution. G. pH meter.
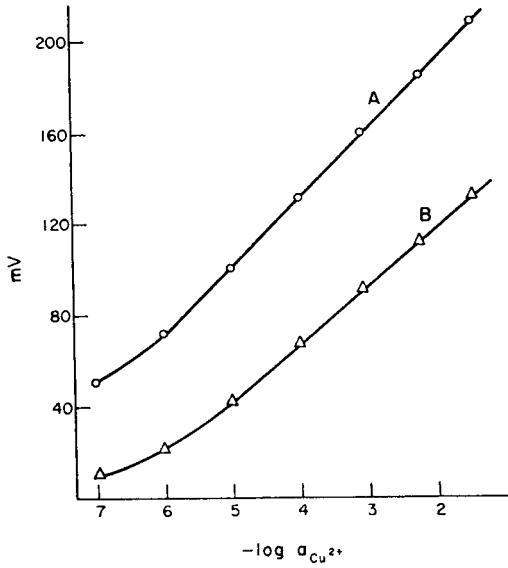
FIG. 3.—Potential responses of silicone rubber membranes impregnated with (*A*) copper(I) sulphide and (*B*) copper(II) sulphide.
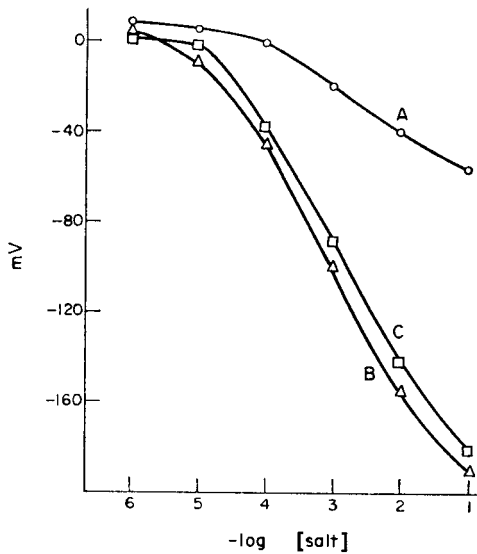
FIG. 4.—Potential responses of copper(I) sulphide-impregnated epoxy resin membranes in the solutions of (*A*) copper sulphate, (*B*) copper nitrate and (*C*) potassium chloride.
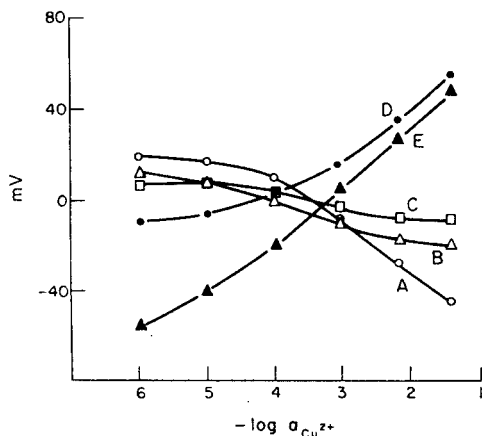
FIG. 5.—Potential responses of pressed epoxy resin membranes.
A. 10% epoxy resin. *B*. 5% epoxy resin. *C*. 2% epoxy resin. *D*. 1% epoxy resin. *E*.
Copper(I) sulphide only.

range 10^{-1}–$10^{-6}M$. The electrode can be used to determine copper in the concentration range 10^{-1}–$10^{-7}M$. The response time of the measuring cell was a few sec for $10^{-1}M$ copper(II) and about 10 min for a $10^{-7}M$ solution. The membrane had to be soaked in a $10^{-2}M$ solution of copper(II) for more than 5 days after its preparation. However, once the membrane was soaked, the potentials were stable and steady even if the membrane was exposed to air for more than two weeks. They were also stable after the membrane was soaked in the solution of copper sulphate for more than a month.

When the fraction of silicone rubber in the membrane was more than 50% by weight, the potentials were unstable and could not be measured. When it was decreased to less than 50%, the time required for soaking in the solution of copper sulphate decreased and the potentials became more stable, and potential properties similar to those shown in Fig. 3 were obtained. However, the lower the fraction of silicone rubber in the membrane, the lower is the adhesive force.

Copper(II) sulphide was used as precipitate in a silicone rubber membrane instead of copper(I) sulphide and the potential responses of this membrane in the solution of copper sulphate are also shown in Fig. 3. The slope of the potential response is about 5 mV less than that in the case of copper(I) sulphide and the chemical or mechanical stability of the membrane was less satisfactory. This is because the copper(II) sulphide powder had been treated at a temperature below 130° (for fear of decomposition).

Influence of pH

The potentials of copper(I) sulphide-impregnated silicone rubber membrane electrodes in $10^{-4}M$ copper(II) did not change at pH values below 7, but decreased sharply when the pH increased above 7, when the precipitation of copper hydroxide occurred [the pH at which the precipitation begins depends on the concentration of copper(II)].

Influence of other ions

Potassium, sodium, calcium, magnesium, aluminium, cadmium, zinc, iron(II), nickel, cobalt(II), chromium(III), lead and ammonium ions at pH values below 7 and chloride, nitrate, sulphate, bromide, perchlorate and acetate ions did not interfere with the determination of copper, and their selectivity ratios for the copper(II) ion were 10^3 or more. The selectivity ratios of iron(III) and iodide ions were 10^2. Ammonium ions (at pH greater than 7), silver, and mercury(II) interfered. The reason is that ammonium ions form stable complex ions with copper(II) in basic solution, and that silver and mercury deposit on the membrane. The sulphide ion caused interference and the membrane can be used as a selective electrode for sulphide.

Effect of temperature

Copper(I) sulphide-impregnated silicone rubber membrane electrodes could be safely used at temperatures between from 10° and 70° and the potentials of the membrane satisfied the Nernst equation within experimental error.

Inert matrices

Epoxy resin was examined as an inert matrix for a copper(I) sulphide-impregnated membrane. The fraction of epoxy resin in the membrane was varied from 10 to 70% by weight and the potential responses developed in the solutions of copper sulphate, copper nitrate and potassium chloride are shown in Fig. 4. Epoxy resin membrane electrodes responded toward anions and the slopes in Fig. 4 were almost independent of the fraction of epoxy resin within the range used. Silver chloride- or barium sulphate-impregnated epoxy resin membranes also responded to anions. In the case of pressed epoxy resin membranes which contain up to 10% of epoxy resin, the lower the fraction of epoxy resin, the smaller the slope of the potential response and the membrane responds to copper(II) when the fraction of resin is less than 2% (Fig. 5), although the Nernst equation is not satisfied.

Polyvinyl chloride, polyvinyl acetate, polyurethane and phenolic resins were examined as inert matrices, and similar results were obtained.

From these results, the membrane impregnated with copper(I) sulphide responds to copper(II)-ion only when the particles of copper(I) sulphide are in contact with each other from one surface of the membrane to the other. When the direct contact of the particles is broken, the potential of the electrode is produced by processes which do not ensure ion-selectivity.

Wireless Research Laboratory   Hiroshi Hirata
Matsushika Electric Industrial Co. Ltd.   Kenji Date®
Kadoma, Osaka, Japan

Summary—Silicone rubber membranes impregnated with copper(I) sulphide have been developed as selective electrodes for copper(II) ions. The internal electrode and solution were eliminated. The Nernst equation was satisfied in the concentration range from 10^{-1} to $10^{-6}M$ copper(II) and the analytical range was from 10^{-1} to $10^{-7}M$. The interference of other ions was examined. Other resins were compared with silicone rubber as inert matrices.

Zusammenfassung—Mit Kupfer(I) sulfid imprägnierte Silikongummimembranen wurden als für Kupfer(II)-Ionen selektive Elektroden entwickelt. Die innere Elektrode und die Lösung wurden weggelassen. Die Nernstsche Gleichung wurde bei Konzentrationen von 10^{-1} bis $10^{-6}M$ Kupfer(II) erfüllt; der analytische Bereich erstreckt sich von 10^{-1} bis $10^{-7}M$. Die Störung durch andere Ionen wurde geprüft. Andere Harze wurden als inerte Träger mit Silikongummi verglichen.

Résumé—On a élaboré des membranes en caoutchouc se silicone imprégnées de sulfure de cuivre(I) comme électrodes sélectives pour les ions cuivre(II). On a éliminé l'électrode et la solution internes. L'équation de Nernst a été satisfaite dans le domaine de concentrations 10^{-1} à $10^{-6}M$ en cuivre(II) et le domaine analytique va de 10^{-1} à $10^{-7}M$. On a examiné l'interférence d'autres ions. On a comparé d'autres résines avec le caoutchouc de silicone comme matrices inertes.

REFERENCES

1. E. Pungor, *Anal. Chem.*, 1967, **39**, 28A.
2. G. A. Rechnitz, *Chem. Eng. News*, 1967, **45**, 146.
3. B. Chatterjee and D. K. Mitra, *J. Indian Chem. Soc.*, 1955, **32**, 751.
4. S. Morrazzani-Pelletier and M. A. Baffier, *J. Chim. Phys.*, 1965, **62**, 429.
5. E. B. Buchanan, Jr. and J. L. Seago, *Anal. Chem.*, 1968, **40**, 517.
6. J. Kielland, *J. Am. Chem. Soc.*, 1937, **59**, 1675.

Some interferences in atomic-absorption spectrometry and extraction of
iron and copper

MUCH has been written on the application of solvent extraction in atomic-absorption spectrometry to overcome interference from other metals. Takeuchi *et al.*[1] have compared the effect of complexing agents on the atomic absorption of metals and found various effects. Sastri *et al.*[2] have demonstrated that metal–oxygen-bonded species contribute to the total amount of metal oxide in flames and hence depopulate the atomic ground-state of the metal in flames.

This paper describes the interferences of the complexing agent in extracted species, in the atomic absorption determination of iron; copper was tested for comparison.

EXPERIMENTAL

Apparatus

A Nippon Jarrell-Ash Model AA-1E atomic-absorption spectrophotometer was used with a Hitachi burner-nebulizer assembly, 75 × 0·5 mm burner, HTV R-136 photomultiplier tube, and Yanagimoto Model RA-2511S recorder. The light sources were iron–chromium and copper hollow-cathode lamps.

Instrument settings

Iron. Wavelength 248·3 nm: slit-width 0·10 mm: lamp current 10 mA: burner height adjusted so that optical pass is 2, 8 or 12 mm above burner top: flow-rates, air 6·0 l./min, acetylene 0·9–1·5 l./min for air–acetylene flame; nitrous oxide 6·0 l./min, acetylene 4·0 l./min for nitrous oxide–acetylene flame: sample uptake 3·8 ml/min for isobutyl methyl ketone extracts.

Copper. Wavelength 324·8 nm: slit-width 0·10 mm: lamp current 10 mA: flame parameters as for iron.

Reagents

Iron standard solution. Dissolve 1 g of pure iron metal in a minimum excess of hydrochloric acid and oxidize with a few drops of nitric acid, boil out nitrogen oxides, and dilute to 1 litre. Prepare dilute standards just before use.

Copper standard solution. Dissolve 1 g of pure copper metal in a minimum excess of nitric acid, boil out nitrogen oxides, and dilute to 1 litre. Prepare dilute standards just before use.

8-Hydroxyquinoline solution. A 0·5% solution in isobutyl methyl ketone.

Sodium diethyldithiocarbamate solution, 2%.

Buffer solution. Acetate and borate buffer solutions for pH 5 and pH 9 respectively.

All reagents used were of analytical-reagent grade. Isobutyl methyl ketone (IBMK) was purified by distillation.

Procedure

Solvent extraction methods were used to prepare the solutions of the iron(III) complexes. The following reagents were used to produce the corresponding complexes of iron(III): potassium thiocyanate, 8-hydroxyquinoline, sodium diethyldithiocarbamate, hydrochloric acid.

Each complex was extracted with two 20-ml portions of IBMK from 30 ml of buffered solution containing 250 μg of iron(III) and the combined extracts were diluted to 50 ml with IBMK.

RESULTS AND DISCUSSION

The effects of complexing agents on iron absorption are summarized in Fig. 1. A marked depressive effect was shown in an air-acetylene flame when thiocyanate was used as complexing agent, increasing with increasing concentration of thiocyanate in the aqueous phase.

Flame conditions were also an important parameter. The fuel-lean flame (for $CO + H_2$ stoichiometry) is seen to be effective for atomization of iron from its thiocyanate complexes. The increased depression of absorption in fuel-rich flames may be derived first from incomplete dissociation and then from compound formation. Iron sulphide is a likely product from decomposition of the thiocyanate complex because the bond energy of CS (272 kJ/mole) is much lower than that of CN (865 kJ/mole) and a CN-band appears in the flame. The depressive effect was also observed when iron chloride complexes and free thiocyanic acid were separately extracted into IBMK and mixed before spraying.
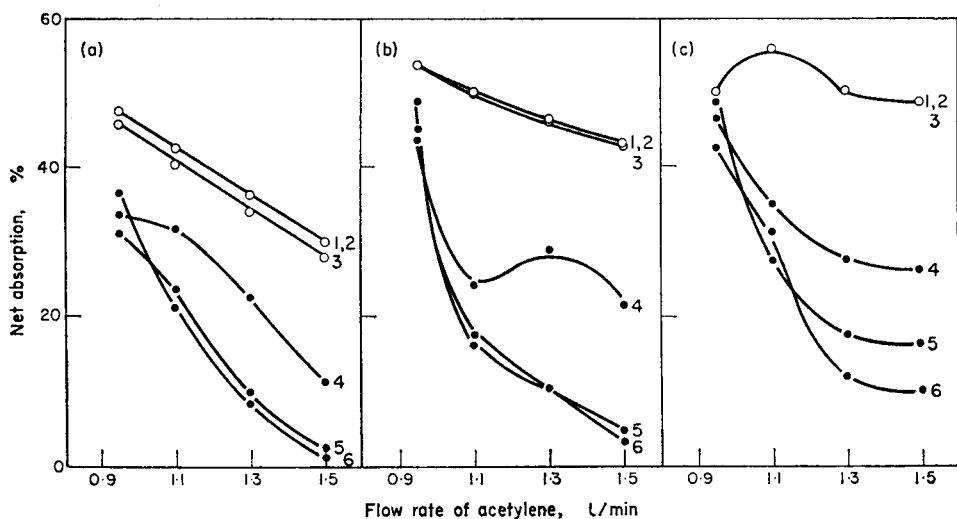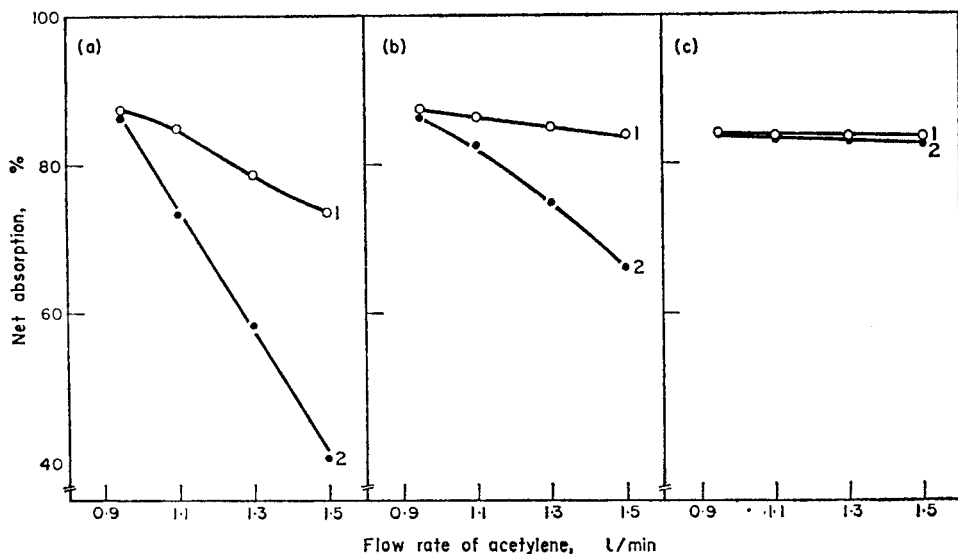
FIG. 1.—Effect of complexing agents on iron absorption.
(a) 2 mm above burner top; (b) 8 mm above burner top; (c) 12 mm above burner top; (1) chloride complex extracted from $6M$ HCl; (2) diethyldithiocarbamate complex extracted at pH 9; (3) hydroxyquinoline complex extracted at pH 5; (4) thiocyanate complex from $0.1M$ SCN$^-$ $0.5M$ HCl; (5) thiocyanate complex from $2M$ SCN$^-$ $0.5M$ HCl; (6) thiocyanate complex from $5M$ SCN$^-$ $0.5M$ HCl.

FIG. 2.—Effect of complexing agents on copper absorption.
(a) 2 mm above burner top; (b) 8 mm above burner top; (c) 12 mm above burner top; (1) diethyldithiocarbamate complex extracted at pH 5; (2) pyridine-thiocyanate complex.

Chloride, diethyldithiocarbamate and 8-hydroxyquinoline complexes of iron(III) behaved alike, but differently from thiocyanate, irrespective of flame conditions. The depressive effect of thiocyanate was reduced if a nitrous oxide–acetylene flame was used. The effect of thiocyanate on copper absorption was investigated for comparison. Copper was extracted into IBMK as the pyridine–thiocyanate complex. A depressive effect was also observed for copper absorption, but similar absorptions were found for both pyridine–thiocyanate and diethyldithiocarbamate complexes, provided the measurements were made for a fuel-lean flame or in higher regions of the flame (Fig. 2). No interference was observed on addition of pyridine to the extracted diethyldithiocarbamate complex before spraying. The depression of copper absorption may also be due to the formation of sulphide in the flame. However, copper sulphide will dissociate during the passage of the aerosol particles into the higher regions of the flame. Furthermore, copper has a higher atomic population in all regions of the flame,[3] and this may be the reason for no depressive effect occurring if measurements are made with the light-path well above the burner top.

Department of Synthetic Chemistry   MASAAKI YANAGISAWA
Faculty of Engineering   HITOSHI KIHARA
Nagoya University   MASAMI SUZUKI
Chikusa-ku, Nagoya, Japan   TSUGIO TAKEUCHI

Summary—The effect of complexing agents on the atomic-absorption spectrometry of iron and copper extracts was investigated Thiocyanate complexes gave a marked depression of absorption by iron and copper, especially in fuel-rich flames. Chloride, diethyldithiocarbamate and hydroxyquinoline complexes of iron behaved alike, but differently from the thiocyanate complex.

Zusammenfassung—Der Einfluß von Komplexbildnern auf die Atomabsorptionsspektrometrie von Eisen- und Kupferextrakten wurde untersucht. Thiocyanatkomplexe gaben eine merkliche Verminderung der Absorption von Eisen und Kupfer, besonders in fetten Flammen. Chlorid-, Diäthyldithiocarbamat- und Hydroxychinolinkomplexe von Eisen verminderten sie ebenfalls, aber in anderem Ausmaß als der Thiocyanatkomplex.

Résumé—On a étudié l'influence d'agents complexants sur la spectrométrie d'absorption atomique d'extraits de fer et de cuivre. Les complexes du thiocyanate donnent une dépression marquée de l'absorption par le fer et le cuivre, spécialement dans des flammes riches en combustible. Les complexes chlorure, diéthyldithiocarbamate et hydroxyquinoléine du fer se comportent de la même façon, mais différemment du complexe thiocyanate.

REFERENCES

1. T. Takeuchi, M. Suzuki and M. Yanagisawa, *Anal. Chim. Acta*, 1966, **36**, 258.
2. V. S. Sastri, C. L. Chakrabarti and D. E. Willis, *Can. J. Chem.*, 1969, **47**, 587.
3. C. S. Rann and A. N. Hambly, *Anal. Chem.*, 1965, **37**, 879.

ANNOTATION

Mass spectrometric investigation of copper chelates with
1-(2-pyridylazo)-2-naphthol

IN A RECENT investigation Betteridge and John[1] (B & J) examined the mass spectra of several transition metal chelates in order to establish their stoichiometry. In the case of the copper chelate with 1-(2-pyridylazo)-2-naphthol (o-β-PAN) the stoichiometry was inferred to correspond to the 1:2 Cu(o-β-PAN)$_2$ chelate. In an earlier solution study however, Betteridge, Fernando and Freiser[2] proposed the extraction of the 1:1 Cu(o-β-PAN) (OH) chelate over the pH range from 4 to 10, rather than the Cu(o-β-PAN)$_2$ chelate which would only be formed in a solution containing a very large proportion of o-β-PAN relative to OH$^-$. Galík[3] has found that copper can be extracted as Cu(o-β-PAN)Z where Z$^-$ is Br$^-$, SCN$^-$ *etc*, over the pH range 4–10 and as Cu(o-β-PAN)$_2$ over the pH range 8–10 from solutions in which the supporting anion is sulphate. Without certain supporting anions there would be virtually no extraction below pH 8.

    B & J were puzzled by the fact that the mass spectrum was like that expected for Cu(o-β-PAN)$_2$ except that there were no peaks corresponding to species containing copper-65, and were unable to explain this peculiarity. Being interested in the application of this chelate for quantitative determinations of copper at the ng and pg levels,[4,5] we investigated the stoichiometry as well as the isotopic abundance of this chelate in more detail.

EXPERIMENTAL

Chelates

    The copper chelates were prepared from commercially obtained o-β-PAN samples (recrystallized from methanol) in the following ways:

    (*i*) analogously to the procedure given by B & J, *i.e.*, recrystallization from the precipitate obtained by the reaction of copper(II) and o-β-PAN at pH 8;

    (*ii*) following the same procedure as described above, in this case however, extracting the aqueous phase with chloroform until colourless, and combining the extracts;

    (*iii*) in order to investigate possible extraction of the Cu(o-β-PAN) (OH), solutions buffered at pH 4 and 9 were extracted by a procedure analogous to that described by Betteridge, Fernando and Freiser,[2] but with a smaller PAN:Cu^{2+} ratio of 7:1 in order to obtain more evidence for the proposed Cu(o-β-PAN) (OH) extraction.

Apparatus

    All measurements were made with an AEI MS 9 mass spectrometer fitted with an insertion lock and a direct evaporation probe. Samples were admitted by evaporating 10 μl of a solution of the chelate in chloroform (*i, ii*) or carbon tetrachloride (*iii*) on the tip of a quartz sample probe.

RESULTS AND DISCUSSION

The stoichiometry

    Whereas the mass spectrum of the chelating agent is identical with that reported by B & J,[1] the spectrum of the chelate shows some interesting discrepancies (a part of this spectrum is given in Fig. 1). In the spectrum reported by B & J only two peaks were attributed to copper-containing ions, *viz.* the peaks at $m/e = 311$ and $m/e = 559$, corresponding to the ions CuX$^+$* and CuX$_2$$^+$ respectively. The spectrum recorded for the present work, however, shows at least nine copper-containing ions of reasonable abundance. Exact mass and isotopic abundance measurements showed the triplet at $m/e = 622$, 624 and 626† to correspond with the formula Cu$_2$X$_2$, yielding evidence for a 1:1 stoichiometry. Likewise, the peaks at $m/e = 559$ and $m/e = 311$ correspond with the formulae CuX$_2$ and CuX, indicating a 1:2 and 1:1 stoichiometry for these ions.

    * X means o-β-PAN

    † Henceforth, reference to isotopic clusters will be made by use of the lowest m/e value only.

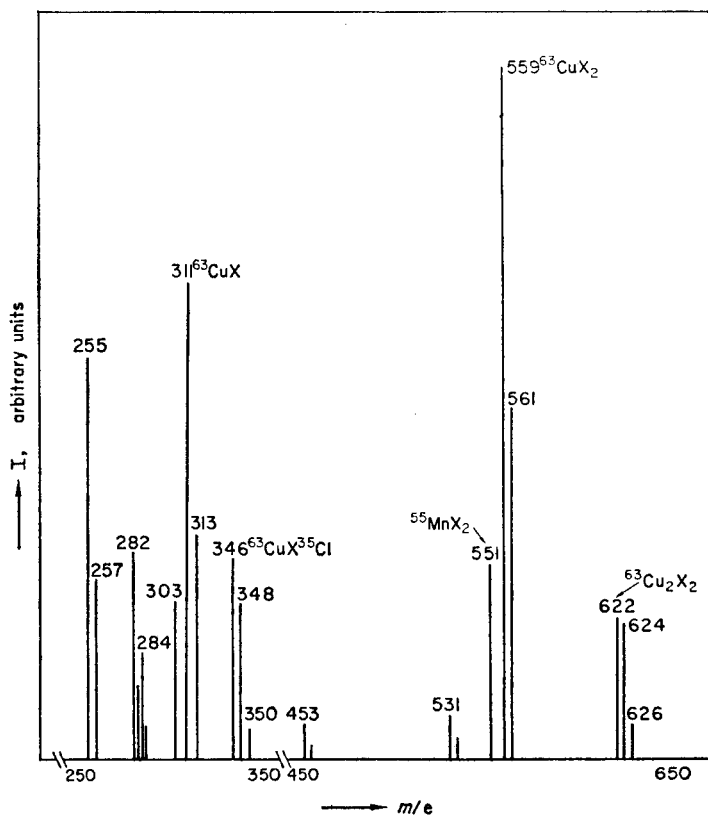   ‡ 180° is the lowest temperature at which the chelate evaporates.

FIG. 1.—Part of mass spectrum of copper chelate with PAN. T = 200°C.

It should, however, be questioned whether these ions correspond to chelates originally present in the sample or to reactions in the mass spectrometer. Samples prepared in different ways (see experimental) showed a constant intensity ratio of the peaks at $m/e = 622$ and $m/e = 559$ during the evaporation at constant temperature. Moreover, this ratio appeared to be independent of the ion-source temperature in the region of 180–280°‡. Consequently the presence of a mixture of Cu_2X_2 and CuX_2 seems less plausible. A plot of the intensity ratio 622/559 vs. the electron beam energy showed the ionization potential of $Cu_2X_2^+$ to be lower than that of the CuX_2^+ ion; if we are dealing with a compound and not with a mixture, the CuX_2^+ ion is most probably formed by loss of copper from the $Cu_2X_2^+$ molecular ion. Metastable peaks originating in either field-free region of the mass spectrometer were not found, however, for this reaction.

In the work of B & J the CuX_2^+ ion is proposed to be the molecular ion, while the CuX^+ ion at $m/e = 311$ should be exclusively the result of fragmentation. This would be indicated by the close resemblance of the intensity ratio CuX_2^+/CuX^+ to the MeX_2^+/MeX^+ ratios for other metal o-β-PAN chelates, known from solution studies to have a 1:2 stoichiometry. However, apart from the fact that this ratio may vary considerably for a single component, depending on ion-source conditions, several other metal chelates, $e.g.$, acetylacetonates[6] and dibenzoylmethanates[7] of a known 1:2 stoichiometry in solution show very different MeX_2^+/MeX^+ ratios, so that no reliance can be placed upon this ratio as an indication of stoichiometry. We have found metastable transitions from the $Cu_2X_2^+$ and CuX_2^+ ions into the CuX^+ ion, while furthermore the appearance potential of the CuX^+ ion exceeds that of $Cu_2X_2^+$ and CuX_2^+, but this does not rule out the possibility that the ion at $m/e = 311$ is partly a molecular ion.

The spectra were examined for peaks due to the species CuXOH. The spectra obtained from solutions prepared at pH 4 by procedure (iii) had no peaks due to copper-containing species but those obtained from solutions prepared at pH 9 by the same procedure were analogous with spectra obtained by procedures (i) and (ii). It is possible indeed that in solution a chelate of the composition CuX^+OH^- is formed, which decomposes in the ion-source. However the presence of ions at $m/e = 346, 348$ and

350, which correspond (according to exact mass and isotopic abundance measurements) with the composition CuX^+Cl^- makes this less plausible. The relative intensity of this ion was strongly dependent on the temperature (elevated temperatures probably cause decompostion) and the sample. It is probably formed in solution by ion-pair formation with chloride ion impurities in the chelating agent and/or decomposition of the solvent (chloroform). In the recrystallized sample [preparation (i), see experimental] its presence was negligible. All other copper-containing ions in the mass spectrum can be easily understood by a comparison with the fragmentation of the pure chelating agent. Because of the results noted above we concur with B & J, that the use of mass spectrometry for the establishment of chelate stoichiometry is limited; however, we do not agree with their stoichiometric conclusions derived from the mass spectra of the copper chelate.

Isotopic abundance measurements

Copper has two stable isotopes of comparable abundance, viz. copper-63 (69·09 %) and Copper-65 (30·91 %). B & J stated that copper in $Cu(o$-β-$PAN)_2$ and related chelates behaved as though copper-63 were the only stable isotope. In our investigation, the isotopic abundance of copper as measured from all copper-containing molecular and fragment ions of sufficient intensity (8), showed the expected natural abundance. This was also the case with samples prepared in a way analogous to that described by B & J.

As can be seen from Fig. 1 there are also peaks at $m/e = 551$ and $m/e = 303$. If the temperature is increased to 230–250°, the intensity of these ions is greatly enhanced with respect to that of the copper-containing ions. Exact mass measurements showed these peaks to correspond with the mono-isotopic manganese chelate. At higher temperatures (280–300°) intense peaks at $m/e = 552$, 554 and 556 appear (about 5–10 times as intense as the copper ion at $m/e = 559$), which we attribute to the presence of iron and nickel. However, X-ray fluorescence analyses of the sample showed these metals only in vanishing by small quantities. We suppose these ions are the result of exchange reactions with hot metal surfaces in the ion-source, like the manganese-containing heater wires. A similar effect has been observed by Holtzclaw et al.[8] in their investigation of 1-methyl-3-alkyl-1,3-dione–copper(II) chelates.

Considering the (unnecessary) excessively high temperature of 380° used by B & J, we suppose the peaks, given by the dotted lines in their Figs. 12 and 13, to be merely the result of other (mono-isotopic) metal chelate ions, rather than copper-containing ions.

Utrecht University   J. K. TERLOUW
Laboratory for Analytical Chemistry   J. J. DE RIDDER
Croesestraat 77-A, Utrecht
The Netherlands

Summary—The mass spectra of copper chelates of 1-(2-pyridylazo)-2-naphthol, HX, prepared by different methods, are discussed. Peaks due to $Cu_2X_3^+$, CuX_2^+ and $CuXCl^+$ have been positively identified and all copper-containing species have the expected isotopic ratios. The significance of probe temperature and impurities are discussed and it is concluded that the spectra are more in accordance with the known chemical facts than those reported earlier by Betteridge and John.

Zusammenfassung—Die Massenspektren von verschieden hergestellten Kupferchelaten mit 1-(2-Pyridylazo-2-naphthol, HX, werden diskutiert. Die Peaks von $Cu_2X_3^+$, CuX_2^+ und $CuXCl^+$ wurden sicher identifiziert; alle Kupfer enthaltenden Spezies haben die erwarteten Isotopenverhältnisse. Die Bedeutung der Temperatur an der Einspritzstelle und von Verunreinigungen werden diskutiert und es wird der Schluß gezogen, daß die Spektren mit den bekannten chemischen Tatsachen besser übereinstimmen als die früher von Bettridge und John mitgeteilten.

Résumé—On discute les spectres de masse des chélates de cuivre du 1 (2-pyridylazo) 2-naphtol, HX, préparées par différentes méthodes. Les pics dûs à $Cu_2X_3^+$, CuX_2^+ et $CuXCl^+$ ont été positivement identifiés, et toutes les espèces contenant du cuivre ont les rapports isotopiques attendus. On discute l'importance de la température de

l'essai et des impuretés et l'on conclut que les spectres sont plus en accord avec les faits chimiques connus que le spectre rapporté antérieurement par Betteridge et John.

REFERENCES

1. D. Betteridge and D. John, *Talanta*, 1968, **15**, 1227.
2. D. Betteridge, Q. Fernando and H. Freiser, *Anal. Chem.*, 1963, **35**, 294.
3. A. Galík, *Talanta*, 1969, **16**, 201.
4. J. K. Terlouw, J. J. de Ridder, W. Heerma and G. Dijkstra, *Z. anal. Chem.*, 1970, **249**, 296.
5. J. K. Terlouw and J. J. de Ridder, *ibid.*, 1970, **250**, 166.
6. C. G. Macdonald and J. S. Shannon, *Australian J. Chem.*, 1966, **19**, 1545.
7. M. J. Lacey, C. G. Macdonald and J. S. Shannon, *Org. Mass Spectr.*, 1968, **1**, 115.
8. H. F. Holtzclaw, Jr., R. L. Lintvedt, H. E. Baumgarten, R. G. Parker, M. M. Bursey and P. F. Rogerson, *J. Am. Chem. Soc.*, 1969, **91**, 3774.

PAPERS RECEIVED

Design of olfactory detection reactions based on isocyanide formation: E. J. POZIOMEK. (11 *June* 1970)

Massenspektrometrische Untersuchungen zur Elementaranalyse organischer Verbindungen—I. Einlass-system zur Analyse von Gasgemischen in grossen Temperatur- und Druckbereichen: W. WALISCH and O. JAENICKE. (12 *June* 1970)

Massenspektrometrische Untersuchungen zur Elementaranalyse organischer Verbindungen—II. Bestimmung von Verbrennungsprodukten in Trägergasstrom durch Peakintegration: OTTAKAR JAENICKE and W. WALISCH. (12 *June* 1970)

Spectrophotometric determination of ruthenium with 3,4-diaminobenzoic acid: G. H. AYRES and J. A. ARNO. (22 *June* 1970)

The determination of zinc in copper by atomic-fluorescence flame spectroscopy: P. D. WARR. (22 *June* 1970)

Fluorimetric determination of aluminium and lead: D. R. HAWORTH and E. A. LAMSARGES. (22 *June* 1970)

Determination of noble metals by neutron-activation analysis: R. GIJBELS. (22 *June* 1970).

Extraction with long-chain amines—IV. Separation and colorimetric determination of gold: JIŘÍ ADAM and RUDOLF PŘIBIL. (23 *June* 1970)

The possibilities for separation and simultaneous determination of *N*-unsubstituted- and *N*-substituted nitroimidazoles and criteria for distinguishing between them: D. DUMANOVIĆ and S. PERKUČIN. (23 *June* 1970)

Determination of dimetridazole in reaction mixtures: D. DUMANOVIĆ and S. PERKUČIN. (23 *June* 1970)

Infrared determination of barium, strontium, sodium, and potassium sulphates by the pellet technique: DAVID E. CHASAN and GEORGE NORWITZ. (26 *June* 1970)

Anion-exchange separations of metal ions in thiocyanate media: JAMES S. FRITZ and EDWARD E. KAMINSKI. (29 *June* 1970)

Chromatographic separation and colorimetric determination of gold: J. S. FRITZ and W. G. MILLEN. (9 *July* 1970)

Spectrophotometric determination of EDTA: S. N. BHATTACHARYYA and K. P. KUNDU. (14 *July* 1970).

Gas chromatography of metal chelates with carrier gas containing ligand vapour: TAITIRO FUJINAGA, TOORU KUWAMOTO and SHIGEO MURAI. (14 *July* 1970)

Professor L. Erdey: GYULA SVEHLA. (15 *July* 1970)

Application of displacement reactions in flame photometry—I. Determination of phosphate by a flame emission method: E. SZEBENY, P. J. SLEVIN, G. SVEHLA and L. ERDEY. (15 *July* 1970)

Application of displacement reactions in flame photometry—II. Flame-photometric determination of alkaline earth metals in the presence of interfering anions: P. J. SLEVIN, E. GYÖRY-SZEBENYI and G. SVEHLA. (15 *July* 1970)

Identification of some polyatomic inorganic anions as their diphenyliodonium salts by infrared spectroscopy, and interpretation of the spectra: A. J. BOWD, D. THORBURN BURNS and R. GRZESKOWIAK. (20 *July* 1970)

PUBLICATIONS RECEIVED

The Determination of Carboxylic Functional Groups: R. D. Tiwari and J. P. Sharma, Pergamon, Oxford, 1970. Pp. vii + 132. 60s, $8.00.

One of the most commonly encountered problems in the analysis of natural products is the determination of carboxylic acid functional groups. This monograph reviews the very large number of methods which have been devised for the solution of this problem. In addition to the many chemical procedures which have been reported in the literature there is an account of the application of physical methods to the determination of acidic groups. Derivatives of carboxylic acids such as acid chlorides, anhydrides, amides and esters may also be determined by many of these techniques and chapters are devoted to descriptions of the appropriate analytical methods. There is also a section dealing with the much more difficult problem of binary and multicomponent mixtures.

The Determination of Organic Peroxides: R. M. Johnson and I. W. Siddiqi, Pergamon Press, Oxford, 1970. Pp. ix + 119. 50s, $6.75.

The ever increasing industrial use of organic peroxides and hydroperoxides as initiators in polymerization processes makes the publication of a review of methods for their analysis particularly welcome at the present time. Because of their reactive nature, peroxides are comparatively simple to detect and there are a large number of methods which rely upon this fact. The book devotes chapters to the more familiar chemical methods based on the release of iodine and the oxidation of iron (II) but the more recent work on chromatographic procedures is also included. There are sections dealing with other physical techniques such as spectrophotometry, polarography and gas chromatography. A particularly useful feature of the book is a chapter on the selection of the most appropriate method for any particular peroxide mixture.

Ion Exchange in Analytical Chemistry: William Rieman III and Harold F. Walton, Pergamon, Oxford, 1970. Pp. xiii + 295. 130s, $17.50.

The object of this volume in the well known Pergamon Monographs in Analytical Chemistry series is to give a broad survey of all aspects of ion-exchange methods, covering preparation, structure, properties, and applications of all kinds of exchangers, and giving a useful account of the basic theory in a form calculated to be of most use to the analyst. From simple demineralization to use of ion-exchange membranes and studies on complex ions, there is something for everyone in this book.

Activation Analysis: A Bibliography: Part I, Addendum 1—Issued December 1969; Part 2, Revision 1—Issued December 1969; edited G. J. Lutz, R. J. Borenj, R. S. Maddock and W. W. Meinke *NBS Technical Note* 467. U.S. Department of Commerce, Washington D.C., 1970 Pp. 264. $8.50 per set, sold in sets only.

Errors, Measurement and Results in Chemical Analysis: K. Eckschlager, Van Nostrand-Reinhold, London, 1969. Pp. 155, 60s.

This book should be close to the hand of all analytical chemists. It discusses the sources of error inherent in the most common methods and gives an account of the statistical procedures necessary for the evaluation of experimental results. The statistical methods are described in a down to earth way and are illustrated by exemplary treatments of analytical results. Methods for handling small numbers of results are given their due as are rapid graphical methods. Parts are uneven, e.g., errors in colorimetry due to stray light are not mentioned and the tiro who wished to compute a simple regression curve would be advised to consult one of the more formal works listed in the bibliography. Despite its blemishes, the range of coverage and its practical approach make it a most valuable book.

Chemistry of Complex Equilibria: M. T. BECK, Van Nostrand-Reinhold, London, 1970. Pp. 285, 90s.

The author provides an extensive and realistic review of complex equilibria. The methods available for the determination of equilibrium constants are outlined and critically evaluated. He considers that the formation of mononuclear complexes with one ligand only is abnormal and consequently he gives a welcome emphasis to polynuclear complexes, protonation of chelates and mixed ligand complexes. He also discussed the factors which determine the value of the stability constant of a metal complex. The text contains many graphs and experimental data taken from original papers, which are used to exemplify an approach to a particular problem and there are over 1000 references. Workers in the field will find it very useful and it will be of value to those who wish to widen their background, since the style is clear and the coverage good.

SUMMARIES FOR CARD INDEXES

Practical analysis of high-purity chemicals—I. Preparation and characterization of high-purity EDTA: A. J. BARNARD JR., E. F. JOY, K. LITTLE and J. D. BROOKS, *Talanta*, 1970, **17**, 785. (Research Analytical Services, J. T. Baker Chemical Company, Phillipsburg, New Jersey 08865, U.S.A.)

Summary—Advanced laboratories have requirements for high-purity chemicals with less than 500 ppm total impurities (ultrapure chemicals) and with broad analytical definition of each lot. Some economically feasible approaches to the practical analysis of such chemicals, both inorganic and organic, are delineated. Compounds used in the study of lunar samples and in other advanced programmes are noted. EDTA, as the free acid, has been prepared by dissolution in water with base and precipitation by addition of acid. The product has been broadly characterized. Precision assay is achieved by weight titrimetry, potentiometrically as a triprotic acid and photometrically as a chelating agent. Other tests applied include elemental analysis, ash, loss on drying, particulate matter, and tests for nitrilotriacetate, arsenic, and chloride. Boron, silicon, and trace metals are determined by emission spectrography. Many of the procedures are applicable to other high-purity organic chemicals.

Extractions with long-chain amines—I. Extraction of some metal–Xylenol Orange complexes into methyltrioctylammonium chloride (Aliquat 336-S): RUDOLF PŘIBIL and VLADIMÍR VESELÝ, *Talanta*, 1970, **17**, 801. (Laboratory for Analytical Chemistry, J. Heyrovský Polarographic Institute, Czechoslovak Academy of Sciences, Prague 1, Jilská 16, Czechoslovakia.)

Summary—The extraction of traces of metals forming intensely coloured complexes with Xylenol Orange in acidic medium (pH 0–3) has been studied. For such extractions, in the presence of sulphates, chlorides and nitrates, a solution of methyltrioctylammonium chloride (Aliquat 336-S) in chloroform has been used. It is shown that it is possible to detect small amounts of gallium in indium and *vice versa*, and titanium or zirconium in thorium. These reactions should be capable of adaption to spectrophotometric determinations. The principle of the extraction of metals as their complexes with various metallochromic indicators is briefly discussed.

ПРАКТИЧЕСКИЙ АНАЛИЗ ВЫСОКОЧИСТОТНЫХ
ХИМИКАЛИЙ—I. ПРИГОТОВЛЕНИЕ И
ХАРАКТЕРИЗОВАНИЕ ВЫСОКОЧИСТОТНОЙ ЭД ТА:

A. J. BARNARD JR., E. F. FOY, K. LITTLE and J. D. BROOKS, *Talanta*,
1970. **17**, 785.

Резюме—Прогрессивные лаборатории требуют высокочистот-
ных химикалий с общим содержанием примесей меньше чем
500 частей на миллион (ультрачистотные химикалии),
сопровожденных широкой аналитической характеристикой
для каждойо партии. Приведены некоторые экономически
осуществимые пути практического анализа таких химикалий,
органических как и неорганических. Упомянуты соединения
использованные в исследовании лунарных образцов и в
других прогрессивных программах. ЭДТА в форме свобод-
ной кислоты была приготовлена растворением в воде с
щелочью и осаждением прибавлением кислоты. Продукт
широко охарактеризован. Прецизионный анализ проведен
использованием весовой титриметрии, потенциометрического
определения трипротической кислоты и фотометрическим
путем в качестве хелатообразующего агента. Также опреде-
лены элементарный анализ, зола, потеря при высушивании,
присутствие частиц и проведены испытания на нитрилотр-
иацетат, мышьяк и хлорид. Бор, кремний и следы металлов
определены методом емиссионной спектрографии. Ряд
описанных методов применымы на другие высокочистотные
органические химикалии.

ЭКСТРАКЦИИ С АМИНАМИ С ДЛИННОЙ ЦЕПЬЮ—I.
ЭКСТРАКЦИЯ НЕКОТОРЫХ КОМПЛЕКСОВ МЕТАЛ-
ЛОВ С КСИЛЕНОЛОВЫМ ОРАНЖЕВЫМ В
МЕТИЛТРИОКТИЛАММОНИЙХЛОРИД
(АЛИКВАТ 336-S):

RUDOLF PŘIBIL and VLADIMÍR VESELÝ, *Talanta*, 1970 **17**, 801.

Резюме—Изучена экстракция следов металлов образующих
сильноокрашенные комплексы с ксиленоловым оранжевым
в кислой среде (рН 0–3). Для таких экстракций, в присутст-
вии сульфатов, хлоридов и нитратов, пользовались раствором
метилтриоктиламмонийхлорида (Аликват 336-S) в хлоро-
форме. Показана возможность обнаружения следов галлия
в индие и наоборот, и титана или циркония в тории. Эти
реакции должны служить основой для спектрофотометри-
ческого определения этих металлов. Кратко обсуждены
принципы экстракции металлов в форме их комплексов с
разными металлохромными индикаторами.

Interaction of palladium with sulphaguanidine: W. F. RITTNER, A. GULKO and G. SCHMUCKLER, *Talanta*, 1970, **17**, 807. (Department of Chemistry, Technion, I.I.T., Haifa, Israel.)

Summary—The formation constants of palladium with chloride ions have been determined by a new approach to the interpretation of the ultraviolet spectra. The interaction of $PdCl_4^{2-}$ with sulphaguanidine (SG) has been interpreted and evaluated quantitatively. The formation constants of the mixed ligand complex $Pd(SG)_2Cl_2$, were determined spectrophotometrically. The stability constants for the stepwise formation of the palladium chloride complexes are: $\log k_1 = 3.48$; $\log k_2 = 2.79$; $\log k_3 = 2.35$; $\log k_4 = 1.1$, and for the interaction of $PdCl_4^{2-}$ with SG, $\log k_1 = 5.42$; $\log k_2 = 4.38$.

Colorimetric determination of traces of selenium, tellurium, manganese and cerium: P. P. NAIDU and G. GOPALA RAO, *Talanta*, 1970, **17**, 817. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—Methods are described for the colorimetric determination of micro- and semi-micro quantities of selenium, tellurium, cerium and manganese. The test solution in 0.35–$3M$ condensed phosphoric acid medium is oxidized with an excess of permanganate. The colour intensity of the unreacted permanganate is measured at 530 nm.

Sulphoxides as solvating reagents for the separation of metal ions: DAVID C. KENNEDY and J. S. FRITZ, *Talanta*, 1970, **17**, 823. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—The solvent extraction properties of the following sulphoxides have been evaluated: di-n-octyl sulphoxide (DOSO), bis(n-octylsulphinyl)methane (BOSM), bis(n-octylsulphinyl)ethane (BOSE) and *p*-tolyl sulphoxide (PTSO). By use of reversed-phase paper chromatography as a qualitative surveying technique, the interactions of these sulphoxides with some fifty metal ions were investigated in several acid–ligand systems. All sulphoxides were studied in 1–$10M$ hydrochloric and nitric acids; DOSO and BOSM were also studied in perchloric acid and ammonium thiocyanate–perchloric acid mixtures. Observations are made concerning sulphoxide–metal interactions and the existence of several useful analytical separation systems is pointed out. The synthesis and characterization of BOSM and BOSE are described.

ВЗАИМОДЕЙСТВИЕ ПАЛЛАДИЯ С СУЛЬФАГУАНИДИНОМ:

W. F. Rittner, A. Gulko and G. Schmuckler, *Talanta*, 1970, 17, 807.

Резюме—Определены константы образования палладия с хлоридионами, пользуясь новым подъемом к интерпретации ультрафиолетовых спектров. Истолковано и количественно изучено взаимодействие $PdCl_4^{2-}$ с сульфагуанидином (СГ). Константы образования комплекса $Pd(СГ)_2Cl_2$ с смешанными лигандами определены спектрофотометрическим методом. Константы устойчивости для шагового образования комплексов хлорида палладия равны: $\lg k_1 = 3{,}48$; $\lg k_2 = 2{,}79$; $\lg k_3 = 2{,}35$; $\lg k_4 = 1{,}1$, а для взаимодейстствия $PdCl_4^{2-}$ с СГ—$\lg k_1 = 5{,}42$; $\lg k_2 = 4{,}38$.

КОЛОРИМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЛЕДОВ СЕЛЕНА, ТЕЛЛУРА, МАРГАНЦА И ЦЕРА:

P. P. Naidu and G. Gopala Rao, *Talanta*, 1970, 17, 817.

Резюме—Описаны методы колориметрического определения микро- и семимикроколичеств селена, теллура, цера и марганца. Анализируемый раствор в 0,35–3M конденсированной фосфорной кислоте окисляют избытком перманганата и измеряют светопоглощение нереагированного перманганата при 530 нм.

СУЛЬФОКСИДЫ В КАЧЕСТВЕ СОЛЬВАТИЗИРУЮЩИХ АГЕНТОВ ДЛЯ РАЗДЕЛЕНИЯ ИОНОВ МЕТАЛЛОВ:

David C. Kennedy and J. S Fritz, *Talanta*, 1970, 17, 823.

Резюме—Изучены экстрационные характеристики следующих сульфоксидов: ди-н-октилсульфоксид (ДОСО), бис-(н-октилсульфинил)метан (БОСМ), бис(н-октилсульфинил)-этан (БОСЭ) и п-толилсульфоксид (ПТСО). Используя бумажную хроматографию в качестве метода качественного контроля, исследованы взаимодействия этих сульфоксидов с 50 ионов металлов в разных системах кислота-лиганд. Все сульфоксиды изучены в 1–10 М растворах соляной и азотной кислот; ДОСО и БОСМ также изучены в хлорной кислоте и в смесях тиоцианата аммония и хлорной кислоты. Изучены взаимодействия сульфоксида с металлом и обнаружен ряд разделительных систем используемых в анализе. Описаны синтез и характеристики БОСМ и БОСЭ.

Extraction chromatography of uranium with dioctyl sulphoxide: JAMES S. FRITZ and DAVID C. KENNEDY, *Talanta*, 1970, **17**, 837. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—Uranium(VI) is quantitatively extracted from aqueous perchlorate media into dioctyl sulphoxide in 1,2-dichloroethane. The extracted species contains four sulphoxides for each uranium. Most other metal ions are not appreciably extracted. On columns containing a solid support impregnated with dioctyl sulphoxide in 1,2-dichloroethane, uranium(VI) may be separated quantitatively from metal ions such as thorium(IV), zirconium(IV) and rare earths(III).

Determination of silver, gold and palladium by a combined fire-assay atomic-absorption procedure: SILVE KALLMANN and EVERETT W. HOBART, *Talanta*, 1970, **17**, 845. (Ledoux & Co., Teaneck, N.J. 07666, U.S.A.)

Summary—A method is described which combines the best features of the fire-assay procedure with an atomic-absorption technique. The precious-metal bead resulting from the fire-assay concentration step is dissolved in acids, the solution evaporated to dryness and the residue dissolved in a measured quantity of cyanide solution. The atomic-absorption measurement of this solution allows the determination of as little as 0·017 ppm of silver, 0·08 ppm of gold, and/or 0·08 ppm of palladium in various precious-metal-bearing materials with a precision of ±1%.

Absorptiometric determination of sulphide ion: S. A. RAHIM and T. S. WEST, *Talanta*, 1970, **17**, 851. (Department of Chemistry, Imperial College of Science and Technology, London, S.W.7.)

Summary—An absorptiometric method is described for sulphide ion, based on the green colour which is formed when sulphide ions are treated in ammoniacal solution with iron(III) and an excess of nitrilotriacetic acid. The recommended procedure can be applied from 1200 down to 8 ppm of sulphide and is interfered with seriously only by selenite from amongst seventeen other anions examined. The colour system is stabilized by an excess of sulphite. Suggestions are made about the nature of the colour body and its mechanism of production.

ЭКСТРАКЦИОННАЯ ХРОМАТОГРАФИЯ УРАНА ДИОКТИЛСУЛЬФОКСИДОМ:

JAMES S. FRITZ and DAVID C. KENNEDY, *Talanta*, 1970, **17**, 837.

Резюме—Уран(VI) экстрагируется количественно из водных растворов перхлората раствором сульфоксида в 1,2-дихлорэтане. Эктсрагированный комплекс содержит четыре молекулы сульфоксида для каждого атома урана. Большинство других ионов металлов не экстрагируются в значительной мере. На колонках содержащих носитель пропитанный раствором диоктилсульфоксида в 1,2-дихлорэтане, удается отделять уран(VI) количественно от таких ионов металлов как на пример тория(IV), циркония(IV) и редкоземельных элементов(III).

ОПРЕДЕЛЕНИЕ СЕРЕБРА, ЗОЛОТА И ПАЛЛАДИЯ КОМБИНИРОВАННЫМ МЕТОДОМ СУХИМ ПУТЁМ И АТОМНО-АБСОРБЦИОННОЙ СПЕКТРОСКОПИИ:

SILVE KALLMANN and EVERETT W. HOBART, *Talanta*, 1970, **17**, 845.

Резюме—Описан метод комбинирующий наиучшие характеристики определения металлов сухим путём и методом атомно-абсорбционной спектроскопии. Шарик благородного металла полученный концентрацией сухим путем растворяют в кислотах, выпаривают раствор до сухого, а остаток растворяют в измеренном объеме раствора цианида. Анализ этого раствора методом атомно-абсорбционной спектроскопии позволяет опраделять до 0,017 мкг (г серебра, 0,08 мкг) г золота и (или 0,08 мкг) г палладия в разных веществах содержащих благородные металлы с воспроизводимостью ±1%.

АБСОРБЦИОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СУЛЬФИДИОНА:

S. A. RAHIM and T. S. WEST, *Talanta*, 1970, **17**, 851.

Резюме—Описан абсорбциометрический метод определения сульфидиона, основанный на зеленой окраске образующейся если сульфидионы реагируют в аммиачном растворе с железом(III) и избытком нитрилотриуксусной кислоты. Предложенным методом можно пользоваться от 1200 до 8 частей на миллион сульфида, а среди исследованных 17 других анионов только селенитион мешает определению. Система окраски стабилизируется избытком сульфитиона. Предложено объяснение природы окрашенного вещества и механизма его образования.

Column chromatographic separation of gallium, indium and thallium: JAMES S. FRITZ, R. THOMAS FRAZEE and GARY L. LATWESEN, *Talanta*, 1970, **17**, 857. (Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.)

Summary—Distribution ratios are given for the extraction of gallium-(III), indium(III) and thallium(III) from aqueous solutions of hydro-bromic acid into di-isopropyl ether and isobutyl methyl ketone. Based on the results obtained, a scheme is presented for the quantitative separation of these elements from each other by liquid–liquid partition chromatography. The effect of a number of other metal ions upon the separation is also studied. The separation method has been applied to the analysis of a series of lead–indium alloys.

Spectrophotometric determination of nickel(II) with molybdophosphoric acid: R. L. HELLER and J. C. GUYON, *Talanta*, 1970, **17**, 865. (Department of Chemistry, University of Missouri, Columbia, Missouri 65201, U.S.A.)

Summary—A sensitive spectrophotometric method for the determination of nickel, based on the reduction of a complex formed between molybdophosphoric acid and Ni(II) at pH 4·3 has been developed. Excess of molybdophosphoric acid is eliminated by complexation with sodium citrate. The method is rapid and the system obeys Beer's law up to 5 ppm of Ni(II). The molar absorptivity is $1·30 \times 10^3$ $1.\text{mole}^{-1}.\text{mm}^{-1}$. The technique compares favourably with existing photometric methods for nickel in sensitivity and is reasonably selective.

Pyridine-2-aldoxime and 6-methylpyridine-2-aldoxime as gravimetric reagents for estimation of palladium(II) and uranium(VI): NARAYAN KUMAR, G. S. MANKU, A. N. BHAT and B. D. JAIN, *Talanta*, 1970, **17**, 873. (Department of Chemistry, University of Delhi, Delhi-7, India.)

Summary—Pyridine-2-aldoxime (I) has been found to be a sensitive reagent for the gravimetric determination of palladium(II). From chloride medium, precipitation is complete at pH 3·0–11·0, and in solution containing 1 N HNO$_3$ to pH 6·0. The compositions of the precipitates (dried at 130°) correspond to PdL$_2$ and PdL$_2$·HNO$_3$ (HL representing the reagent respectively. Pd(II) can be estimated gravimetrically in presence of acetate, oxalate, tartrate, phosphate, fluoride, borate, perchlorate, Cu(II), Cd, Co(II), Fe(III), Ni, Zn, Pb, Bi, Sb(III), Pt(IV), Ir(IV), Ru(III), Rh(III); Os(IV) in quantities more than twice that of Pd(II), and Ag(I), Au(III) and Fe(II) even in traces cause serious interference. The yellow uranium(VI) complex with (I) is precipitated quantitatively over the pH range 3·5–10·0 and, after washing and drying corresponds to the composition UO$_2$(C$_6$H$_5$N$_2$O)$_2$. The uranium-(VI) complex with 6-methylpyridine-2-aldoxime (II) is precipitated quantitatively over the pH range 3·0–10·5, and after washing and drying at 120–130° corresponds to UO$_2$(C$_7$H$_7$N$_2$O)$_2$. Both (I) and (II) are suitable for the estimation of 1–50 mg of uranium(VI) in the presence of up to 10-fold quantities of Th(IV), La(III) and Ce(III) even when present together. Ce(IV) in quantities more than three times that of U must be reduced to Ce(III). Tartrate, citrate, phosphate, Ti(IV) and Zr interfere, but acetate, oxalate, and borate do not.

РАЗДЕЛЕНИЕ ГАЛЛИЯ, ИНДИЯ И ТАЛЛИЯ МЕТОДОМ ХРОМАТОГРАФИИ НА КОЛОНК:

James S. Fritz, R. Thomas Frazee and Gary L. Latwesen, *Talanta*, 1970, **17**, 857.

Резюме—Приведены отношения распределения в экстракции галлия(III), индия(III) и таллия(III) из водных растворах бромистоводородной кислоты диизопропиловым эфиром и изобутилметилкетоном. На основе полученных результатов предложена схема количественного отделения этих элементов одного от другого методом разделительной хроматографии в жидкой фазе. Так же исследован эффект ряда других ионов металлов на разделение. Метод применен в анализе ряда сплавов свинца и индия.

СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИКЕЛЯ(II) МОЛИБДОФОСФОРОВОЙ КИСЛОТОЙ:

R. L. Heller and J. C. Guyon, *Talanta*, 1970, **17**, 865.

Резюме—Разработан чувствительный спектрофотометрический метод определения никеля, основанный на восстановлении комплекса образующегося из молибдофосфоровой кислоты и никеля(II) при pH 4,3. Избыток молибдофосфоровой кислоты удаляется комплексированием с цитратом натрия. Метод является быстрым а система повинуется закону Бера до 5 мкг/мл Иi(II). Молярное светопоглощение равно $1,30 \times 10^3$ л.моль$^{-1}$.мм$^{-1}$. Метод является довольно чувствительным и селективным в сравнении с существующими фотометриуескими методами.

ПИРИДИН-2-АЛЬДОКСИМ И 6-МЕТИЛПИРИДИН-2-АЛЬДОКСИМ КАК РЕАГЕНТЫ ДЛЯ ВЕСОВОГО ОПРЕДЕЛЕНИЯ ПАЛЛАДИЯ(II) И УРАНА(VI):

Narayan Kumar, G. S. Manku, A. N. Bhat and B. D. Jain, *Talanta*, 1970, **17**, 873.

Резюме—Пиридин-2-альдоксим (I) оказался чувствительным реагентом для определения палладия(II). Осаждение комплетно из хлоридной среды при pH 3,0–11,0, а из нитратной среды—при pH 0–6,0. Состав осадков (осушенных при 130°) соответствует формулами PdL_2 и $PdL_2 \cdot HNO_3$, соответственно, где HL представляет реагент. Pd(II) можно определять весовим методом в присутствии ацетата, оксалата, тартрата, фосфата, фторида, бората, перхлората, Cu(II), Cd, Co(II), Fe(III), Ni, Zn, Pb, Bi, Sb(III), Pt(IV), Ir(IV), Ru(III) Rh(III); Os(IV) в количествах больше чем дважды количества Pd(II), а Ag(I), Au(III) и Fe(II) даже в следовых количествах серезно мешают определению. Желтый комплекс урана(VI) с (I) осажднется количественно в области pH 3,5–10,0 и, после промывки и осушки, соответствует формуле $UO_2(C_6H_5N_2O)_2$. Комплекс урана(VI) с 6-метилпиридин-2-альдоксимом (II) осаждается количественно в области pH 3,0–10,5 и—после промывки и осушки—соответствует формуле $UO_2(C_7H_7N_2O)_2$. Оба реагента (I) и (II) можно использовать для определения 1–50 мг урана(VI) в присутствии до 10-кратного избытка Th(IV), La(III) и Ce(III), даже если они присутствуют одновременно. Ce(IV) нужно восстановить до Ce(III) если присутствует в количествах больше чем трижды количества U. Тартрат, цитрат, фосфат, Ti(IV) и Zr мешают, но ацетат, оксалат и борат не мешают определению.

Separation and determination of mixtures containing *p*-aminosalicylic acid and *m*-aminophenol: MARTIN I. BLAKE and JAMES HUNT, *Talanta*, 1970, **17**, 876. (Department of Pharmacy, University of Illinois at the Medical Center, Chicago, Illinois 60612, U.S.A.)

Summary—A procedure is described for separating and determining *p*-aminosalicylic acid and *m*-aminophenol in mixtures. Separation is effected by passing a solution of the mixture in dimethylformamide through a column of strong cation-exchange resin. The eluate containing the *p*-aminosalicylic acid is titrated with sodium methoxide. The *m*-aminophenol is eluted from the column with ethanolic HCl. The eluate is evaporated to dryness, the residue dissolved in acetic acid, and the solution titrated with perchloric acid.

The complexes of bismuth(III) and nitrilotriacetic acid: B. P. KARADAKOV and D. I. VENKOVA, *Talanta*, 1970, **17**, 878. (Institute of Chemical Technology, Sofia-56, Bulgaria.)

Summary—The reaction between bismuth(III) and nitrilotriacetic acid (NTA or H_3X) has been investigated by ultraviolet spectrophotometry. It has been established that bismuth(III) and NTA form two complexes with compositions bismuth(III): NTA = 1:1 and 1:2. The absorption maxima are at 243 nm (1:1) and 271 nm (1:2), the molar absorptivities being 8.00×10^3 and 8.20×10^3 l.mole^{-1}.cm^{-1} respectively. The stability constants (ar $\mu = 1.0$) are: log $\beta_{BiX} = 17.53 \pm 0.06$ and log $\beta_{BiX_2}{}^{3-} = 26.56 \pm 0.07$. The possibility of the analytical application of BiX is briefly discussed.

Copper(I) sulphide-impregnated silicone rubber membranes as selective electrodes for copper(II) ions: HIROSHI HIRATA and KENJI DATE, *Talanta*, 1970, **17**, 883. (Wireless Research Laboratory, Matsushika Electric Industrial Co. Ltd., Kadoma, Osaka, Japan.)

Summary—Silicone rubber membranes impregnated with copper(I) sulphide have been developed as selective electrodes for copper(II) ions. The internal electrode and solution were eliminated. The Nernst equation was satisfied in the concentration range from 10^{-1} to $10^{-6}M$ copper(II) and the analytical range was from 10^{-1} to $10^{-7}M$. The interference of other ions was examined. Other resins were compared with silicone rubber as inert matrices.

РАЗДЕЛЕНИЕ И ОПРЕДЕЛЕНИЕ СМЕСЕЙ СОДЕРЖАЩИХ П-АМИНОСАЛИЦИЛОВУЮ КИСЛОТУ И М-АМИНОФЕНОД:

MARTIN I. BLAKE and JAMES HUNT, *Talanta*, 1970, **17**, 876

Резюме—Описан метод разделения и определения п-амино-салициловой кислоты и м-аминофенола в смеси. Разделение получается пропусканием раствора смеси в диметилфор-мамиде через колонку сильной катионообменной смолы. Элюат содержащий п-аминосалициловую кислоту титруют метоксидом натрия. м-Аминофенол элюируют из колонки спиртовым раствором HCl. Элюат выпаривают до сухого, остаток растворяют в уксусной кислоте и раствор титруют хлорной кислотой.

КОМПЛЕКСЫ ВИСМУТА(III) И НИТРИЛОТРИУКСУСНОЙ КИСЛОТЫ:

B. P. KARADAKOV and D. I. VENKOVA, *Talanta*, 1970, **17**, 878.

Резюме—Изучена методом ультрафиолетовой спектрофото-метрии реакция висмута(III) и нитрилотриуксусной кислоты (НТА или H_3X). Обнаружено что висмут(III) и НТА обра-зуют два комплекса состава висмут(III):НТА = 1:1 и 1:2. Максимумы светопоглощения при 243 нм (1:1) и 271 нм (1:2), а молярные светопоглощения равны $8,00 \times 10^3$ и $8,20 \times 10^3$ л.моль$^{-1}$.мм$^{-1}$, соответственно. Константы устойчивости (при $\mu = 1\,0$) равны: $\lg \beta_{BiX} = 17,53 \pm 0,06$ и $\lg \beta_{BiX_2}{}^{3-} = 26,56 \pm 0,07$. Кратко обсуждена применимость BiX в анализе.

ПРОПИТАННЫЕ СУЛЬФИДОМ МЕДИ(I) МЕМБРАН ИЗ КРЕМНИЙОРГАНИЧЕСКОЙ РЕЗИНЫ В КАЧЕСТВЕ ЭЛЕКТРОДОВ ИЗБИРАТЕЛЬНЫХ ДЛЯ ИОНА МЕДИ(II):

HIROSHI HIRATA and KENJI DATE, *Talanta*, 1970, **17**, 883.

Резюме—Разработаны пропитанные сульфидом меди(I) мемб-раны из кремнийорганической резины в качестве электродов избирательных для ионов меди(II), за исключением внутрен-него электрода и раствора. Уравнение Нернста соблюдалось в области концентраций 10^{-1} до 10^{-6} М меди(II), а аналити-ческий диапазон был 10^{-1} до 10^{-7} М. Изучено влияние других ионов. Другие смолы сравнены с кремнийорганической резиной в качестве инертной матрицы.

Some interferences in atomic-absorption spectrometry and extraction of iron and copper: MASAAKI YANAGISAWA, HITOSHI KIHARA, MASAMI SUZUKI and TSUGIO TAKEUCHI, *Talanta*, 1970, **17**, 888. (Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan.)

Summary—The effect of complexing agents on the atomic-absorption spectrometry of iron and copper extracts was investigated. Thiocyanate complexes gave a marked depression of absorption by iron and copper, especially in fuel-rich flames. Chloride, diethyldithiocarbamate and hydroxyquinoline complexes of iron behaved alike, but differently from the thiocyanate complex.

Mass spectrometric investigation of copper chelates with 1-(2-pyridylazo)-2-naphthol: J. K. TERLOUW and J. J. DE RIDDER, *Talanta*, 1970, **17**, 891. (Utrecht University, Laboratory for Analytical Chemistry, Croesestraat 77-A, Utrecht, The Netherlands).

Summary—The mass spectra of copper chelates of 1-(2-pyridylazo)-2-naphthol, HX, prepared by different methods, are discussed. Peaks due to $Cu_2X_2^+$, CuX_2^+ and $CuXCl^+$ have been positively identified, and all copper-containing species have the expected isotopic ratios. The significance of probe temperature and impurities are discussed and it is concluded that the spectra are more in accordance with the known chemical facts than those reported earlier by Betteridge and John.

НЕКОТОРЫЕ ВЛИЯНИЯ НА ОПРЕДЕЛЕНИЕ АТОМНО-АБСОРБЦИОННЫМ МЕТОДОМ И ЭКСТРАГИРОВАНИЕ ЖЕЛЕЗА И МЕДИ:

MASAAKI YANAGISAWA, HITOSHI KIHARA, MASAMI SUZUKI and TSUGIO TAKEUCHI, *Talanta*. 1970, **17**, 888.

Резюме—Исследовано влияние комплексообразующих агентов на определение методом атомно-абсорбционной спектроскопии экстрактов железа и меди. Тиоцианаткомплексы в значительной мере подавляют абсорбцию железа и меди, особенно в богатых топливом пламенах. Комплексы железа с хлоридом, диэтилдитиокарбаминатом и оксихинолином показали то же поведение, но различное от комплекса с тиоцианатом.

ИССЛЕДОВАНИЕ ХЕЛАТОВ МЕДИ С 1-(2-ПИРИДИЛАЗО)-2-НАФТОЛОМ МЕТОДОМ МАСС-СПЕКТРОМЕТРИИ:

J. K. TERLOUW and J. J. DE RIDDER, *Talanta*, 1970, **17**, 891.

Резюме—Обсуждены масс-спектры хелатов меди с 1-(2-пиридилазо)-2-нафтолом, HX, приготовленные разными методами. Идентифицированы пики соответствующие $Cu_2X_2^+$, CuX_2^+ и $CuXCl^+$ а все мед-содержащие соединения имели ожиданные соотношения изотопов. Обсуждено влияние температуры датчика и примесей и сделан вывод что спектры лучше соглашаются с химическими фактами чем спектры опубликованные Беттериджем и Джоном.

Books for Analytical Chemists

Contents