

# ANALYTICA CHIMICA ACTA

*International monthly devoted to all branches of analytical chemistry*  
*Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique*  
*Internationale Monatsschrift für alle Gebiete der analytischen Chemie*

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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA  
Vol. 30, No. 3, March 1964

THE USE OF A DISCHARGE TUBE AS AN ABSORPTION  
SOURCE FOR THE DETERMINATION OF LITHIUM-6 AND  
LITHIUM-7 ISOTOPES BY ATOMIC ABSORPTION  
SPECTROPHOTOMETRY

An atomic absorption technique was used to determine the natural abundance ratio,  ${}^7\text{Li}/{}^6\text{Li}$ , in a normal sample of C.P. grade lithium hydroxide prepared in 1942. The result obtained,  $12.1 \pm 3.3\%$ , compares favorably with a mass spectrometer value of 12.3 used by the Oak Ridge Isotope Division for reporting the lithium isotope abundance ratio, and it is the first time the  ${}^7\text{Li}/{}^6\text{Li}$  abundance ratio has been reported with accuracy by atomic absorption methods. A Schüler-Göllnow water-cooled hollow-cathode tube was used to obtain the resonance doublet of lithium at 6708 Å, while a modified Schüler-Göllnow water-cooled hollow-cathode tube was used to vaporize the natural lithium and related standards in microgram quantities and to absorb the resonance radiation. Helium was used as a carrier gas in both tubes at low pressures for the purpose of sputtering samples and exciting the lithium resonance lines. Regulated d.c. current power supplies, and conventional, independent circulating systems were used with each tube; and a Jarrell-Ash monochromator, Model 82-000, of relatively low dispersion, was used to isolate the resonance lines, along with other readily available commercial recording equipment.

J. A. GOLEB AND Y. YOKOYAMA,

*Anal. Chim. Acta*, 30 (1964) 213-222.

SIMULTANEOUS DETERMINATION OF NICKEL AND COBALT  
TRACES BY NEUTRON ACTIVATION ANALYSIS

Nickel and cobalt traces may be determined by measuring the  ${}^{58}\text{Co}$  and  ${}^{60}\text{Co}$  activities produced in a nuclear reactor. Solvent extraction of cobalt, and  $\gamma$ -spectrometry on the extracted phase allow a rapid and simple analysis of both metals. The method is applied to the determination of nickel (100-0.2 p.p.m.) and cobalt (0.15-0.001 p.p.m.) in various materials (petroleum, polyphenyls, aluminium).

R. MALVANO AND G. B. FASOLO,

*Anal. Chim. Acta*, 30 (1964) 223-226.

## MICRODETERMINATION OF CAFFEINE USING THE RING OVEN TECHNIQUE

A rapid and highly selective method for the microdetermination of caffeine of special interest for air pollution studies is presented. With the ring oven technique and with solutions of acetylacetone in sodium hydroxide and *p*-dimethylaminobenzaldehyde in hydrochloric acid, as little as 0.5  $\mu\text{g}$  caffeine on the ring can be determined with an average error of 3%. Compounds containing purine bases which would be likely to give the same color reaction as caffeine do not interfere. Of the organic air pollutants which might be collected from the atmosphere during the sampling for caffeine, benzo( $\alpha$ )pyrene and formic acid do not interfere. Interferences from formaldehyde and urea are easily eliminated.

F. ORDOVEZA AND P. W. WEST,

*Anal. Chim. Acta*, 30 (1964) 227-233.

## THERMOGRAVIMETRIC INVESTIGATION OF THE ALKALINE EARTH DILITURATES

Thermolysis curves for calcium, strontium and barium diliturates were obtained. Calcium diliturate forms an octahydrate from aqueous solution while strontium diliturate forms a heptahydrate and barium diliturate forms a tetrahydrate.

Methods for the thermogravimetric determination of strontium and barium were developed and found to be quite accurate; calcium can only be determined semi-quantitatively by precipitation as the diliturate salt.

M. W. GOHEEN AND R. J. ROBINSON,

*Anal. Chim. Acta*, 30 (1964) 234-239.

## EFFECTS OF SURFACE-ACTIVE SUBSTANCES ON POLAROGRAPHIC WAVES OF SOME COMPLEXES

The effect of the charge type of surface-active substances on the polarographic waves of various complexes has been investigated. The results indicate that the polarograms are practically unaffected by the presence of a surfactant, provided that the adsorbed layer has a charge opposite to that of the depolariser. Polarographic waves of depolarisers with the same charge as the adsorbed layer are, however, shifted to more negative values or greatly distorted. The distorting effect is qualitatively interpreted in terms of an electrostatic repulsion between the adsorbed layer and the depolariser. The charge type of a surfactant seems to be important for the appropriate choice of a nondistorting maximum suppressor.

E. JACOBSEN AND G. KALLAND,

*Anal. Chim. Acta*, 30 (1964) 240-247.

### SINE-WAVE POLAROGRAPHIC DETERMINATION OF SMALL AMOUNTS OF INDIUM IN THE PRESENCE OF LARGE AMOUNTS OF CADMIUM, LEAD OR TIN

The sine-wave polarographic determination of small amounts of indium in the presence of large amounts of cadmium, lead or tin was investigated. The determination of indium in cadmium was possible down to 0.01% in 1 *M* potassium iodide at pH 2, the determination of indium in lead was possible down to 0.02% in 1 *M* potassium chloride at pH 2, and the determination of indium in tin was possible down to 0.3% in 1 *M* hydrochloric acid and down to 0.2% in 2 *M* perchloric acid with 0.5 *M* sodium chloride.

M. KASAGI AND C. V. BANKS,

*Anal. Chim. Acta*, 30 (1964) 248-254.

### SIMULTANEOUS DETERMINATION OF LEAD AND NICKEL IN URANIUM BY SQUARE-WAVE POLAROGRAPHY

A sensitive method for the simultaneous determination of trace lead and nickel in uranium is described. These elements are separated from uranium by anion exchange and then determined by square-wave polarography using the alkaline cyanide solution as supporting electrolyte. The procedure is applicable to uranium metal and its compounds containing as little as 1 p.p.m. of lead and nickel.

F. NAKASHIMA,

*Anal. Chim. Acta*, 30 (1964) 255-260.

### SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM(III) WITH COMPLEXANS

Selective spectrophotometric determinations of milligram amounts of chromium(III) with complexans are described, based on the fact that the chromium(III) complexes are formed rapidly at boiling temperatures, but very slowly at room temperature, while the formation of some interfering complexes takes place instantaneously. Determinations with EDTA are more sensitive, but the combined presence of cobalt and other metals still interferes; there is no interference with the less sensitive NTA. The combined presence of a 100-fold amount of copper, nickel, cobalt and iron generally has no effect on the results. The use of DCTA, DTPA and HEDTA is discussed.

G. DEN BOEF AND B. C. POEDER,

*Anal. Chim. Acta*, 30 (1964) 261-268.

### *n*-PENTYL-2-PYRIDYL KETOXIME AS A SELECTIVE COLORIMETRIC REAGENT FOR COPPER

*n*-Pentyl-2-pyridyl ketoxime hydrochloride has been prepared and examined as a colorimetric reagent for copper. It is less sensitive than some reagents, but shows a remarkable selectivity toward copper. The copper(I)-oxime compound can be extracted into isoamyl alcohol or into chloroform. In isoamyl alcohol the colored compound conforms to Beer's law in concentrations up to  $5.6 \cdot 10^{-4}$  *M* and has a molar absorptivity of 2650 at 360 m $\mu$ . A procedure for the colorimetric determination of copper is given and its reliability is shown.

F. TRUSELL AND K. LIEBERMAN,

*Anal. Chim. Acta*, 30 (1964) 269-272.

## THE SEPARATION OF THE ALKALINE EARTHS WITH EDTA ON ION-EXCHANGE COLUMNS

(in French)

The quantitative separation of a few mg of strontium and barium from several g of calcium is described. The alkaline earth carbonates are dissolved in 0.1 M EDTA, fixed at pH 4.8 on an ammoniacal Dowex column, and eluted, also with 0.1 M EDTA, calcium at pH 5.25, strontium at pH 6.0, barium at pH 9.0. The end of the calcium elution can be followed accurately by a sudden pH increase in the eluate (from 4.8 up to 5.25).

J. J. BOUQUIAUX ET J. H. C. GILLARD,  
*Anal. Chim. Acta*, 30 (1964) 273-279.

## THEORY OF TITRATION CURVES

### V. LOCATIONS OF EXTREMA ON CONDUCTOMETRIC, AMPEROMETRIC, SPECTROPHOTOMETRIC, AND OTHER LINEAR ("SEGMENTED") TITRATION CURVES

For both isovalent and heterovalent single-step ion-combination reactions whose products do not make any contributions to the property measured, this paper presents the results of a rigorous investigation of the conditions required for the existence of extrema on linear titration curves and their locations. These results are applied to various conductometric, amperometric, and spectrophotometric titrations.

J. A. GOLDMAN AND L. MEITES,  
*Anal. Chim. Acta*, 30 (1964) 280-292.

## ELECTRODE PROBLEMS IN POTENTIOMETRY

(in German)

The variations of the potential, calculated and observed during a potentiometric titration, are independent of the nature of the electrode used. The influence of changing the rate of agitation upon the potential of silver electrodes of different surfaces is studied. A halide-free reference electrode is described as a suitable simplification in argentometric titrations.

F. L. HAHN,  
*Anal. Chim. Acta*, 30 (1964) 293-296.

## SELECTIVE HYDROXYL GROUP DETERMINATION BY DIRECT TITRATION WITH LITHIUM ALUMINUM AMIDE

The selective determination of hydroxyl groups in most complex alcohol systems by direct titration with standard lithium aluminum amide solution is described. The titration is carried out in ether solvent under nitrogen with N-phenyl-*p*-aminoazobenzene as reversible indicator. The accuracy is better than  $\pm 1\%$ ; less than 6 min are required for a complete determination of alcohols up to triacontanol. Aldehydes, ketones, esters, amines and alkoxy groups do not interfere, but organic and inorganic acids, and water and molecular oxygen, interfere. Water and acid interferences can be corrected for after a Karl Fischer titration and neutralization reactions respectively.

D. E. JORDAN,  
*Anal. Chim. Acta*, 30 (1964) 297-302.

APPLICATIONS OF INFRARED SPECTROSCOPY

PART XIII. THE DETERMINATION OF SMALL AMOUNTS OF ALCOHOLS IN  
AQUEOUS SOLUTION

Recent developments in methods of analysing dilute solutions of alcohols are briefly reviewed, and a simple modification to the Zeisel reaction is described. This permits the analysis, on a 1-ml aliquot, of dilute aqueous solutions of alcohols alone or in admixture

D. M. W. ANDERSON AND S. S. H. ZAIDI,

*Anal. Chim. Acta*, 30 (1964) 303-307.

A SIMPLE METHOD FOR THE DISSOLUTION OF  
PLATINUM METALS

(*Short Communication*)

D. R. GABBE AND D. N. HUME,

*Anal. Chim. Acta*, 30 (1964) 308-309.

PAPER CHROMATOGRAPHIC SEPARATION OF SILVER(I),  
LEAD(II), MERCURY(II) AND THALLIUM(I) WITH  
SOLVENTS CONTAINING CHLOROFORM

(*Short Communication*)

R. P. BHATNAGAR AND K. D. SHARMA,

*Anal. Chim. Acta*, 30 (1964) 310-312.

POLAROGRAPHIC DETERMINATION OF N-PHTHALYL-  
GLUTAMIC ACID IMIDE (THALIDOMIDE)

(*Short Communication*)

J. S. HETMAN,

*Anal. Chim. Acta*, 30 (1964) 313-315.

## THE USE OF A DISCHARGE TUBE AS AN ABSORPTION SOURCE FOR THE DETERMINATION OF LITHIUM-6 AND LITHIUM-7 ISOTOPES BY ATOMIC ABSORPTION SPECTROPHOTOMETRY\*

JOSEPH A. GOLEB AND YU YOKOYAMA\*\*

*Argonne National Laboratory, Argonne, Illinois (U.S.A.)*

(Received September 20th, 1963)

In a preceding paper<sup>1</sup>, a water-cooled hollow-cathode discharge tube was investigated as a possible atomic absorption source. A modified Schüler-Gollnow tube was convenient to use for the investigation because a number of Schüler-Gollnow tubes were readily available at this laboratory, being used for problems concerning nuclear spin and term analysis in line spectra. It was thought the sputtering action in the tube might dissociate refractory as well as non-refractory elements from their compounds, and thus extend atomic absorption techniques to include more elements. The results of that investigation indicated that microgram quantities of refractory and non-refractory elements deposited in the crater of the absorption tube were detected; therefore it is thought atomic absorption techniques can be extended not only to the determination of more elements but also to isotope determination, because the isotope displacement for many elements is greater than the spectral line width of about 0.01 Å obtained with a water-cooled hollow-cathode emission source.

For this paper the water-cooled discharge tubes used for the previous investigations<sup>1</sup> were again tested for their usefulness as atomic absorption sources, this time for isotope determination. To expedite obtaining data to investigate the usefulness of a discharge tube as an absorption source for isotope determination, the first element selected for investigation was lithium, since it has a well-known resonance doublet at 6708 Å, displaying an appreciable isotope displacement of 0.16 Å. Also both lithium isotopes, <sup>6</sup>Li and <sup>7</sup>Li, can be purchased inexpensively from the Oak Ridge Isotope Division in the purest form, > 99.9%.

Some previous work done with lithium isotopes by atomic absorption techniques is reported by ZAIDEL AND KORENNOI<sup>2</sup> and MANNING AND SLAVIN<sup>3</sup> using flames as absorption sources. The former workers showed no results for the lithium natural abundance ratio while the latter's results were reported to be preliminary and were considerably higher than the ratio used by Oak Ridge Isotope Division. Much work, however, has been done in the past to determine the lithium isotopes by emission spectrographic techniques<sup>4-11</sup>, using expensive and sophisticated high-resolution instruments. In contrast, the work described in this paper employs a relatively

\* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

\*\* Presently at Tokai Refinery, Atomic Fuel Corp., Tokai-mura, Ibaraki-ken, Japan.



inexpensive monochromator of low dispersion to obtain the natural abundance ratio in a lithium sample. The precision obtained for the lithium abundance ratio using this atomic absorption technique is comparable to the precision obtained by the emission spectrographic methods.

Other recent unique techniques used for the analysis of the lithium isotopes are reported by AMIEL AND WELWART<sup>12</sup>, using a counting delayed neutron method; ĆIRIĆ AND PUPEZIN<sup>13</sup> separated lithium isotopes on Amberlite IR-120 cation exchanger, and the isotopic analysis was made using a double-collector mass spectrometer.

#### EXPERIMENTAL

The spectroscopic arrangement used to obtain the lithium natural abundance ratio by atomic absorption techniques was basically the same as described in previous work<sup>1</sup>. Incident lithium light from a hollow-cathode emission tube was modulated by a 60-cycle mechanical chopper, and focussed on the hole of the cathode electrode of the absorption tube containing an evaporated sample. The transmitted light was then focussed on the  $500 \mu$  slit of a monochromator equipped with a 1P21 photomultiplier tube. The a.c. signal was amplified, rectified, and then transmitted to a recorder. To obtain the lithium results, however, a few changes were necessary.

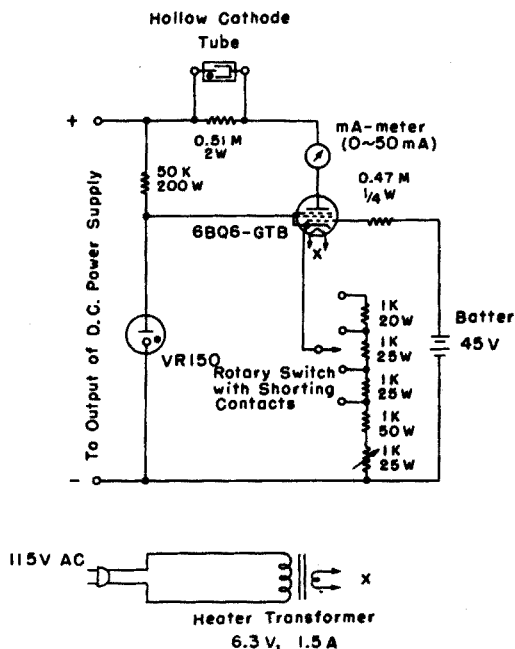


Fig. 1. Stabilized current supply.

Instead of using aluminum electrodes and neon as a carrier gas in the tubes, copper electrodes and helium were used to obtain precision and sensitivity. Also, to improve the over-all stability of the method, the commercial-type 1500 V rectifiers were provided with current stabilizers built at this laboratory, shown in Fig. 1, which provided

currents up to 50 mA through the two tubes with an accuracy of 0.5% when the tubes were operated at about 300 V. The a.c. ripple was less than 0.2%. Figure 2 shows a master cathode electrode and a copper insert that were used in the absorption tube for the purpose of retaining an evaporated liquid sample. The insert had a 0.25" inside diameter, and a length of 1". This insert, made from inexpensive copper tubing, purity > 99.9%, served the need of having well-machined pure electrodes available when individual samples needed analyzing.

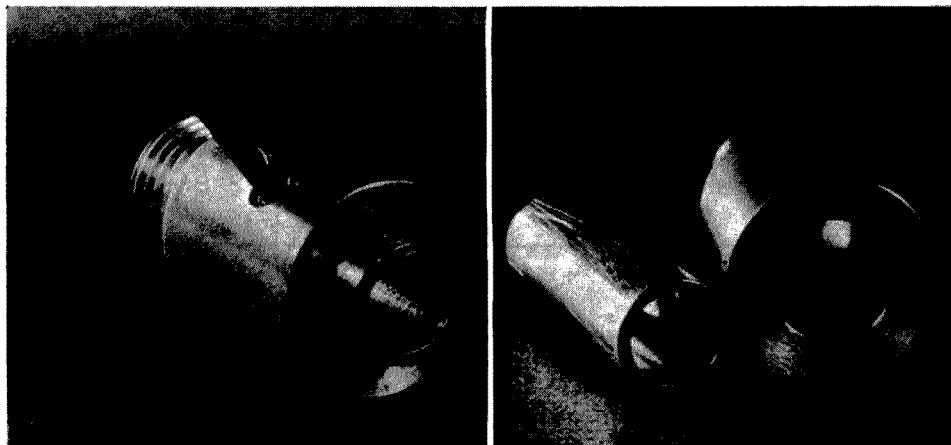


Fig. 2. Absorption tube electrodes.

To find a satisfactory lithium compound to be used in the emission and absorption tubes to obtain an accurate lithium natural abundance ratio, a number of lithium compounds, lithium carbonate, lithium sulfate, lithium fluoride, and lithium hydroxide, were tested in the emission and absorption tubes. To minimize the spreading of lithium contamination in the tubes and circulating systems, normal lithium compounds were used instead of lithium compounds containing  ${}^6\text{Li}$  and  ${}^7\text{Li}$ , respectively, since it was assumed that behavior of the mentioned  ${}^6\text{Li}$  and  ${}^7\text{Li}$  compounds and natural lithium compounds in the tubes would be essentially the same. It was found that 10 mg of lithium fluoride, placed in the crater of the emission tube, using 10–20 mA current and helium at 2 mm Hg, was sufficient to produce a stable discharge lasting 2–3 days after the sample was sputtered on the walls of the cathode crater for about 1–2 h. Lithium carbonate gave the poorest reproducibility and sensitivity when tested in the emission tube. It was observed that after lithium carbonate was sputtered in the tube for about 0.5 h, the lithium intensity started to diminish appreciably, as was seen on a recorder. It is thought the presence of carbon monoxide in the discharge<sup>14</sup>, due to the sputtering action of helium on lithium carbonate, had a suppressing effect on the lithium emission intensity. Of the same compounds tested in the absorption tube, using 40 mA current and helium at 2 mm Hg, lithium hydroxide worked the best, since the greatest amount of incident radiation, about 70%, was absorbed. It was thus decided to use lithium hydroxide in the absorption tube and limit the sample size to give approximately 90  $\mu\text{g}$  of total lithium (300  $\mu\text{g}$  of lithium

hydroxide). The results in Fig. 3 show that the copper electrode in the absorption tube was saturated with lithium when 50  $\mu\text{g}$  of lithium was present, since the absorption readings did not change essentially when as much as 1000  $\mu\text{g}$  of lithium was present in the electrodes. Experience showed by using 90  $\mu\text{g}$  of lithium in the absorption tube, a number of reproducible absorption readings were obtained and lithium

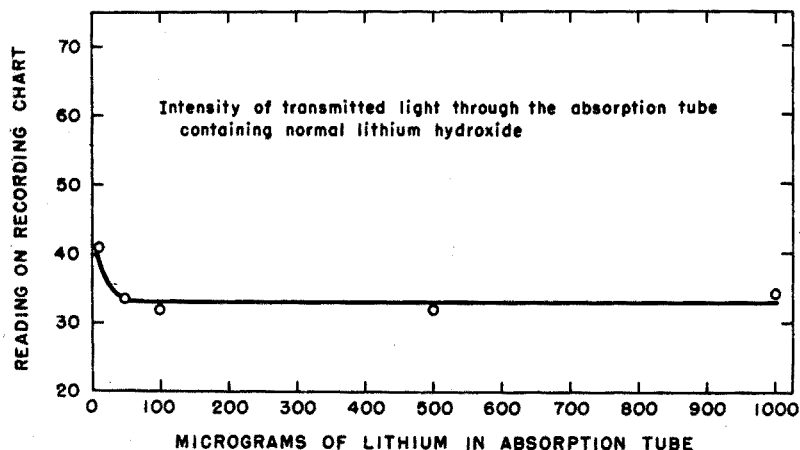


Fig. 3. Effect of sample size on absorption.

contamination was minimized in the system. Thus, as a result of determining the operating conditions of the tubes using normal lithium compounds in the emission and absorption tubes, a minimum amount of lithium contamination was spread in the tubes and vacuum system before standards and normal sample were analyzed. A blank correction was not necessary when the standards and samples were finally analyzed.

#### *Investigation of helium pressure in tubes*

In previous investigations<sup>1</sup> using sodium in the emission and absorption tubes with neon as a carrier gas, results indicated that the self-absorption of the sodium resonance line, 5890  $\text{\AA}$ , was minimized for a given current and sample using the carrier gas, neon, at a low pressure of 2 mm of Hg. Thus, absorption was obtained for 1  $\mu\text{g}$  of sodium. To obtain the maximum absorption for the lithium resonance line at 6708  $\text{\AA}$  for a given current and sample, the emission and absorption tubes were also operated at the lowest helium pressure possible, 2 mm Hg. The results shown for lithium in Fig. 4 agree with the results found for sodium. The bottom curve of Fig. 4 shows that when incident lithium light was passed through an active absorption tube containing lithium, the greatest absorption was obtained when the absorption tube was operated at the lowest helium pressure, while the smallest absorption was obtained when the absorption tube was operated at the highest pressure. The top curve of Fig. 4 shows that the emission intensity of the lithium line from the absorption tube, used independently, was the strongest at the lowest helium pressure and the weakest at

the highest pressure. Thus, this experimental evidence from the two curves of Fig. 4, indicates that as the carrier gas pressure is increased in the absorption tube, relatively fewer atoms capable of absorbing incident radiation are present in the light path, which is in agreement with observations made with sodium<sup>1</sup>.

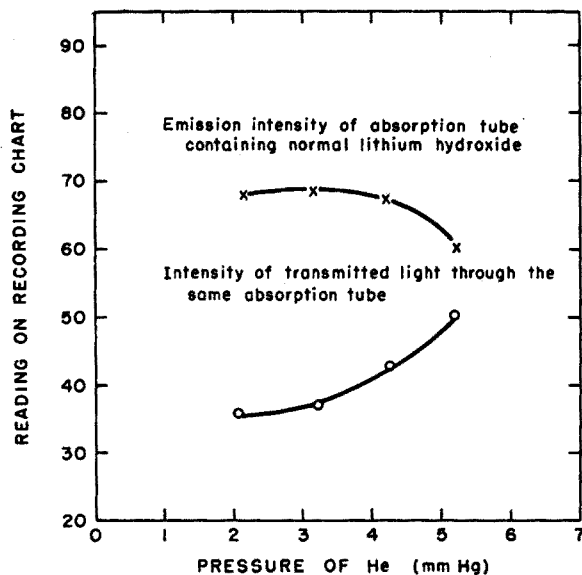


Fig. 4. Influence of helium pressure in tubes.

## RESULTS

### *Preparation of analytical curve and method of analysis*

The  $^6\text{Li}$  and  $^7\text{Li}$  hydroxide compounds used to prepare standards for the absorption tube were made by dissolving high purity  $^6\text{Li}$  and  $^7\text{Li}$  metals, purchased from the Oak Ridge Isotope Division, in distilled water using polyethylene beakers. The solutions were taken to dryness on a hot plate and dried at  $160^\circ$  for 8 h in a drying oven. A chemical analysis was made of the two compounds to determine the lithium content. Using the  $^6\text{Li}$  and  $^7\text{Li}$  hydroxides, two standard water solutions were prepared containing  $^6\text{Li}$  and  $^7\text{Li}$ , respectively. From these two solutions, four standards were prepared, covering a range of 2.5 to 10.0 atomic per cent  $^6\text{Li}$  in  $^7\text{Li}$ , to establish an analytical curve. An aliquot of 0.1 ml of a standard solution, containing 90  $\mu\text{g}$  of total lithium, was placed in a copper electrode of the absorption tube, and the solution taken to dryness uniformly in the electrode by adding about 0.1 ml of acetone to it while the electrode was rotating at 60 rev./min on a Fisher "Minimill" machine, Model 8-413. A heat lamp was also used over the electrodes to speed the evaporation processes. This drying technique proved to be a very significant part of this atomic absorption procedure, because when the copper electrode containing the uniformly deposited sample on its wall was excited by the discharge in the absorption tube, a reproducible and uniform absorption column of lithium vapor was produced in the electrode.

The  ${}^6\text{Li}$  and  ${}^7\text{Li}$  fluoride compounds used in the emission tube to produce incident radiations were prepared from the  ${}^6\text{Li}$  and  ${}^7\text{Li}$  hydroxide solutions mentioned above. Pure hydrofluoric acid was added to the respective hydroxide solutions, until a pink acid color was observed on litmus paper; subsequently, the solutions were taken to dryness and dried for 8 h at  $160^\circ$ .

Respective  ${}^6\text{Li}$  and  ${}^7\text{Li}$  absorption readings were obtained for the four standards by passing  ${}^6\text{Li}$  and  ${}^7\text{Li}$  incident light independently through the discharge of the absorption tube containing the standards. Reproducible and accurate absorption readings were obtained by operating the emission and absorption tube at some

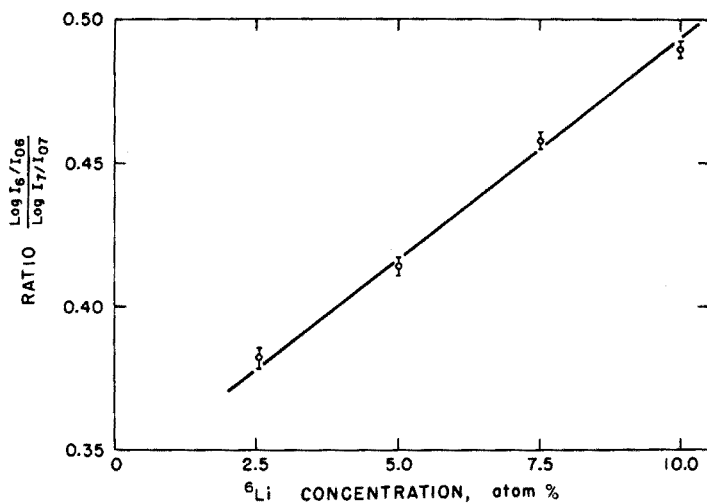


Fig. 5. Analytical curve.

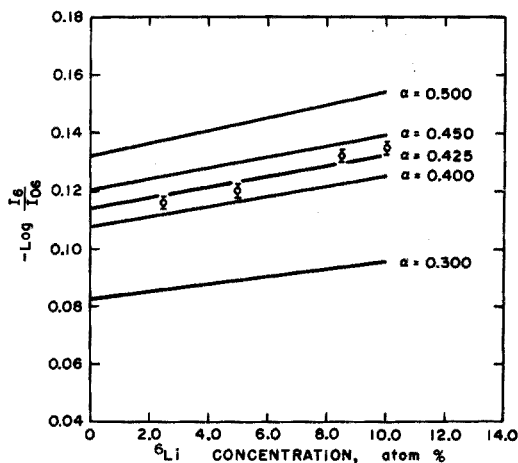


Fig. 6. Comparison of experimental absorbance results to results predicted by Zaidel and Korennoi<sup>2</sup>.

fixed lithium intensity for a constant current previously mentioned. The fixed lithium emission intensities for a given current were observed on a recorder by operating each tube independently just before absorption readings were taken. As a result of carefully controlling the currents and lithium emission intensities for the two tubes, a valid analytical curve, shown in Fig. 5, was established by plotting  $\log(I_6/I_{06})/\log(I_7/I_{07})$  against  ${}^6\text{Li}$  concentration, where  $I_{06}$  and  $I_{07}$  are the respective  ${}^6\text{Li}$  and  ${}^7\text{Li}$  incident intensities, and  $I_6$  and  $I_7$  are respective transmitted intensities. Each point used to draw the analytical curve was an average of 5 values for the same sample.

It was decided to plot a ratio of the two absorbance values,  $\log(I_6/I_{06})/\log(i_7/i_{07})$ , against  ${}^6\text{Li}$  concentration in preference to one absorbance value,  $\log(I_6/I_{06})$ , against  ${}^6\text{Li}$  concentration, used by ZAIDEL AND KORENNOI<sup>2</sup>, to obtain a lithium analytical curve, because investigations showed that more reproducibility and accuracy were obtained with the additional data. However, a plot of  $\log(I_6/I_{06})$  against  ${}^6\text{Li}$  concentration for the 4 standards also gave a straight-line analytical curve, as shown in Fig. 6, for the concentrations covered, and it essentially coincides with a lithium analytical curve predicted by ZAIDEL AND KORENNOI<sup>2</sup> for a particular absorption coefficient, 0.425.

#### PRECISION

To determine the natural abundance ratio  ${}^7\text{Li}/{}^6\text{Li}$ , a normal lithium hydroxide sample, prepared in 1942, was analyzed a number of times by the technique described for the standards. The absorbance ratios,  $\log(I_6/I_{06})/\log(I_7/I_{07})$ , obtained for the samples were converted to  ${}^6\text{Li}$  concentration by reference to an analytical curve. Table I shows the comparison of results obtained on a number of independent analyses using a new sample in the absorption tube for each analysis. Each result is an average of about 5 determinations for a sample in the absorption tube. The average of the 5 calculated natural abundance ratios is  $12.1 \pm 3.3\%$ .

TABLE I  
RESULTS FOR A NUMBER OF INDEPENDENT ANALYSES USING A NEW SAMPLE IN THE  
ABSORPTION TUBE

Sample no.	Atomic ratio ${}^7\text{Li}/{}^6\text{Li}$	Deviation from average
1	11.58	-0.52
2	11.84	-0.26
3	12.61	+0.51
4	11.84	-0.26
5	12.61	+0.51
Average	12.10	$\pm 0.41$
% Average deviation from mean atomic ratio 3.3%		

Additional experimental data obtained with the two tubes showed good stability of the method and negligible cross-contamination among samples in each tube. As an example, an absorbance,  $\log(I_6/I_{06})$ , was obtained when only  ${}^6\text{Li}$  was present in the tubes and subsequently compared to an absorbance,  $\log(I_7/I_{07})$ , when only

${}^7\text{Li}$  was present in the tubes at the same concentration. Results of this test showed that the respective absorbances for  ${}^6\text{Li}$  and  ${}^7\text{Li}$  were the same.

#### DISCUSSION

In some recent neutron activation work carried out at this laboratory, it became apparent to an investigator that the isotopic composition of lithium in reagent-grade lithium nitrate was not the same as that observed in other lithium compounds previously tested. The lithium nitrate sample was submitted for a mass spectrometric analysis along with the lithium hydroxide sample that was used for the determination of the lithium natural abundance ratio reported in this paper. The isotopic abundance of  ${}^6\text{Li}$  in the lithium nitrate was found to be 2.55 atomic per cent. The  ${}^6\text{Li}$  abundance in the lithium hydroxide was essentially normal, 7.42 atomic per cent. This indicated that the atomic weight for lithium in the depleted sample, lithium nitrate, was different from the normal lithium hydroxide atomic weight by 0.7 per cent. Since a user of lithium compounds might not normally be aware of the large variation in isotopic composition of some reagent-grade lithium salts, it seems appropriate to draw attention to this problem. The unknowing use of reagent-grade lithium salts that have a large variation in isotopic composition can lead to indeterminate errors in the preparation of standards to determine the total lithium content in normal lithium samples. Indeterminate errors will also arise in obtaining absorption readings of the doublet lithium resonance lines at 6708 Å since, as was pointed out earlier in this paper, the isotopic shifts of these lines are greater than the line widths.

The reliability of the atomic absorption technique reported in this paper depended on (1) obtaining a uniformly deposited sample in the crater of the absorption tube, resulting in a reproducible gaseous medium capable of absorbing maximum incident radiation when the discharge was started in the absorption tube; (2) operating the tubes at some stable predetermined fixed lithium emission intensity for a given constant current, so that the ratio of the emitting atoms in the emission tube to the atoms in the absorption tube would be the same for standards and samples. The problem of obtaining a uniformly deposited sample appeared to be solved by using acetone and by rotating the tube to help spread the sample uniformly on the walls of the crater until dried. Close visual inspection of the lithium deposits in the copper electrodes used to obtain the results for this investigation showed that one prepared electrode could not be distinguished from another. The operation of the absorption tube at some stable predetermined lithium emission intensity worked well but for a few loaded electrodes. When the predetermined lithium intensity was not obtained for a given current, the electrode containing the sample was discarded and replaced with a new one. Since valid results were obtained with new samples, when the previously mentioned techniques for the tubes were applied, the problem was minor. The emission tube gave no problems whatever since stable  ${}^6\text{Li}$  and  ${}^7\text{Li}$  emission intensities were constantly obtained for a given current.

At this stage of our work, it is evident from results shown in Table I and a comparison of data with ZAIDEL AND KORENNOI<sup>2</sup> that a water-cooled hollow-cathode discharge tube can be useful as an absorption source for the determination of lithium isotopes and possibly isotopes of other elements. The advantages of using a water-cooled hollow-cathode discharge as an absorption source for lithium isotope analysis instead of flames are numerous:

- (1) Microgram quantities of sample are used in the absorption electrode.
- (2) A number of absorption readings can be obtained on a microgram-size sample and the sample stored away for possible future reference.
- (3) The closed tube and vacuum system minimize the spreading of toxic materials.
- (4) Cost of standard samples is relatively low since the tube uses small samples.

In retrospect, it is felt a one-piece glass absorption tube, having a removable, water-cooled electrode assembly, might have some advantages over the Schüler-Gollnow absorption tube used for this work, since the discharge might be observed more easily using the former assembly and thus studied in greater detail. The ease of cleaning a glass tube periodically in preference to a number of metal parts of the Schüler-Gollnow absorption tube would simplify operation.

It is a pleasure to express our gratitude to Dr. HOWARD CLAASSEN for numerous helpful consultations, Dr. ATHOS GIACCHETTI for informative discussions, and Dr. DON STEWART for encouragement in carrying out this work.

#### SUMMARY

An atomic absorption technique was used to determine the natural abundance ratio,  $^7\text{Li}/^6\text{Li}$ , in a normal sample of C.P. grade lithium hydroxide prepared in 1942. The result obtained,  $12.1 \pm 3.3\%$ , compares favorably with a mass spectrometer value of 12.3 used by the Oak Ridge Isotope Division for reporting the lithium isotope abundance ratio, and it is the first time the  $^7\text{Li}/^6\text{Li}$  abundance ratio has been reported with accuracy by atomic absorption methods. A Schüler-Gollnow water-cooled hollow-cathode tube was used to obtain the resonance doublet of lithium at 6708 Å, while a modified Schüler-Gollnow water-cooled hollow-cathode tube was used to vaporize the natural lithium and related standards in microgram quantities and to absorb the resonance radiation. Helium was used as a carrier gas in both tubes at low pressures for the purpose of sputtering samples and exciting the lithium resonance lines. Regulated d.c. current power supplies, and conventional, independent circulating systems were used with each tube; and a Jarrell-Ash monochromator, Model 82-000, of relatively low dispersion, was used to isolate the resonance lines, along with other readily available commercial recording equipment.

#### RÉSUMÉ

Une méthode par absorption atomique a été utilisée pour déterminer le rapport de la teneur isotopique naturelle  $^7\text{Li}/^6\text{Li}$  dans un échantillon d'hydroxyde de lithium, préparé en 1942. Les résultats correspondent aux valeurs obtenues à l'aide du spectromètre de masse, utilisé par la "Oak Ridge Isotope Division". On utilise un tube cathodique creux, refroidi à l'eau, de Schüler-Gollnow, pour obtenir le doublet de résonance du lithium à 6708 Å, tandis qu'un tel tube, modifié, a été utilisé pour vaporiser le lithium naturel, les étalons correspondants (en microquantités) et pour absorber les radiations de résonance.

#### ZUSAMMENFASSUNG

Mit einer atomaren Absorptionstechnik wurde in einem im Jahre 1942 hergestellten Lithiumhydroxid das natürliche Isotopenverhältnis  $^7\text{Li}/^6\text{Li}$  bestimmt. Das Ergebnis  $12.1 \pm 3.3\%$  stimmt ausgezeichnet mit einem Massenspektrometerwert von 12.3 der "Oak Ridge Isotope Division" überein. Es wurde eine wassergekühlte Schüler-Gollnowsche Hohlkathodenröhre benutzt, um das Resonanzdoublet des Lithiums bei 6708 Å zu erhalten, während mit einer modifizierten Röhre dieser Art das natürliche Lithium und Vergleichsstandards (in Mikrogramm-Mengen) verdampft und die Resonanzstrahlung absorbiert wurden. Helium wurde in beiden Röhren bei niedrigen Drucken als Trägergas verwendet, um die Proben zu versprühen und die Lithiumresonanzlinien anzuregen.

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*Anal. Chim. Acta*, 30 (1964) 213-222

SIMULTANEOUS DETERMINATION OF NICKEL AND COBALT TRACES  
BY NEUTRON ACTIVATION ANALYSIS

R. MALVANO AND G. B. FASOLO

SORIN, *Centro Ricerche Nucleari, Saluggia-Vercelli (Italy)*

(Received August 8th, 1963)

The usual neutron activation techniques allow an accurate determination of traces of cobalt and nickel. For the determination of cobalt both radionuclides, 10.5-min  $^{60m}\text{Co}$  and 5.27-year  $^{60}\text{Co}$ , are used; for nickel the measurement of 2.56-h  $^{65}\text{Ni}$  is the basis of the only widely applied method<sup>1-4</sup>. Anyway, when suitable irradiations in a fast neutron flux are performed (*e.g.* in a water-pool reactor), it is sometimes advantageous to use the  $^{58}\text{Ni}$  (n,p)  $^{58}\text{Co}$  reaction for the determination of nickel. The analytical sensitivity of the method using the 72-day nuclide  $^{58}\text{Co}$  may be easily made at least of the same order of magnitude as that based on  $^{65}\text{Ni}$  measurement, and, moreover, is not so critical with respect to the time required for cooling and treating samples.

In Table I nuclear data<sup>5</sup> for nickel and cobalt, and related analytical sensitivities

TABLE I  
NUCLEAR DATA<sup>5</sup> AND CALCULATED SENSITIVITIES

Element	Target nuclide	Isotopic abundance (%)	Nuclear reaction and cross-section (barns)	Produced radionuclide	Half-life	Energy of $\gamma$ -radiation (MeV)	Analytical sensitivity (g)
Ni	$^{64}\text{Ni}$	1.16	<sup>a</sup> (n, $\gamma$ ) 1.6	$^{65}\text{Ni}$	2.56 h	0.6, 1.45, 1.09	$1.0 \cdot 10^{-7}$
	$^{58}\text{Ni}$	67.8	<sup>b</sup> (n,p) $9.2 \cdot 10^{-2}$	$^{58}\text{Co}$	72 d	0.51 ( $\beta^+$ annihilation) 0.81	$6.5 \cdot 10^{-8}$
Co	$^{59}\text{Co}$	100	<sup>a</sup> (n, $\gamma$ ) 16	$^{60m}\text{Co}$	10.5 min	0.059	$1.1 \cdot 10^{-7}$
			<sup>a</sup> (n, $\gamma$ ) 20	$^{60}\text{Co}$	5.27 y	1.17, 1.33	$1.2 \cdot 10^{-9}$

<sup>a</sup> Thermal activation cross-section.

<sup>b</sup> Activation cross-section averaged over a fission spectrum.

are reported. The sensitivity values are calculated for easily obtained experimental conditions: 200-h irradiation, or at saturation for shorter-lived radionuclides, at a flux level of  $1 \cdot 10^{13}$  neutrons/cm<sup>2</sup>/sec both for thermal and (fission) fast neutrons; active material measured at a distance of 5 mm from a 3''  $\times$  3'' NaI(Tl) scintillator; minimum detectable activity equal to detector background; time required for separation taken into account.

It is possible to determine nickel and cobalt simultaneously through the long-lived radionuclides  $^{58}\text{Co}$  and  $^{60}\text{Co}$  produced in the pile at high fluxes of both fast and thermal

neutrons, by means of a simple separation of cobalt followed by  $\gamma$ -spectrometry: in fact the  $^{58}\text{Co}$  and  $^{60}\text{Co}$  activities are well resolved in the  $\gamma$ -spectrum (see Fig. 1).

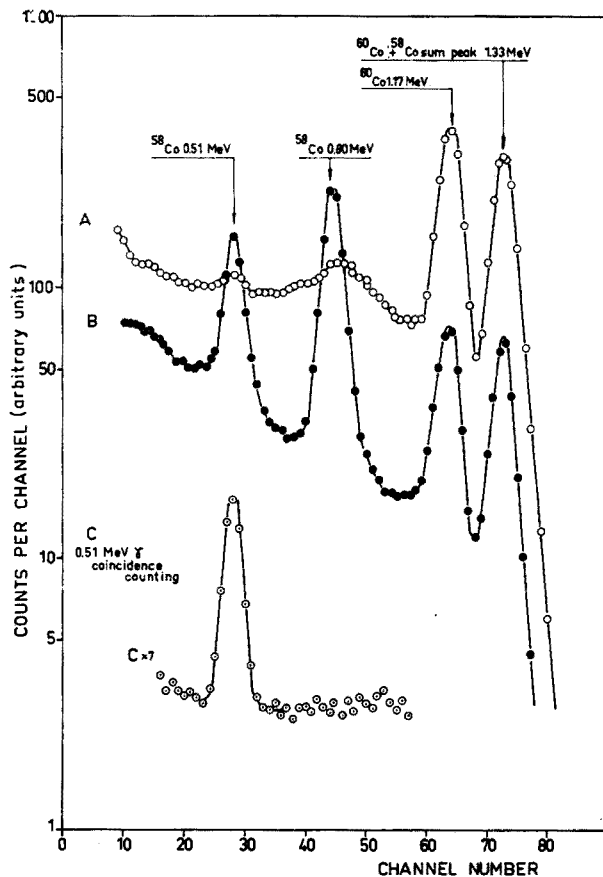


Fig. 1. Spectra of Ni + Co irradiated samples (synthetic samples): A, Ni 1 p.p.m., Co 1 p.p.m.; B, Ni 100 p.p.m., Co 0.1 p.p.m.; C, Ni 1 p.p.m., Co 1 p.p.m.

Solvent extraction of cobalt and a direct spectrophotometric control of chemical recovery on the extracted phases form the basis for a simple, selective separation from other interfering activities.

#### EXPERIMENTAL

##### *Apparatus and materials*

The irradiations were carried out in the core of the Avogadro RSr pool reactor, at thermal fluxes of  $(2.0-4.1) \cdot 10^{13}$  neutrons/cm<sup>2</sup>/sec, fast fluxes of  $(0.6-1.2) \cdot 10^{13}$  neutrons/cm<sup>2</sup>/sec (for in-core irradiations the fast neutron spectrum was found to be very similar to a fission spectrum in the used energy range).

The counting equipment consisted of a  $\gamma$ -spectrometer, with 200-channel pulse analyser (Laben C-31), and 3"  $\times$  3" NaI(Tl) scintillator (Harshaw).

Chemical yields were checked by a Beckman DU spectrophotometer. Reagents

and carriers were selected from B.D.H. chemicals for laboratory use; standards were B.D.H. AnalaR  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$  as solutions.

### General procedure

Weighed samples (0.2–1 g) of the various studied materials were irradiated in quartz vials together with nickel and cobalt standards, for 100–200 h at high neutron fluxes. After a 10-day cooling period, the vials were opened and the samples transferred and treated. The aluminium samples were dissolved in hydrochloric acid containing cobalt carrier (1 mg) solution. For organic substances the attack was carried out by alkaline fusion, the petroleum samples being previously coked with concentrated sulphuric acid; after the addition of cobalt carrier and leaching with hydrochloric acid, the pH was adjusted with sodium hydroxide and the extraction of cobalt was performed.

Both the extraction of the thiocyanate complex by methylisobutylketone and of the 1-nitroso-2-naphthol complex by benzene<sup>6</sup> were used. Because of the interferences of  $^{65}\text{Zn}$  and  $^{59}\text{Fe}$  in the measurement of the  $^{60}\text{Co}$  activity, when the non-selective thiocyanate method was used, previous separations of zinc and iron were performed, as described elsewhere<sup>7</sup>. On the other hand, the 1-nitroso-2-naphthol extraction allowed a good single-step decontamination (< 1% of zinc and iron present in the organic phase, as found by radioactive tracer tests). The chemical yields (70–96%) were determined by spectrophotometric measurements on aliquots of the extracted phase (at 625  $m\mu$  for the thiocyanate, and 350  $m\mu$  for the 1-nitroso-2-naphthol complexes).

The activity was measured by  $\gamma$ -spectrometry on the extracted organic solution and on the aqueous standard solution. For  $^{58}\text{Co}$  the 0.8 MeV peak and for  $^{60}\text{Co}$  the 1.17 MeV peak were evaluated; the 1.33 MeV peak of  $^{60}\text{Co}$  was not taken into account because of the interference from  $^{58}\text{Co}$  activity (1.31 MeV sum-peak), though this contribution may be estimated in a standard  $^{58}\text{Co}$  spectrum. The Compton background under the photopeaks was subtracted by suitable interpolation.

### DISCUSSION AND RESULTS

The precision of the method was tested by a series of analyses on synthetic nickel-cobalt samples (standardized nickel and cobalt-aluminium alloys); the criterion of subtracting the Compton background and the Ni/Co concentration range in which determinations can be performed were evaluated. With a straight-line subtraction of the Compton background for both 0.80 and 1.17 MeV photopeaks, reproducible data within 2.5% were found. For the above-mentioned experimental conditions, quite good results for both nickel and cobalt were obtained, in the range of Ni/Co concentration ratios 3–2500 (3% maximum deviation); for lower values of the ratio either a 0.51 MeV  $\gamma$ -coincidence counting (see Fig. 1), or irradiation at a higher fast to thermal flux ratio (e.g. by shielding with cadmium foils) can be useful.

The possible spurious contribution to the  $^{60}\text{Co}$  activity arising from both the  $^{60}\text{Ni}$  (n,p) $^{60}\text{Co}$  and  $^{63}\text{Cu}$ (n, $\alpha$ ) $^{60}\text{Co}$  reactions was evaluated. From the known amount of the interfering element and the published cross-section values<sup>8</sup> the copper contribution is stated to be less than 1% in any case. With regard to the contribution from nickel, some of the (n,p) cross-section values reported in the literature<sup>8</sup> could suggest that determinations of cobalt would be affected by serious errors: however, negligible

spurious effects were found from an experimental evaluation on irradiated high purity nickel, as well as from the mentioned precision tests on synthetic samples.

In Table II analytical results are shown (average values on 2-5 independent determinations); the reproducibility of the data was found to be within  $\pm 4\%$  for the aluminium sample, and within  $\pm 12\%$  for the petroleum and polyphenyl samples.

TABLE II  
RESULTS OF NICKEL AND COBALT DETERMINATIONS

Materials	Concentrations (p.p.m.)	
	Ni	Co
Crude oil A	0.20	0.0015
B	3.0	0.0030
C	0.31	<0.001
Crude asphalt A	101	0.11
B	78.1	0.055
C	89.0	0.14
D	93.5	0.12
Polyphenyl A	0.14	0.0031
B	0.75	0.0045
Refined (99.995) Al	0.71	0.0052

#### SUMMARY

Nickel and cobalt traces may be determined by measuring the  $^{58}\text{Co}$  and  $^{60}\text{Co}$  activities produced in a nuclear reactor. Solvent extraction of cobalt, and  $\gamma$ -spectrometry on the extracted phase allow a rapid and simple analysis of both metals. The method is applied to the determination of nickel (100-0.2 p.p.m.) and cobalt (0.15-0.001 p.p.m.) in various materials (petroleum, polyphenyls, aluminium).

#### RÉSUMÉ

Une méthode est proposée pour le dosage de traces de nickel et de cobalt par mesure des activités de  $^{58}\text{Co}$  et  $^{60}\text{Co}$ , produits dans un réacteur nucléaire. Une extraction du cobalt et une spectrométrie  $\gamma$  permettent une analyse simple et rapide de ces deux métaux. La méthode a été appliquée au dosage du nickel et du cobalt dans diverses substances.

#### ZUSAMMENFASSUNG

Nickel und Kobalt können in Spuren durch Messung der im Reaktor erzeugten  $^{58}\text{Co}$ - und  $^{60}\text{Co}$ -Aktivitäten bestimmt werden. Die Extraktion des Kobalts und anschließende  $\gamma$ -spektrometrische Untersuchung der extrahierenden Phase erlauben eine schnelle und einfache Analyse beider Metalle. Die Methode wurde zur Bestimmung von 0.2-100 p.p.m. Nickel und 0.001-0.15 p.p.m. Kobalt in verschiedenen Materialien angewendet.

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MICRODETERMINATION OF CAFFEINE USING THE RING OVEN  
TECHNIQUE

FE ORDOVEZA AND PHILIP W. WEST

*Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana (U.S.A.)*

(Received August 18th, 1963)

The presence of organic matter in the atmosphere is generally recognized. Until quite recently, however, analytical methods for the study of such materials have been limited to a relatively few direct methods for individual compounds. With the development of gas chromatography, a powerful tool for the detection and determination of gaseous organic pollutants has been made available. Infrared spectroscopy has also proved very useful in some studies. Still, the identification and estimation of air-borne organic particulates remains a real problem<sup>1</sup>. However, as demonstrated by the present studies, the combination of the spot test and the ring oven techniques holds promise for solving this problem.

Although no special significance is attached to the presence of caffeine in air at this time, the fact that its presence had already been shown<sup>1</sup> influenced its choice as the substance for initial study on the ring oven. WEST and coworkers<sup>2</sup> have previously described the ring oven technique as a tool for studying inorganic air-borne particulates, and the same general procedures now apply to the study of organic particles.

A number of sensitive color reactions are available for the detection of caffeine. However, most of these give similar color reactions with the other purines, the most common interferences resulting from theobromine and theophylline. WACHSMUTH AND VAN KOECKHOVEN<sup>3</sup> obtained a reaction for caffeine with an alkaline solution of acetylacetone and an acidic solution of *p*-dimethylaminobenzaldehyde in which a blue solution formed upon the addition of water. The reaction can be used for the spectrophotometric determination of caffeine and has now been adapted for use in the estimation of traces of caffeine by means of the ring oven technique. The method is free of interferences from theobromine, theophylline and other purine-containing compounds. Application to the study of air-borne organic particulates is suggested.

## EXPERIMENTAL

*Reagents*

Solution A is a freshly prepared solution of 0.5 ml of acetylacetone in 5 ml of 2 *N* sodium hydroxide.

Solution B is a freshly prepared solution of 0.05 g of *p*-dimethylaminobenzaldehyde in 2 ml of 12 *N* hydrochloric acid.

### *Apparatus*

Weisz ring oven.

Capillary pipets calibrated to 1  $\mu$ l and 5  $\mu$ l.

Schleicher and Schuell analytical filter paper No. 595, 5.5 cm diameter.

### *Sample collection*

The proposed method is especially suited for use in air pollution studies. For such applications, samples of air-borne particulates can be collected by any of the standard techniques, such as filtration using high volume samplers or sequential tape samplers or by electrostatic precipitation. Bulk samples collected by electrostatic precipitation or on glass filters can be extracted with chloroform and the dissolved caffeine transferred to the ring oven as described under *Preparation for analysis*. Where filtration on paper is employed, a representative portion of the filter can be cut out with a cork borer, the disc placed on filter paper with the dust side down, and the sample extracted to the ring by means of 10–15 washes with chloroform. This method is convenient for detection and rough estimation, but does not apply to quantitative measurement as described here. Preferably, the entire sample can be isolated, dissolved and treated as described below whereby three rings of the sample are prepared and statistically evaluated.

### *Preparation for analysis*

Caffeine may be extracted from the gross sample with chloroform. The chloroform extract is then transferred in small portions to a 5-ml test tube and evaporated to dryness over a water bath at 60°. The residue is then ready for subsequent analysis.

### *Procedure*

Treat the caffeine sample in the test tube with 0.2 ml of solution A. Stopper the test tube and heat over a water bath at 80° for 7 min. Cool.

Place two 5- $\mu$ l drops of solution B in the center of a piece of Schleicher and Schuell filter paper 595, positioned on the ring oven heated to 80°. Add a 1- $\mu$ l drop of the treated sample. More 1- $\mu$ l drops of the treated sample may be added if necessary, but the quantity should not exceed ten 1- $\mu$ l drop portions. Add in addition two 5- $\mu$ l drops of solution B. Wash the spot reaction to the ring zone with 8 to 10 5- $\mu$ l drops of 0.1 N hydrochloric acid. In washing, care should be taken to avoid flooding the ring. Heat the filter paper on the ring oven at 80° for 1 min. Remove the paper and immediately dip with agitation in a bath of 95% by volume acetone until the definite blue color of the ring appears. Blot off the excess solvent between thick absorbant papers and dry the ring at room temperature. The color of the ring is observed in both transmitted and direct light.

### *Analysis of an unknown*

The above procedure is followed for the preparation of each ring. The standard scale is prepared by making rings with 1, 2, 4, 6, 8 and 10 drops containing 1  $\mu$ l per drop of a solution (caffeine treated with solution A) containing 1.0  $\mu$ g caffeine. The size of drops used in preparing the standard scale should also be used in making the rings of the unknown solution. Three rings made from different numbers of  $\mu$ l drops

of the solution are sufficient for each unknown. The color of each of the three rings is compared visually with that of the standard scale, and it is decided if it matches one of the rings or if it falls between two rings of the standard scale. The sum of the numbers of  $\mu\text{l}$  drops of the three matching rings of the standard divided by the sum of the numbers of  $\mu\text{l}$  drops of the three rings made from the unknown solution used equals the concentration of the unknown solution referred to the standard solution<sup>4</sup>. When this quotient is multiplied by the concentration of the standard solution used to prepare the standard scale, the concentration of the unknown sample is obtained. The preparation of the standard scale and the analysis of the unknown solution take about 1-1.5 h.

#### RESULTS AND DISCUSSION

##### *Factors affecting the color reaction*

The reaction for caffeine using solutions of acetylacetone in sodium hydroxide and *p*-dimethylaminobenzaldehyde in hydrochloric acid to form a blue-colored solution upon the addition of water<sup>3</sup> provided a guide for the development of a spot reaction for caffeine on filter paper suitable for use in microquantitative analysis by the ring oven technique. In the development of this test, several factors were investigated. The formation of a definite and stable colored ring on the paper for the purpose of quantitative determination of caffeine depended on the concentrations of all the reagents used, the order of their addition to form the ring, the temperature of the media, the length of time in which the reaction was carried out and the type of filter paper employed.

The two reagents used in the procedure were solutions of acetylacetone in sodium hydroxide (solution A) and *p*-dimethylaminobenzaldehyde in hydrochloric acid (solution B). Varying concentrations of each constituent of the two reagents were tried as color-producing reagents with caffeine on the filter paper. A temperature range of 60-90° was used to determine the appropriate temperature condition for the reaction. For the preliminary experiment, spotting was done on Whatman No. 40 filter paper, and an ordinary laboratory oven was used for heating. Approximately 10  $\mu\text{g}$  of caffeine was spotted on the center of the filter paper, followed by a drop of solution A. This was heated for about 2 min and cooled. A drop of solution B was added to the same spot, heated for 2 min and cooled. Distilled water was used for the dipping bath to develop the color reaction. Of all the conditions tried, 0.5 ml of acetylacetone in 5 ml of 2 *N* sodium hydroxide and 0.05 g of *p*-dimethylaminobenzaldehyde in 2 ml of hydrochloric acid with the reaction carried out at 80° for 2 min gave the best test: a definite blue spot on the paper which tended to diffuse and to turn yellow-green on standing.

The above reaction was tried on the ring oven. However, spotting the test solution in the center of the filter paper on the ring oven heated to 80°, followed by the addition of the reagents, washing to the ring zone with 0.1 *N* hydrochloric acid and heating for 2 min, resulted in the formation of an irregular and indefinitely colored ring, which remained unchanged on dipping in distilled water. Varying the temperature of the ring oven (60° to 90°), the time of heating (1 to 7 min), the number of  $\mu\text{l}$  drops of the reagent and changing the order of addition of the reagent solutions all failed to yield satisfactory test rings.

It was then decided to treat the caffeine first in a 5-ml test tube with 0.2 ml of



solution A and then to heat for 5 to 7 min in a water bath at 80°. After cooling, the mixture was added to the center of the filter paper fixed in place on the ring oven. After adding two 5- $\mu$ l drops of reagent solution B, the spot reaction was washed to the ring zone with 0.1 *N* hydrochloric acid and treated at 80° for 1 min. Heating for more than 2 min tended to destroy the reaction ring. An unstable green colored ring was formed which turned to a definite blue when dipped in a bath of distilled water. Though water gave a good blue colored reaction, the ring formed was unstable and tended to diffuse from the paper and to lose its color on standing. The color of the test ring varied in stability according to the dipping bath used. Ethanol, methanol, propanol, ether and acetone were unsatisfactory in developing the color of the ring. Dipping baths containing 50, 75, 90 and 95% by volume of each of the above solvents were studied, but only 95% by volume acetone gave satisfactory results in the formation of the blue colored ring.

The sensitivity and proportionality of color intensity of the ring with increasing quantity of caffeine were determined. From 10 to 200  $\mu$ g of caffeine were treated with 0.02 ml of solution A. This gave a concentration range of 0.050  $\mu$ g to 1.0  $\mu$ g of caffeine per  $\mu$ l. When the procedure was used on 1-10  $\mu$ l drops of each of the test solutions, blue rings with uncertain proportionality and with a significant blank resulted. Since different filter papers may affect certain color reactions, a study of the performance of several analytical filter papers was undertaken. Among the filter papers tried, Schleicher and Schuell analytical filter paper no. 595 proved to give the most satisfactory result. A sensitivity of 1  $\mu$ l of caffeine on the ring was obtained, and no blank was observed. Table I shows the characteristics of the filter papers studied.

TABLE I  
CHARACTERISTICS OF SELECTED FILTER PAPER

<i>Paper</i>	<i>Speed</i>	<i>Strength</i>	<i>Remarks</i>
Whatman 40	Good	Fair	Gives a blank reaction and uncertain proportionality of increase in color intensity with increasing quantity of caffeine
Whatman 41	Very good	Poor	Gives a blank reaction and uncertain proportionality of increase in color intensity with increasing quantity of caffeine
Munktells O	Good	Fair	Gives a good sensitive reaction, without blank, but has a tendency to form an irregular ring
Munktells OK	Good	Good	Gives a yellow-colored ring
Schleicher and Schüll White Ribbon 589	Good	Good	Gives a weak color for caffeine and a blank reaction
Schleicher and Schüll Blue Ribbon 589	Slow	Good	Gives a weak color for caffeine and a blank reaction
Schleicher and Schüll 595	Good	Good	Gives a definite color for caffeine with good sensitivity, no blank and certain proportionality

The sensitivity of the test on the ring was further improved to  $0.5 \mu\text{g}$  by putting two  $5\text{-}\mu\text{l}$  drops of reagent solution B on the paper on the ring oven before spotting the test solution (caffeine treated with solution A) and followed by another two  $5\text{-}\mu\text{l}$  drops of solution B, before finally washing the spot reaction to the ring zone. A lower limit of  $10 \mu\text{g}$  of caffeine could be treated with  $0.2 \text{ ml}$  of solution A in the test tube, in which case  $10\text{-}\mu\text{l}$  drops of the treated caffeine would be needed to make a ring of  $0.5 \mu\text{g}$  of caffeine. Drops of not more than  $10 \mu\text{l}$  of the test solution could be put on the paper. A weaker color resulted when more than  $10\text{-}\mu\text{l}$  drops were used. This fact determined the upper limit ( $10 \mu\text{g}$ ) of caffeine that could be treated in the test tube with solution A. With  $20 \mu\text{g}$  of caffeine or more on the paper, the color intensity of the ring tended to become so very dark that a loss of proportionality resulted, and dilution of the sample was required before treatment with reagent solution A. A sample with  $10\text{--}400 \mu\text{g}$  of caffeine would be satisfactory for treatment with  $0.2 \text{ ml}$  of reagent solution A. In this case the lower limit of  $0.5 \mu\text{g}$  on the ring could be obtained by using  $10\text{-}\mu\text{l}$  drops of the treated sample with  $10 \mu\text{g}$  of caffeine, and the upper limit of  $20 \mu\text{g}$  of caffeine on the ring would not be exceeded.

In the procedure finally developed, the period of stability of the ring was studied and determined. Rings containing  $0, 1, 2, 4, 6, 8$  and  $10 \mu\text{g}$  of caffeine were made, and any change in color was observed by comparing visually with a similar freshly prepared scale. No change of color was noted until the fourth day.

#### *Study of interferences*

Investigation of organic compounds which usually give a color reaction similar to that of caffeine was made to find out if they would interfere with the test. Theobromine (3,7-dimethylxanthine), theophylline (1,3-dimethylxanthine), xanthine (2,6-dioxypurine) and uric acid (2,6,8-trioxypurine) were non-interfering. Benzo( $\alpha$ )pyrene, formaldehyde, formic acid and urea which could possibly be collected from the atmosphere during the sampling for caffeine were also tested. Benzo( $\alpha$ )pyrene and formic acid did not interfere. Formaldehyde interfered at all levels of concentration by producing an orange-colored solution when treated with solution A and heated to  $80^\circ$ . A blue-violet ring on the paper resulted. However, preliminary evaporation of the sample to complete dryness over an  $80^\circ$  water bath before treatment with solution A eliminated the interference from formaldehyde. Urea did not interfere positively, but with caffeine, it formed a yellow-green ring. However, when the ring was dipped with constant agitation for 2–3 min in 95% by volume acetone, the blue color of the caffeine ring would appear. All of the above interference studies were done with  $10 \mu\text{g}$  caffeine and  $500 \mu\text{g}$  of the other compounds in the test tube and using  $1 \mu\text{g}$  caffeine and  $50 \mu\text{g}$  of the other compounds in the ring.

#### *Quantitative estimation*

The accuracy and reproducibility of the test for use in the microdetermination of caffeine were ascertained by the study of several standard scales and by the analysis of two test solutions. A range of concentration which had observable differences in color intensity was determined and used in the preparation of the standard scales. Several standard scales containing  $0, 1, 2, 4, 6, 8$  and  $10 \mu\text{g}$  of caffeine were prepared using  $1\text{-}\mu\text{l}$  drop portions of standard solution containing  $1 \mu\text{g}$  of caffeine per  $\mu\text{l}$ . A study of two test solutions of known caffeine content was made. Fifteen rings were

made for each of the solutions. The rings contained 1, 2, 2, 3, 4, 4, 5, 6, 6, 7, 8, 8, 9, 10 and 10 1- $\mu$ l drop portions of each of the test solutions. The rings were divided into sets of three, and each group of three rings was treated as a separate sample with the rings compared visually to the standard scale. The average value for the ratio of the test solution to the standard was computed by the method of WEISZ<sup>4</sup> as described in the section, *Analysis of an unknown*.

The results of these determinations are presented in Table II.

TABLE II  
DETERMINATION OF CAFFEINE  
(Ratio of test to standard solution)

<i>Taken</i>	<i>Found</i> <sup>a</sup>
0.85	0.860 $\pm$ 0.006 <sup>b</sup>
1.00	1.010 $\pm$ 0.003

<sup>a</sup> Based on averaging 5 values calculated from 3 rings, each according to the method of WEISZ<sup>2</sup>.

<sup>b</sup> Calculated at 90% confidence level.

Statistical analysis of the values obtained in the above determinations gave average values of 0.86 and 1.01 with sample standard deviations of 0.098 and 0.055, and sample standard errors of 0.0438 and 0.0246, respectively. All units of measurement used were ratio of the test solution concentration to standard solution.

In the work of WEISZ<sup>4</sup>, it was pointed out that the general technique of microanalysis using the ring oven should give results having 5 to 10% error or even less. In the analysis of the two test solutions of caffeine, of the 30 rings studied, 11 did not match exactly any ring of the standard scale. In spite of this high proportion of deviation in visual matching, an average error of 3% resulted which proved the efficacy of the averaging technique developed by WEISZ.

This investigation was supported in whole by Public Health Service Research Grant AP 00117 from the Division of Air Pollution, Bureau of State Services.

#### SUMMARY

A rapid and highly selective method for the microdetermination of caffeine of special interest for air pollution studies is presented. With the ring oven technique and with solutions of acetylacetone in sodium hydroxide and *p*-dimethylaminobenzaldehyde in hydrochloric acid, as little as 0.5  $\mu$ g caffeine on the ring can be determined with an average error of 3%. Compounds containing purine bases which would be likely to give the same color reaction as caffeine do not interfere. Of the organic air pollutants which might be collected from the atmosphere during the sampling for caffeine, benzo( $\alpha$ )pyrene and formic acid do not interfere. Interferences from formaldehyde and urea are easily eliminated.

#### RÉSUMÉ

Une méthode rapide et très sélective est proposée pour le microdosage de la caféine, d'un intérêt tout particulier pour des études de pollution de l'air. Il est possible, en utilisant la technique four anneau et les solutions: acétylacétone dans de l'hydroxyde de sodium, et *p*-diméthylaminobenzaldéhyde dans l'acide chlorhydrique, de doser jusqu'à 0.5  $\mu$ g de caféine, avec une erreur moyenne de 3%. Les substances renfermant des bases puriques, le benzo( $\alpha$ )pyrène et l'acide formique ne gênent pas. Les interférences dues au formaldéhyde et à l'urée peuvent être facilement évitées.

## ZUSAMMENFASSUNG

Eine schnelle und sehr empfindliche Methode zur Mikrobestimmung von Coffein, besonders zur Untersuchung von Luftverunreinigungen, wird beschrieben. Mit der Ringofentechnik und mit Lösungen von Acetylaceton in Natriumhydroxid und *p*-Dimethylaminobenzaldehyd in Salzsäure können 0.5  $\mu\text{g}$  Coffein mit einem mittleren Fehler von 3% bestimmt werden. Verbindungen die Purinbasen enthalten, welche dieselbe Farbreaktion geben, stören nicht. Von den organischen Luftverunreinigungen, die zusammen mit dem Coffein aus der Luft geholt werden, stören Benzopyren und Ameisensäure nicht. Störungen durch Formaldehyd und Harnstoff werden leicht eliminiert.

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*Anal. Chim. Acta*, 30 (1964) 227-233

## THERMOGRAVIMETRIC INVESTIGATION OF THE ALKALINE EARTH DILITURATES

MILTON W. GOHEEN AND REX J. ROBINSON

*Chemistry Department, University of Washington, Seattle 5, Washington (U.S.A.)*

(Received August 28th, 1963)

The alkaline earth salts of dilituric acid (5-nitrobarbituric acid) are known to be quite insoluble. REDEMANN AND NIEMANN<sup>1</sup> have reported the solubilities in water at 25° of a number of the diliturates including those of the alkaline earth group. Magnesium is the least soluble while calcium diliturate is the most soluble. BERLIN AND ROBINSON<sup>2</sup> reported the utilization of dilituric acid for the thermogravimetric determination of magnesium and included a thermolysis curve of magnesium diliturate. The present paper extends the work of BERLIN AND ROBINSON by including the thermolysis curves of calcium, strontium and barium diliturates and the investigation of the thermogravimetric determination of calcium, strontium and barium by precipitation as the diliturates.

MIHAI AND ROCH<sup>3</sup> in 1960 published thermolysis curves for calcium and strontium diliturates which differ markedly from our findings. In the case of calcium diliturate they reported an octahydrate which, when exposed to air at room temperature, lost weight quite rapidly. We have kept the octahydrate open to the laboratory atmosphere for 3 months at a temperature of about 24° with no apparent change in degree of hydration. They reported that the calcium diliturate dihydrate was stable between 80° and 110° and that the anhydrous form was stable between 180° and 210° while we found that the dihydrate was stable between 80° and 160° and that the anhydrate was stable from 210° to 270°. They also found a region between 400° and 600° which exhibited a plateau corresponding to calcium carbonate while we observed only an inflection point for the carbonate at 615°. MIHAI AND ROCH found an octahydrate for strontium diliturate which dehydrated in one step while we found that strontium diliturate formed a heptahydrate which dehydrated in two steps. Our results showed that anhydrous strontium diliturate is stable over a 120° range while they reported that it was stable only at 160–170°. Again we found only an inflection point on the curve for strontium carbonate rather than a long stable region for the carbonate as reported by MIHAI AND ROCH.

### EXPERIMENTAL AND RESULTS

#### *Equipment*

An ADAMEL recording thermobalance (Chevenard system) was used to obtain the thermolysis curves.

Coors porcelain crucibles, No. 00000, and Coors porcelain filtering crucibles, No. 00000, of 15  $\mu$  porosity were used.

### Reagents

*Calcium diliturate* was prepared by treating an aqueous 0.1 *M* solution of reagent-grade calcium chloride with an equivalent amount of saturated aqueous dilituric acid. The precipitate was collected in a fritted glass filtering crucible, washed first with water, then with 95% ethanol and then air-dried (water pump).

*Strontium diliturate* was prepared by treating an aqueous 0.005 *M* solution of reagent-grade strontium nitrate (Mallinckrodt Chemical Works) with an equivalent amount of 0.05 *M* dilituric acid in 50% ethanol. After standing for one day, the precipitate was collected in a fritted glass filtering crucible, washed first with water, then with 95% ethanol and then with acetone and finally vacuum-dried (water pump). The salt was also prepared from completely aqueous solutions using an 0.1 *M* reagent-grade solution of strontium nitrate and an excess of aqueous saturated dilituric acid. This time the precipitate was washed with water, then 95% ethanol and air-dried (water pump).

*Barium diliturate* was prepared by treating an aqueous 0.005 *M* solution of reagent-grade barium chloride (Baker and Adamson) with an equivalent amount of 0.05 *M* dilituric acid in 50% ethanol. The salt was allowed to stand for one day, then collected in a fritted glass filtering crucible and washed with water, then with 95% ethanol and finally with acetone. The salt was dried by vacuum desiccation (water pump). Barium diliturate was also prepared by treating an 0.1 *M* aqueous solution of reagent-grade barium chloride with a slight excess of a saturated aqueous solution of dilituric acid. The salt was allowed to stand overnight, then collected in a fritted glass filtering crucible. The salt was washed in the filter with water, then with 95% ethanol and air-dried (water pump).

*Nitrogen* gas was purified by passing through solid calcium sulfate to free it of moisture. The flow rate was 3 l/h.

### Solutions

Saturated dilituric acid solution (0.05 *M*) in 50% ethanol was prepared from recrystallized, white-label dilituric acid (Eastman Kodak Company), as described by BERLIN AND ROBINSON<sup>2</sup>.

A calcium solution was prepared by dissolving reagent-grade calcium chloride in water and found to be 0.0603 *M* by standardization by the oxalate-permanganate method. This solution was diluted with water to give a 0.00603 *M* solution and also was diluted with water and ethanol to give a 0.00603 *M* solution in 50% ethanol.

Primary standard solutions of 0.00996 *M* and 0.00502 *M* strontium were prepared from Mallinckrodt reagent-grade anhydrous strontium nitrate dried at 135°. Solutions of 0.00251 *M*, 0.001003 *M* and 0.000502 *M* were prepared from the 0.00502 *M* solution by dilution with water.

A primary standard solution of 0.00543 *M* barium was prepared from Baker and Adamson reagent-grade barium chloride dihydrate. This solution was used to prepare 0.00272 *M*, 0.00136 *M* and 0.000543 *M* solutions by dilution with water.

Calibrated volumetric apparatus was used for measuring all volumes of solutions.

*Thermolysis curves*

The thermolysis curves in Fig. 1 were obtained by heating the diliturates in No. 00000 porcelain crucibles. The weights of the samples and the corresponding rates of heating for each curve are recorded on Fig. 1. All samples were run in dry nitrogen flowing at a rate of 3 l/h.

Calcium diliturate octahydrate lost 6 moles of water starting at 33° and terminating at 90°. The dihydrate was stable to 165°. The second dehydration occurred from 165° to 210° where the anhydrous salt was produced. Anhydrous calcium diliturate was stable to 270°. At 270° the salt began decomposing slowly until between 360° and 410° a rapid decomposition occurred. From 410° to 800° the decomposition was slow with the final production of calcium oxide. An inflection point at 615° corresponding to calcium carbonate occurred.

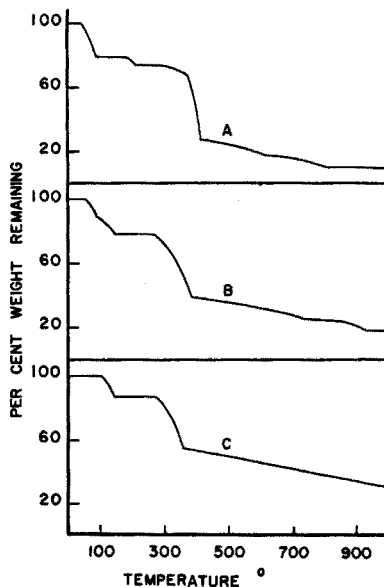


Fig. 1. Thermolysis curves of alkaline earth diliturates: (A) calcium diliturate, 21.4 mg heated at 300°/h; (B) strontium diliturate, 25.2 mg heated at 300°/h; (C) barium diliturate, 28.6 mg heated at 300°/h.

Strontium diliturate heptahydrate dehydrated in two steps of 3.5 moles of water each. The first step started at 50° and terminated at about 95° producing the semi-stable 3.5-hydrate. The second step terminated at 150° with the production of the anhydrous salt. The anhydrous strontium diliturate was stable to 275°. From 275° to 390° a rapid decomposition occurred. From 390° to 925° the decomposition was slow with an inflection point at 720° corresponding to strontium carbonate. The product at 925° was strontium oxide. Since no stable region for strontium carbonate was reached between 500° and 800° as expected from the work of MIHAI AND ROCH<sup>3</sup> as well as DUVAL<sup>4</sup>, a sample of reagent strontium carbonate powder was run. We found that the strontium carbonate started to decompose slowly at 550° and that at 825° the decomposition became quite rapid and quickly produced the strontium oxide.

Barium diliturate tetrahydrate dehydrated in one step starting at 95° and terminating at 125°. The anhydrate was stable from 125° to 275°. At 275° the diliturate decomposed quite rapidly to 365° and then more slowly with no region of stability up to 1000°. On a run on reagent barium carbonate the carbonate was stable to 850° and then slowly decomposed to 1050° which is the upper limit of our thermobalance.

*Thermogravimetric analysis for strontium*

Aliquots (10 ml) of strontium solutions were treated with enough 0.05 M dilituric acid (50% ethanol) solution to give a 1:4 mole ratio of Sr:D. The precipitate was allowed to form overnight and then cooled for 3 h on ice. The precipitate was collected in No. 00000 filtering crucibles, washed with 0.01 M dilituric acid (50% ethanol) solution and then once with 95% ethanol. The precipitate was then weighed after ignition at 160–180°.

TABLE I  
DETERMINATION OF STRONTIUM AS STRONTIUM DILITURATE

<i>SrD<sub>2</sub></i> precipitate (mg)	<i>Sr</i> taken (mg)	<i>Sr</i> found (mg)	Deviation (mg)
43.9	8.72	8.91	+0.19
43.3	8.72	8.78	+0.06
43.2	8.72	8.77	+0.05
21.3	4.40	4.32	-0.08
21.3	4.40	4.32	-0.08
21.6	4.40	4.38	-0.02
21.6	4.40	4.38	-0.02
21.7	4.40	4.40	0.00
21.9	4.40	4.44	+0.04
21.7	4.40	4.40	0.00
10.6	2.20	2.15	-0.05
10.6	2.20	2.15	-0.05
10.7	2.20	2.17	-0.03
4.2	0.88	0.85	-0.03
4.2	0.88	0.85	-0.03
4.1	0.88	0.83	-0.05
1.1	0.44	0.22	-0.22
1.6	0.44	0.32	-0.12

*Results.* Table I lists the results obtained by this method. The precipitate formed slowly and optimum results were obtained by allowing the precipitation to proceed overnight at room temperature and then cooling on ice for a period of about 3 h before filtration. At 8.72 mg/10 ml of solution the deviations were all positive and of the order of 1%. From 4.40 to 2.20 mg/10 ml the method was found to be accurate to 0.9%. The level of 0.88 mg/10 ml appears to be too low for this method, as the results were off by about 3 parts in 80 and at 0.44 mg/10 ml the results were very low. The method yields optimum results for solutions containing about 2–4 mg strontium per 10 ml of solution.



*Thermogravimetric analysis of barium*

Aliquots (10 ml) of barium solutions were treated with enough 0.05 *M* dilituric acid (50% ethanol) solution to give a 1:4 mole ratio of Ba:D. The precipitate was allowed to form for about 30 min and then cooled on ice for another 30 min. The precipitates were then collected in No. 00000 filtering crucibles, washed with 0.01 *M* dilituric acid (50% ethanol) solution, then washed once with 95% ethanol and weighed after ignition at about 160°.

TABLE II  
DETERMINATION OF BARIUM AS BARIUM DILITURATE

<i>BaD<sub>2</sub></i> precipitate (mg)	<i>Ba</i> taken (mg)	<i>Ba</i> found (mg)	Deviation (mg)
26.4	7.46	7.53	+0.07
26.5	7.46	7.56	+0.10
26.3	7.46	7.50	+0.04
13.1	3.73	3.74	+0.01
12.9	3.73	3.69	-0.04
13.1	3.73	3.74	+0.01
13.2	3.73	3.76	+0.03
13.0	3.73	3.71	-0.02
13.0	3.73	3.71	-0.02
13.4	3.73	3.82	+0.09
13.1	3.73	3.74	+0.01
6.5	1.86	1.86	0.00
6.3	1.86	1.80	-0.06
6.5	1.86	1.86	0.00
2.4	0.75	0.68	-0.07
2.2	0.75	0.63	-0.12
1.5	0.75	0.43	-0.32

*Results.* Table II lists the results obtained by this method. The precipitate formed rapidly and was easily handled. From 3.73 to 1.86 mg/10 ml of solution, the method was found to be accurate to 0.8%. At 7.46 mg/10 ml of solution the results were all about 1% high. The results for the 0.746 mg/10 ml level were very low. The optimum range for barium appears to be 1.5–5.0 mg of barium per 10 ml of solution.

*Thermogravimetric analysis of calcium*

An attempt was made to determine calcium as the diliturate. Aliquots (10 ml) of the 0.00603 *M* aqueous solution were treated with enough dilituric acid solution (50% ethanol) to give mole ratios of 1:4, 1:5 and 1:6 Ca:D, and 10-ml aliquots of the 50% ethanol solution of calcium were treated with enough saturated aqueous dilituric acid solution to give a mole ratio of 1:4 Ca:D. The precipitates were allowed to form for about 30 min, then cooled on ice for 1 h and then collected in No. 00000 filtering crucibles. The precipitates were washed with 0.01 *M* dilituric acid (50% ethanol), then with 95% ethanol and finally weighed after ignition at 220–230°.

*Results.* As could have been predicted from the relatively large solubility of calcium diliturate in water at 25° (5.7 mmol/l)<sup>1</sup>, the results (Table III) are all low and approach

TABLE III  
 DETERMINATION OF CALCIUM AS CALCIUM DILITURATE

<i>CaD<sub>2</sub></i> precipitate (mg)	<i>Ca</i> taken (mg)	<i>Ca</i> found (mg)	Deviation (mg)
23.6	2.43	2.20	-0.23
24.4	2.43	2.28	-0.15
1:4 mole ratio using 0.05 M (50% ethanol) dilituric acid			
25.2	2.43	2.34	-0.09
1:5 mole ratio using 0.05 M (50% ethanol) dilituric acid			
25.3	2.43	2.36	-0.07
25.3	2.43	2.36	-0.07
1:6 mole ratio using 0.05 M (50% ethanol) dilituric acid			
25.3	2.43	2.36	-0.07
25.2	2.43	2.34	-0.09
1:4 mole ratio using 50% ethanol calcium solution and an aqueous saturated solution of dilituric acid			

about a 3% negative deviation at the best. But since solubilities for the diliturate salts decrease with decreasing temperature and increasing alcohol content, the investigation was undertaken. The method might find use in quick estimations since it takes only about 2 h for duplicate analysis.

#### SUMMARY

Thermolysis curves for calcium, strontium and barium diliturates were obtained. Calcium diliturate forms an octahydrate from aqueous solution while strontium diliturate forms a heptahydrate and barium diliturate forms a tetrahydrate.

Methods for the thermogravimetric determination of strontium and barium were developed and found to be quite accurate; calcium can only be determined semi-quantitatively by precipitation as the diliturate salt.

#### RÉSUMÉ

Les courbes de thermolyse des diliturates de calcium, strontium et baryum ont été tracées. A partir de solutions aqueuses, le diliturate de calcium obtenu est un octahydrate, celui de strontium un heptahydrate et celui de baryum un tétrahydrate. Les auteurs ont mis au point une méthode de dosage thermogravimétrique pour le strontium et le baryum; le calcium ne peut être dosé ainsi que semi-quantitativement.

#### ZUSAMMENFASSUNG

Thermolysekurven für Calcium-, Strontium- und Barium-Diliturat wurden gemessen. Calcium-Diliturat bildet aus wässriger Lösung ein Octahydrat, Strontium-Diliturat ein Heptahydrat und Barium-Diliturat ein Tetrahydrat. Methoden zur thermogravimetrischen Bestimmung von Strontium und Barium wurden entwickelt. Calcium kann nur halbquantitativ durch Ausfällen des Diliturats bestimmt werden.

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## EFFECTS OF SURFACE-ACTIVE SUBSTANCES ON POLAROGRAPHIC WAVES OF SOME COMPLEXES

EINAR JACOBSEN AND GUNNAR KALLAND

*Department of Chemistry A, University of Oslo, Blindern (Norway)*

(Received September 25th, 1963)

Surface-active substances (surfactants) are usually employed in polarographic analysis in order to eliminate maxima on the waves. In recent years a number of new synthetic detergents has been recommended as maximum suppressors. In some cases, however, the presence of such substances causes undesirable effects such as suppression of the diffusion current, shift in the half-wave potential, splitting of a wave into two parts or a complete inhibition of the electrode reaction. These effects, caused by a strong adsorption of the surface-active material at the electrode, have been described by several authors<sup>1-7</sup>. A literature survey showed, however, that only a few papers are concerned with the effects of the charge type of the surfactants. HAQUE AND MALIK<sup>8</sup> claim that cationic soaps are most effective for the suppression of negative maxima and anionic soaps for the suppression of positive maxima. TANFORD<sup>9</sup> reported that the negatively charged chloro-complexes of lead and cadmium are reversibly reduced in the presence of serum albumin, whereas the uncomplexed metal ions produce irreversible waves in the same medium. He interpreted the results in terms of an electrostatic repulsion between the cations and the positively charged protein molecules. The effects of cationic and anionic surfactants on the polarographic wave of copper(II) in perchlorate medium have been thoroughly investigated by KOLTHOFF AND OKINAKA<sup>10</sup>. They found that the presence of an anionic surfactant makes the copper wave more reversible, whereas cationic and non-ionic substances have a great distorting effect on the wave.

Recently we investigated the polarographic behaviour of the copper-DTPA complex and found that this complex yields a well-defined wave in the presence of the cationic substance dodecylamine perchlorate, whereas the wave of uncomplexed copper was greatly distorted in the same medium. The experiments indicated that the distorting effect of a surfactant depends upon the charge type of the particular depolariser. The present work was carried out in order to investigate the effect of cationic and anionic substances on the polarographic waves of positively and negatively charged complexes.

## EXPERIMENTAL

*Materials*

Diethylenetriaminepentaacetic acid (DTPA) was obtained from Geigy Chemical Corp., New York. A 0.05 *M* stock solution was prepared and standardized as described

previously<sup>11</sup>. Stock solutions of triethylenetetramine (Trien) and of ethylenediamine-tetraacetic acid (EDTA) were prepared by dissolving the appropriate amount of triethylenetetramine disulphate (Baker Analyzed Reagent) and Idranal III (Riedel de Haen AG) respectively, in distilled water.

A 0.5% solution of dodecylamine perchlorate was prepared by dissolving 0.5 g of Armeen 12 D (Armour Chemical Industries, Ltd., U. K.) in 100 ml of perchloric acid containing the equivalent amount of the acid. Sodium dodecyl sulphate (SDS) was a product of L. Light and Co., Ltd., U. K., and Triton X-100 was obtained from Rohm and Haas Co., Philadelphia; 0.1% stock solutions of these substances were prepared by dissolution of the commercial products in distilled water. The remaining chemicals were of reagent grade and used without further purification. 0.2 *M* acetate and phosphate buffers were used as supporting electrolytes.

### Apparatus

All polarograms were recorded with a Tast-Polarograph, Selector D (Atlas Werke, Bremen, West-Germany). The conventional types of dropping mercury electrode and of electrolysis cell were used. The capillary characteristics measured in 0.1 *M* potassium nitrate (open circuit) at a corrected mercury height of 50.7 cm were  $m = 2.998$  mg/sec and  $t = 3.52$  sec. An external saturated calomel electrode (S.C.E.) served as reference electrode. Dissolved air was removed from the solutions with oxygen-free nitrogen. All experiments were performed at  $25 \pm 0.1^\circ$ . The pH of the solutions was measured with a Beckman Zeromatic pH meter.

### RESULTS AND DISCUSSION

The surface-active substances used in this investigation, sodium dodecyl sulphate (SDS), dodecylamine perchlorate (Armeen) and Triton X-100 are all strongly adsorbed at the dropping mercury electrode. As indicated in Fig. 1, the presence of

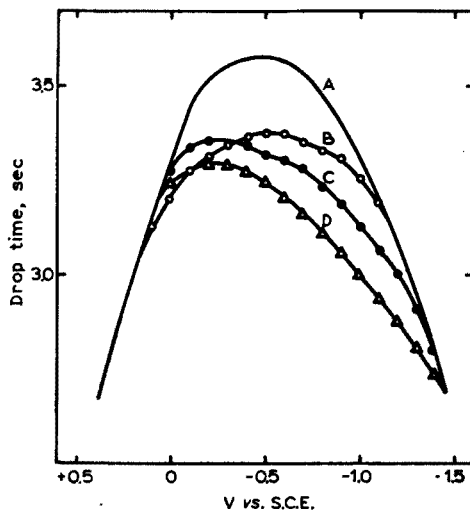


Fig. 1. Electrocapillary curves in 0.2 *M* acetate buffer with pH 3.25 containing A = 0, B = 0.01% SDS, C = 0.01% Armeen and D = 0.01% Triton X-100.

0.01% of either the anionic SDS, the cationic Armeen or the non-ionic Triton X-100 causes a large decrease in the droptime over a considerable potential range. Similar results were obtained in the whole pH range 3-7.5.

*Effects of surfactants on polarograms of negatively charged complexes*

In acetic acid medium the copper-DTPA complex yields a reversible 2-electron wave at the dropping mercury electrode<sup>11</sup>. In the absence of surface-active agents a maximum occurs on polarograms recorded from solutions with pH less than 4. The effects of surfactants on the polarograms of  $10^{-3}$  M copper and  $2 \cdot 10^{-2}$  M DTPA in acetate buffer with pH 3.25 are shown in Fig. 2. The maximum is easily suppressed in the presence of 0.0002% Armeen, 0.0004% SDS or 0.0005% Triton

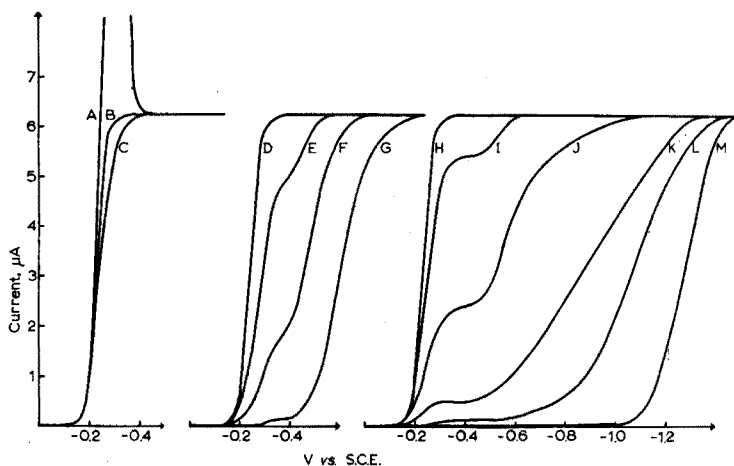


Fig. 2. Polarograms of  $10^{-3}$  M copper and  $2 \cdot 10^{-2}$  M DTPA in acetate buffer pH 3.25 with various amounts of surface-active substances present. A = 0, B = 0.002 and C = 0.02% Armeen; D = 0.0004, E = 0.002, F = 0.004 and G = 0.01% SDS; H = 0.0005, I = 0.002, J = 0.003, K = 0.004, L = 0.006 and M = 0.01% Triton X-100.

X-100. A further increase in the concentration of either of the two latter substances has, however, a great distorting effect on the wave. When the concentration of SDS or Triton X-100 is increased above 0.001%, the wave is broken into two parts and a new wave appears at a more negative potential. The height of the second wave increases with increasing concentration of the surfactant and in the presence of 0.01% SDS or Triton X-100 only the second wave is observed on the polarograms.

Polarograms of the copper-DTPA complex recorded in the presence of various amounts of Armeen showed that this cationic substance has very little influence on the current-voltage curve. Only one wave was observed even in the presence of 0.02% Armeen. In the presence of large amounts of Armeen the wave was slightly drawn out (Fig. 2, curve C) and the plot of  $\log i/(i_a - i)$  vs. the potentials indicated that the electrode reaction is irreversible in the presence of 0.008 to 0.02% Armeen. The half-wave potential is, however, practically constant in absence and in presence of 0.01% Armeen.

Comparison of curves C, G and M in Fig. 2 with the corresponding electrocapillary

curves in Fig. 1, indicates that the electrode reaction is related to a desorption of Triton X-100, but it occurs at potentials much more positive than the desorption of Armeen and SDS. The limiting current of the copper-DTPA complex in the presence of 0.01% SDS and of 0.01% Armeen was measured at different heights of the mercury column. The  $h$ -dependence indicated that the current is controlled by the rates of both diffusion and penetration<sup>12</sup>. Apparently, at a certain potential the complex is able to penetrate the adsorbed layer of these substances. It is of interest to note that the penetration through the Armeen layer takes place almost without any increase in the applied potential, whereas a penetration through the SDS film occurs only at considerably higher potentials.

At pH values above 5 the copper-DTPA complex exhibits two waves even in the absence of surface-active agents. The second wave is assumed to be the result of an inhibited electrode reaction caused by adsorption of the DTPA-species liberated at the electrode during the electrolyses<sup>11</sup>. Figure 3A shows a polarogram of the copper-DTPA complex recorded from phosphate buffer with pH 7.10. The first wave is the reversible reduction of the complex and the second one is the irreversible penetration wave. Experiments showed that the presence of surfactants has a very great effect on the current-voltage curves. Addition of more than 0.0001% SDS resulted in an increase in the height of the second wave at the expense of the first one, indicating that the reversible reduction of the complex is inhibited by the adsorbed SDS film in a similar way as by the DTPA-species (curves E, F and G in Fig. 3).

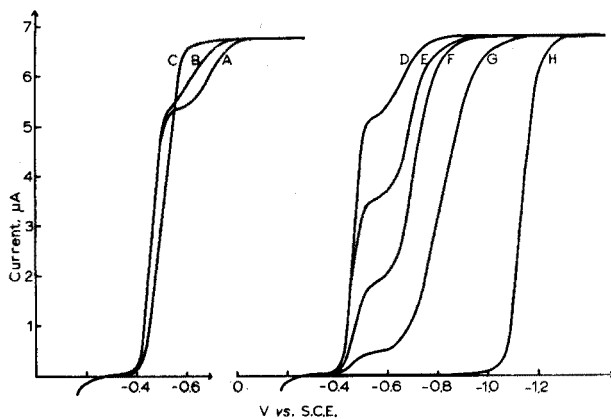


Fig. 3. Effects of Armeen and SDS on the polarograms of  $10^{-3}$  M copper and  $10^{-2}$  M DTPA in phosphate buffer pH 7.10. A = 0, B = 0.001 and C = 0.02% Armeen; D = 0, E = 0.001, F = 0.002, G = 0.003 and H = 0.02% SDS.

As indicated in Fig. 3B the first wave is not affected by the presence of 0.001% Armeen. The second wave, however, is shifted to more positive values upon addition of this cationic substance. In the presence of 0.02% Armeen only one wave is observed on the polarogram. The plot of  $\log i/(i_a - i)$  indicated that the electrode reaction becomes irreversible at Armeen concentrations above 0.001%. At this film thickness the current is probably controlled by the rates of both diffusion and penetration as was observed at lower pH values. The shift in the half-wave potential of the second

wave to more positive values indicates that Armeen is more strongly adsorbed at the electrode than the DTPA-species. Hence, when Armeen is present in sufficiently large amounts to assure complete coverage of the mercury surface from the beginning of the drop formation, this film prevents adsorption of the DTPA-species and only one wave is observed on the polarogram.

The effect of Triton X-100 on the two waves is very similar to that of SDS. Addition of more than 0.0005% Triton resulted in a decrease in the height of the first wave and an increase in the height of the second one. In the presence of 0.008% Triton the electrode reaction was inhibited and only the desorption wave ( $E_{1/2} = -1.5$  V) was observed on the polarogram.

The copper-EDTA complex is nearly reversibly reduced at the dropping mercury electrode<sup>13</sup>. According to SCHMID AND REILLEY<sup>3</sup>, the current-voltage curve is greatly distorted by the presence of Triton X-100. The effects of SDS and of Armeen on the copper-EDTA wave in acetate buffer pH 4.5 were found to be similar to that on the copper-DTPA wave at low pH values. When the concentration of SDS was increased above 0.003% the wave was split into two parts and in the presence of 0.005% SDS only a penetration wave ( $E_{1/2} = -0.8$  V) appeared on the polarogram. The presence of Armeen had no undesirable effect on the copper-EDTA wave. No decrease in the diffusion current or splitting of the wave was observed even in the presence of 0.01% Armeen. The half-wave potential was practically constant in presence and absence of Armeen, indicating that the copper-EDTA complex easily can penetrate the adsorbed Armeen layer.

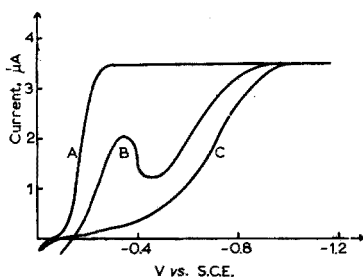


Fig. 4. Effects of surface-active substances on the polarograms of  $10^{-3}$  M iron(III) and  $10^{-2}$  M DTPA in acetate buffer with pH 4.6. A = 0.02% Armeen, B = 0.02% SDS and C = 0.02% Triton X-100.

The iron(III)-DTPA complex exhibits a well-defined wave at the dropping mercury electrode corresponding to a reversible reduction to the divalent state<sup>14</sup>. Polarograms of iron(III)-DTPA in acetate buffer with pH 4.6 indicated that the wave was not affected by the presence of less than 0.007% of SDS or Triton X-100, whereas larger amounts of these substances had a great distorting effect. The presence of Armeen had, however, no effect on the current-voltage curve. Identical polarograms were obtained in absence and presence of 0.02% Armeen (Fig. 4A).

#### *Effects of surfactants on polarograms of positively charged depolarisers*

The effect of surfactants on the polarograms of uncomplexed copper ions was investigated using acetate buffer with pH 4.6 as supporting electrolyte. The result

was in perfect agreement with that obtained by KOLTHOFF AND OKINAKA<sup>10</sup>. The wave was split into two parts in the presence of more than 0.005% Armeen or Triton X-100 whereas a reversible wave was observed in the presence of 0.05% SDS.

The copper-Trien complex is stable in acid medium and is reversibly reduced at the dropping mercury electrode<sup>15</sup>. Polarograms of  $10^{-3}$  M copper and  $10^{-2}$  M Trien in acetate buffer are shown in Fig. 5. As indicated in the Fig. the presence of

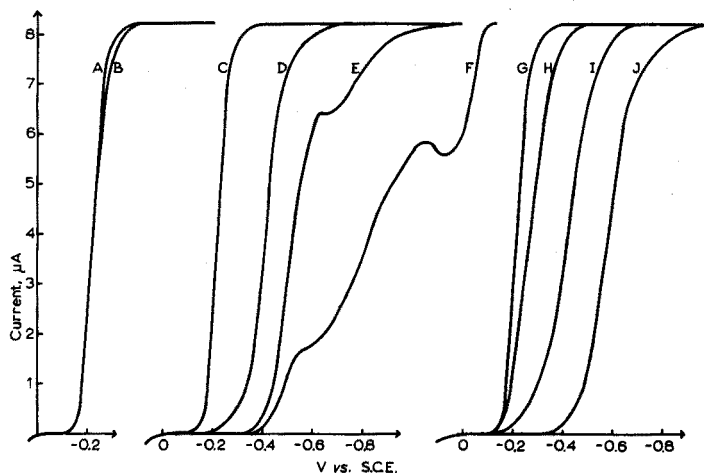


Fig. 5. Polarograms of  $10^{-3}$  M copper and  $10^{-2}$  M Trien in acetate buffer pH 4.6 with various amounts of surface-active substances present. A = 0, B = 0.010% SDS; C = 0, D = 0.002, E = 0.008 and F = 0.010% Armeen; G = 0, H = 0.002, I = 0.004 and J = 0.010% Triton X-100.

Armeen had a great influence on the half-wave potential. In the absence of surfactants the half-wave potential was  $-0.22$  V as compared to  $-0.27$  V and  $-0.42$  V in the presence of 0.008% and 0.002% Armeen respectively. A further increase in the Armeen concentration resulted in a splitting of the wave and in the presence of 0.01% Armeen the whole wave was distorted. The effect of Triton was similar to that of Armeen. As indicated in Fig. 5 the half-wave potential was shifted to more negative values with increasing concentration of Triton X-100.

The presence of SDS, however, had practically no influence on the polarogram. In the presence of large amounts of SDS the upper part of the wave was slightly drawn out, indicating that the electrode reaction becomes irreversible at a certain film thickness (Fig. 5B). The half-wave potential was not affected by addition of 0.01% SDS to the supporting electrolyte, which indicates that the copper-Trien complex can very easily penetrate the adsorbed SDS layer.

#### CONCLUSION

The polarograms of both positively and negatively charged complexes are distorted by the presence of Triton X-100. This effect has previously been reported in the literature<sup>1,3,6,7,14</sup> and is probably due to a very compact structure of the adsorbed layer.



The most interesting result in this paper is the striking difference in the effects of cationic and anionic substances on the polarographic waves. The cationic substance Armeen has no or very little effect on the polarograms of  $(\text{CuH-DTPA})^{2-}$ ,  $(\text{CuDTPA})^{3-}$ ,  $(\text{CuEDTA})^{2-}$  and  $(\text{FeDTPA})^{2-}$  in contrast to the great distorting effect exerted by the anionic substance SDS. On the other hand, well-defined waves of  $\text{Cu}^{2+}$  and  $(\text{CuH-Trien})^{3+}$  are obtained in presence of SDS, whereas the half-wave potentials are shifted to more negative values and the waves distorted in the presence of the same amount of Armeen.

These phenomena can be interpreted by assuming that the adsorbed layer of these positively and negatively charged substances has a loose structure with pores filled with solvent. If the depolariser has a charge opposite to that of the adsorbed layer it may pass through the pores almost without any hindrance. On the other hand, depolarisers with the same charge as the adsorbed layer are electrostatically repelled from the electrode surface. They have to cross a potential energy barrier before they can be reduced and the polarographic waves are therefore shifted to more negative potentials or greatly distorted.

The present results are in excellent agreement with the effect of the negatively charged pepsin and of the positively charged serum and egg albumin on the polarograms of certain cations and of their chloro-complexes<sup>9</sup>. The distorting effect of a surface-active substance is, however, more pronounced on polarograms of large complexes than on the waves of small ions which probably can more easily penetrate the pores in the adsorbed layer.

If the assumption of an electrostatic repulsion between the adsorbed layer and the depolariser has a general validity, it would be of great importance in polarographic analysis. In order to avoid the distorting effects of a maximum suppressor, a cationic substance should be used to suppress maxima on the waves of negatively charged depolarisers and an anionic substance in the case of positively charged depolarisers. Moreover, large amounts of a surface-active substance with the appropriate charge may be used as a selective masking agent in polarographic analysis.

Armeen and SDS form precipitates in alkaline solutions containing the complexing agents used in this investigation and they are therefore not suitable as masking agents in such media. Further work concerning the applicability of other cationic and anionic substances as maximum suppressors and masking agents in polarographic analyses is in progress. A more detailed study of the adsorption of such substances may also result in a more complete interpretation of the phenomena occurring at the electrode surface.

#### SUMMARY

The effect of the charge type of surface-active substances on the polarographic waves of various complexes has been investigated. The results indicate that the polarograms are practically unaffected by the presence of a surfactant, provided that the adsorbed layer has a charge opposite to that of the depolariser. Polarographic waves of depolarisers with the same charge as the adsorbed layer are, however, shifted to more negative values or greatly distorted. The distorting effect is qualitatively interpreted in terms of an electrostatic repulsion between the adsorbed layer and the depolariser. The charge type of a surfactant seems to be important for the appropriate choice of a nondistorting maximum suppressor.

#### RÉSUMÉ

L'influence de substances tensio-actives sur les ondes polarographiques de divers complexes a été examinée. Les résultats montrent que les polarogrammes ne sont pratiquement pas affectés

par la présence de "surfactants", à condition que la couche adsorbée aie une charge opposée à celle du dépolarisant. L'effet de distortion peut être interprété qualitativement par une répulsion entre la couche adsorbée et le dépolarisant. Le type de charge d'un "surfactant" semble être important pour le choix approprié d'un supresseur de maximum.

#### ZUSAMMENFASSUNG

Der Einfluss der Ladungsart von oberflächenaktiven Substanzen auf die polarographischen Stufen verschiedener Komplexe wurde untersucht. Die Versuche zeigen, dass die Polarogramme durch die Anwesenheit solcher Substanzen praktisch nicht beeinflusst werden, vorausgesetzt, dass die absorbierte Schicht entgegengesetzt wie der Depolarisator geladen ist. Besitzt der Depolarisator dieselbe Ladung wie die absorbierte Schicht so werden die polarographischen Stufen zu negativeren Werten verschoben oder stark verzerrt. Die Verzerrung wird qualitativ als Folge der elektrostatischen Abstossung zwischen der absorbierten Schicht und dem Depolarisator gedeutet. Die Ladungsart des aktiven Stoffes scheint für die angemessene Wahl nicht-verzerrender Maximadämpfer wichtig zu sein.

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## SINE-WAVE POLAROGRAPHIC DETERMINATION OF SMALL AMOUNTS OF INDIUM IN THE PRESENCE OF LARGE AMOUNTS OF CADMIUM, LEAD OR TIN\*

MOTOMU KASAGI AND CHARLES V. BANKS

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

(Received August 5th, 1963)

The half-wave potentials for the reduction waves of indium(III), cadmium(II), lead(II) and tin(II) have similar values in conventional supporting electrolytes such as hydrochloric acid or potassium chloride. Therefore, it is not easy to obtain a clearly defined reduction wave for indium in D.C. polarography in the presence of large amounts of these metals. However, the sine-wave polarographic method gave satisfactory results for these determinations.

A satisfactory separation of the reduction waves of indium and cadmium cannot be obtained in the presence of hydrochloric acid or potassium chloride, but can be obtained fairly well in a solution of potassium bromide and still better in a solution of potassium iodide<sup>1-4</sup>. SHIRAI<sup>5</sup> reported that measurable peaks of indium and cadmium in sine-wave polarography were obtained in a solution 0.5 *M* in potassium bromide which contained the same amounts of indium and cadmium, provided that dissolved oxygen was expelled completely. UEHARA<sup>6</sup> determined trace amounts of cadmium in high-purity indium in a 1 *M* solution of potassium iodide by square-wave polarography. Therefore, the sine-wave polarographic determination of small amounts of indium in the presence of large amounts of cadmium was investigated using potassium iodide and bromide as supporting electrolytes, and compared with the D.C. polarographic method. The best results were obtained in a 1 *M* solution of potassium iodide which was also 0.01 *M* in hydrochloric acid.

Small amounts of indium can be determined in lead by the D.C. polarographic method only after almost all of the lead has been precipitated by sulfuric acid<sup>7a</sup>. Therefore, the sine-wave polarographic method was investigated as a possible means of determining indium in the presence of large amounts of lead. A suitable supporting electrolyte for this determination was 1 *M* potassium chloride which was also 0.01 *M* in hydrochloric acid.

The D.C. polarographic determination of small amounts of indium in the presence of large amounts of tin is very difficult<sup>8</sup>, but the sine-wave polarographic method gave acceptable results using 1 *M* hydrochloric or 2 *M* perchloric acid with 0.5 *M* sodium chloride<sup>7b</sup> as the supporting electrolyte.

\* Contribution No. 1375. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

## EXPERIMENTAL

*Apparatus*

The polarograms were obtained with a Yanagimoto AC and DC Polarograph Model PA-101 made in Japan, supplied by the Jarrell-Ash Company. All measurements were made at 25° using a conventional cell with a mercury pool electrode. Nitrogen was used to expel dissolved oxygen from all solutions studied by D.C. polarography. It was not necessary to expel oxygen from solutions containing indium which were used for sine-wave polarography provided the solutions were at least 0.01 *M* in hydrogen ion. The capillary had a drop time of 4.03 sec at the reduction potential of indium in 1 *M* potassium iodide which was also 0.01 *M* in hydrochloric acid, and allowed 0.950 mg of mercury to flow per sec at a height of 70 cm.

*Reagents*

"Baker Analyzed" reagents and de-ionized distilled water were used for the preparation of all solutions.

## PROCEDURE AND RESULTS

*Determination of indium in cadmium*

The determination of 1 through 5% indium in cadmium was investigated in 1 *M* potassium iodide containing 0.01 *M* hydrochloric acid. The concentrations of indium and cadmium in the solutions used for polarography were 0.01 mg In and 0.99 mg Cd through 0.05 mg In and 0.95 mg Cd per ml. A definite peak and wave for indium, well separated from the following reduction wave for cadmium, was observed between -0.1 and -0.2 V *vs.* the mercury pool electrode in the sine-wave and the D.C. polarograms, respectively. The summit potential agreed with the half-wave potential of -0.56 V *vs.* S.C.E. from the literature<sup>1</sup>. A good linear relationship was found between the concentration of indium and the peak height or wave height, though the peak height for 5% In was slightly lower than expected (Table I, Series I).

Solutions containing the above amounts of indium and cadmium in 0.5 *M* KI, 0.2 *M* KI, 0.1 *M* KI, 1 *M* KBr, and 0.5 *M* KBr were investigated also. In 0.5 *M* iodide, a good separation of the reduction waves of indium and cadmium was obtained. In 0.2 *M* iodide, a fairly good separation was obtained. In 0.1 *M* iodide, a good separation was not obtained, especially in the D.C. polarogram. In 1 *M* bromide, a fairly good separation was obtained, but the measurement of the wave height in the D.C. polarogram was quite difficult. In 0.5 *M* bromide, a good separation was not obtained especially in the D.C. polarogram.

The determination of 0.1 through 0.5% indium in cadmium was investigated in 1 *M* potassium iodide containing 0.01 *M* hydrochloric acid. The concentrations of indium and cadmium in the solutions used for polarography were 0.001 mg In and 0.999 mg Cd through 0.005 mg In and 0.995 mg Cd per ml. A fairly definite peak and wave for indium was observed in the sine-wave and the D.C. polarograms, respectively. A good linear relationship was found between the concentration of indium and the peak height or wave height (Table I, Series II). However, the straight line for the sine-wave polarographic method did not pass through the origin because of the appearance of a peculiar peak presumably caused by the mercury dissolving in the iodide solution. This oxidation wave interfered with the measurement of the peak height of indium at the high sensitivity used for these recordings. For obtaining a

TABLE I  
RELATIONSHIP BETWEEN CONCENTRATION OF INDIUM AND THE PEAK HEIGHT OR  
WAVE HEIGHT IN THE PRESENCE OF LARGE AMOUNTS OF CADMIUM<sup>a</sup>

Series	Sample (% In in Cd)	Concn. of In (mg/ml)	Peak height ( $\mu\text{V}$ ) <sup>b</sup>	Wave height ( $\mu\text{A}$ ) <sup>c</sup>
I	1	0.01	510	0.46
	2	0.02	1020	0.90
	3	0.03	1470	1.40
	4	0.04	1970	1.86
	5	0.05	2340	2.34
II	0.1	0.001	22	0.048
	0.2	0.002	64	0.090
	0.3	0.003	100	0.140
	0.4	0.004	132	0.192
	0.5	0.005	176	0.232
III	0.1	0.01	290	0.46
	0.2	0.02	620	1.00
	0.3	0.03	940	1.36
	0.4	0.04	1180	1.86
	0.5	0.05	1470	2.30
IV	0.01	0.001	8	—
	0.02	0.002	23	—
	0.03	0.003	44	—
	0.04	0.004	66	—
	0.05	0.005	81	—

<sup>a</sup> Supporting electrolyte was 1 *M* in KI and 0.01 *M* in HCl.

<sup>b</sup> At sensitivity, 20.0  $\mu\text{V}/\text{mm}$  for Series I, III; 2.0  $\mu\text{V}/\text{mm}$  for Series II, IV.

<sup>c</sup> At sensitivity, 0.020  $\mu\text{A}/\text{mm}$  and parallel capacitance, 100  $\mu\text{F}$  for Series I; 0.004  $\mu\text{A}/\text{mm}$  and 25  $\mu\text{F}$  for Series II; 0.040  $\mu\text{A}/\text{mm}$  and 100  $\mu\text{F}$  for Series III.

high peak and wave of indium, solutions containing 0.01 mg In and 9.99 mg Cd through 0.05 mg In and 9.95 mg Cd per ml were prepared. A definite peak and wave for indium was observed in the sine-wave and the D.C. polarograms, respectively, and a good linear relationship was found between the concentration of indium and the peak height or wave height (Table I, Series III).

The determination of 0.01 through 0.05% indium in cadmium was investigated in 1 *M* potassium iodide containing 0.01 *M* hydrochloric acid. The concentrations of indium and cadmium were 0.001 mg In and 9.999 mg Cd through 0.005 mg In and 9.995 mg Cd per ml. A fairly definite peak and wave for indium was observed in the sine-wave and the D.C. polarograms, respectively, but the measurement of the wave height in the D.C. polarogram was quite difficult. A good linear relationship was found between the concentration of indium and the peak height, though the straight line did not pass through the origin because of the imperfect separation of the peaks of indium and cadmium (Table I, Series IV). The solutions containing still larger amounts of indium and cadmium in the above ratio were not suitable for polarography because the concentration of cadmium was too high for the concentration of the supporting electrolyte.

Consequently, small amounts of indium in the presence of large amounts of cadmium such as 1 through 5% In in Cd can be determined easily in 1 *M* or 0.5 *M* potassium iodide either by the sine-wave (at pH 2) or by the D.C. polarographic

method. Satisfactory results can also be obtained by either method in 0.2 *M* potassium iodide, but only the sine-wave polarographic method gives acceptable results in 1 *M* potassium bromide. The determination of 0.01% indium in cadmium is possible by the sine-wave polarographic method using 1 *M* potassium iodide as the supporting electrolyte. TREINDL<sup>4</sup> has reported that 0.01% indium in cadmium can be determined by the D.C. polarographic method using 3 *M* iodide.

#### *Determination of indium in lead*

The determination of 1 through 5% indium in lead was investigated in 1 *M* potassium chloride containing 0.01 *M* hydrochloric acid. The concentrations of indium and lead in the solutions used for polarography were 0.01 mg In and 0.99 mg Pb through 0.05 mg In and 0.95 mg Pb per ml. A definite peak and wave for indium, well separated from the preceding reduction wave for lead, was observed between -0.6 and -0.7 V *vs.* the mercury pool electrode in the sine-wave and the D.C. polarograms, respectively. The summit potential agreed with the half-wave potential of -0.61 V *vs.* S.C.E. from the literature<sup>1</sup>. Though a good linear relationship was found between the concentration of indium and the wave height in the D.C. polarogram for 2 through 5% In in Pb, the wave height for 1% In in Pb was too low. Therefore, it seemed that the D.C. polarographic determination of less than 2% In in Pb was impractical. The relationship between the concentration of indium and the peak height in the sine-wave polarogram was not linear (Table II, Series I). However, solutions containing 0.005 mg In

TABLE II  
RELATIONSHIP BETWEEN CONCENTRATION OF INDIUM AND THE PEAK HEIGHT OR  
WAVE HEIGHT IN THE PRESENCE OF LARGE AMOUNTS OF LEAD<sup>a</sup>

Series	Sample (% In in Pb)	Concn. of In (mg/ml)	Peak height ( $\mu\text{V}$ ) <sup>b</sup>	Wave height ( $\mu\text{A}$ ) <sup>c</sup>
I	1	0.01	500	0.26
	2	0.02	990	0.82
	3	0.03	1400	1.26
	4	0.04	1630	1.72
	5	0.05	1920	2.14
II	1	0.005	240	—
	2	0.010	490	—
	3	0.015	720	—
	4	0.020	950	—
	5	0.025	1200	—
III	0.1	0.001	44	—
	0.2	0.002	90	—
	0.3	0.003	134	—
	0.4	0.004	182	—
	0.5	0.005	220	—
IV	0.01	0.0001	—	—
	0.02	0.0002	8	—
	0.03	0.0003	12	—
	0.04	0.0004	16	—
	0.05	0.0005	20	—

<sup>a</sup> Supporting electrolyte was 1 *M* in KCl and 0.01 *M* in HCl.

<sup>b</sup> At sensitivity, 20.0  $\mu\text{V}/\text{mm}$  for Series I, II; 4.0  $\mu\text{V}/\text{mm}$  for Series III, IV.

<sup>c</sup> At sensitivity, 0.020  $\mu\text{A}/\text{mm}$  and parallel capacitance, 400  $\mu\text{F}$  for Series I.

and 0.495 mg Pb through 0.025 mg In and 0.475 mg Pb per ml gave a good linear relationship between the concentration of indium and the peak height (Tables II, Series II).

The determination of 0.1 through 0.5% indium in lead was investigated in 1 *M* potassium chloride containing 0.01 *M* hydrochloric acid. The concentrations of indium and lead in the solutions used for polarography were 0.001 mg In and 0.999 mg Pb through 0.005 mg In and 0.995 mg Pb per ml. A definite peak for indium was observed in the sine-wave polarogram, and a good linear relationship was found between the concentration of indium and the peak height (Table II, Series III).

The determination of 0.01 through 0.05% indium in lead was also investigated in 1 *M* potassium chloride containing 0.01 *M* hydrochloric acid. The concentrations of indium in the solutions used for polarography were 0.0001 through 0.0005 mg per ml. A measurable peak for indium was observed in the sine-wave polarogram for 0.02 through 0.05% In in Pb, but was not observed for 0.01% In in Pb (Table II, Series IV). The solutions containing still larger amounts of indium and lead in the above ratio were not suitable for polarography because they were turbid.

Consequently, it was concluded that by using 1 *M* potassium chloride at pH 2 as the supporting electrolyte, the sine-wave polarographic determination of indium in the presence of large amounts of lead was easy down to 0.1% In in Pb, and was possible down to 0.02% In in Pb, and that the D.C. polarographic method was impractical for the determination of less than 2% In in Pb.

The sine-wave and D.C. polarographic methods in 1 *M* potassium chloride were applied to a series of actual samples containing small amounts of indium in lead and zinc which had previously been analyzed by the thiocyanate and by the tartaric acid D.C. polarographic methods<sup>9</sup>. Almost all of the lead had been precipitated from these samples with concentrated sulfuric acid to make it possible to apply the D.C. polarographic method. A comparison of the results obtained by the 4 methods is shown in Table III. The results by sine-wave polarography for comparatively large amounts of indium were slightly low in comparison with the D.C. methods. This is because standard samples containing comparatively small amounts of indium were used and the relationship between the concentration of indium and the peak height is not linear in the range of large amounts of indium. It would be possible to obtain better

TABLE III  
DETERMINATION OF INDIUM IN LEAD WITH 2 % ZINC

% Indium found			
A.C. (1 <i>M</i> KCl)	D.C. (1 <i>M</i> KCl)	D.C. (NH <sub>4</sub> SCN) <sup>9</sup>	D.C. (Tartarate) <sup>9</sup>
0.369	0.371	0.38	0.368
1.144	1.166	1.165	1.173
1.247	1.307	1.295	1.284
1.201	1.258	1.24	1.225
1.226	1.275	1.255	1.237
1.238	1.254	1.27	1.265
1.198	1.206	1.23	1.213
1.112	1.099	1.11	1.108
1.164	1.179	1.19	1.171
1.194	1.219	1.215	1.211

results by comparison with standard samples containing large amounts of indium. However, the D.C. polarographic method gives satisfactory results for the determination of indium in solutions in which almost all of the lead has been removed as lead sulfate. The sine-wave polarographic method is quite satisfactory for determining indium in the presence of large amounts of lead and zinc because these metals do not interfere in the determination of indium.

#### *Determination of indium in tin*

The determination of 1 through 5% indium in tin was investigated using 1 *M* hydrochloric acid as the supporting electrolyte. The concentrations of indium in the solutions used for polarography were 0.002 through 0.010 mg per ml. A definite peak for indium, well separated from the preceding reduction wave for tin(II), was observed between  $-0.5$  and  $-0.7$  V *vs.* the mercury pool electrode in the sine-wave polarogram. The potential of the peak varied somewhat because of the oxidation of tin(II) on the surface of the mercury pool electrode. However, a definite wave for indium in the D.C. polarogram was not observed even for the sample containing 5% In in Sn. The summit potential agreed with the half-wave potential of  $-0.60$  V *vs.* S.C.E. from the literature<sup>1</sup>. Similar results were also obtained using 2 *M* perchloric acid with 0.5 *M* sodium chloride as the supporting electrolyte. With each supporting electrolyte, the relationship between the concentration of indium and the peak height was nearly linear. The slope of the curve increased slightly with concentration in 1 *M* hydro-

TABLE IV  
RELATIONSHIP BETWEEN CONCENTRATION OF INDIUM AND THE PEAK HEIGHT  
IN THE PRESENCE OF LARGE AMOUNTS OF TIN<sup>a</sup>

Series	Sample (% In in Sn)	Concn. of In (mg/ml)	Peak height ( $\mu\text{U}$ ) <sup>b</sup>
I	1	0.002	84
	2	0.004	168
	3	0.006	252
	4	0.008	324
	5	0.010	432
II	1	0.002	84
	2	0.004	174
	3	0.006	264
	4	0.008	333
	5	0.010	408
III	0.1	0.0002	—
	0.2	0.0004	—
	0.3	0.0006	9
	0.4	0.0008	18
	0.5	0.0010	27
IV	0.1	0.0002	—
	0.2	0.0004	12
	0.3	0.0006	21
	0.4	0.0008	30
	0.5	0.0010	39

<sup>a</sup> Supporting electrolyte for Series I, III was 1 *M* in HCl; for Series II, IV was 2 *M* HClO<sub>4</sub> with 0.5 *M* NaCl.

<sup>b</sup> At sensitivity, 6.0  $\mu\text{U}/\text{mm}$ .



chloric acid and decreased slightly with concentration in 2 *M* perchloric acid with 0.5 *M* sodium chloride (Table IV, Series I, II).

The determination of 0.1 through 0.5% indium in tin was investigated with the same procedure as above. The concentrations of indium were 0.0002 through 0.0010 mg per ml. Measurable peaks for indium were not obtained for the samples of 0.1 and 0.2% In in Sn in 1 *M* hydrochloric acid, and for the sample of 0.1% In in Sn in 2 *M* perchloric acid with 0.5 *M* sodium chloride. However, the relationship between the concentration of indium and the peak height was linear for 0.3 through 0.5% In in Sn in 1 *M* hydrochloric acid, and for 0.2 through 0.5% In in Sn in 2 *M* perchloric acid with 0.5 *M* sodium chloride (Table IV, Series III, IV). The solutions containing still larger amounts of indium and tin in the above ratio were not suitable because the break of indium was disturbed by the unstable peak of tin.

Consequently, it was concluded that the sine-wave polarographic determination of indium in the presence of large amounts of tin was possible down to 0.3% In in Sn in 1 *M* hydrochloric acid, and down to 0.2% In in Sn in 2 *M* perchloric acid with 0.5 *M* sodium chloride.

The authors wish to thank Yanagimoto Co., Ltd., in Japan and Jarrell-Ash Company for supplying the sine-wave polarograph.

#### SUMMARY

The sine-wave polarographic determination of small amounts of indium in the presence of large amounts of cadmium, lead or tin was investigated. The determination of indium in cadmium was possible down to 0.01% in 1 *M* potassium iodide at pH 2, the determination of indium in lead was possible down to 0.02% in 1 *M* potassium chloride at pH 2, and the determination of indium in tin was possible down to 0.3% in 1 *M* hydrochloric acid and down to 0.2% in 2 *M* perchloric acid with 0.5 *M* sodium chloride.

#### RÉSUMÉ

Les auteurs ont mis au point une méthode polarographique ("sine-wave polarography") pour le dosage de faibles quantités d'indium, en présence de fortes teneurs en cadmium, plomb ou étain. On peut doser ainsi: 0.01% In dans Cd — milieu iodure de potassium 1 *M*, pH 2; 0.02% In dans Pb — milieu chlorure de potassium 1 *M*, pH 2; 0.3% In dans Sn — milieu acide chlorhydrique 2 *M*; et 0.2% In dans Sn — milieu acide perchlorique 2 *M* + chlorure de sodium 0.5 *M*.

#### ZUSAMMENFASSUNG

Eine polarographische Methode ("sine-wave polarography") zur Bestimmung von kleinen Mengen Indium in Gegenwart von grossen Mengen Cadmium, Blei oder Zinn wurde untersucht. Indium liess sich in Cadmium bis zu 0.01% bestimmen, wenn 1 *M* Kaliumjodid und ein pH-Wert von 2 gewählt wurde, in Blei bis zu 0.02%, wenn 1 *M* Kaliumchlorid und ein pH-Wert von 2 gewählt wurde. Die Bestimmung des Indiums in Zinn war möglich bis zu 0.3% in 1 *M* Salzsäure und bis zu 0.2% in 2 *M* Perchlorsäure mit 0.5 *M* Natriumchlorid.

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SIMULTANEOUS DETERMINATION OF LEAD AND NICKEL IN URANIUM  
BY SQUARE-WAVE POLAROGRAPHY

FUMITO NAKASHIMA

*Hitachi Research Laboratory, Hitachi Ltd., Hitachi City, Ibaraki-ken (Japan)*

(Received July 17th, 1963)

Sensitive methods for the determination of cadmium<sup>1</sup> and manganese<sup>2</sup> in high-purity uranium by the application of square-wave polarography have been already described. In the present paper a method is described for the simultaneous determination of lead and nickel in uranium. Spectrophotometric methods for these impurities in uranium have been proposed by several investigators<sup>3-6</sup>. Lead and nickel are first separated from uranium by solvent extraction of the dithizonate and dimethylglyoxime complexes, respectively. SAMBUCETTI *et al.*<sup>7</sup> and SAITO AND TAKEUCHI<sup>8</sup> have applied conventional and alternating current polarography. A spectrographic carrier distillation procedure<sup>9</sup> is another possibility. BRODY, FARIS AND BUCHANAN<sup>10</sup> proposed a method involving ion-exchange separation and copper spark spectrography. It was decided, however, to investigate the possible application of square-wave polarography, in view of the earlier work in which the combination of ion-exchange separation and square-wave polarography was shown to offer a sensitive analytical technique.

## EXPERIMENTAL

*Apparatus and reagents*

Polarograph, ion-exchange columns and the uranium solution were the same as those described previously<sup>2</sup>. Standard solutions of lead and nickel ( $1.00 \cdot 10^{-3} M$ ) were prepared by dissolving the pure metals in hydrochloric acid with the aid of hydrogen peroxide and diluting suitably. The supporting electrolyte solution, 1 *M* potassium hydroxide-0.1 *M* potassium cyanide, was stored in a bottle fitted with a soda-lime tube to prevent absorption of carbon dioxide. All other reagents were prepared from reagent-grade chemicals by using deionized water.

*Recommended procedure*

Weigh 1 g of sample into a 100-ml conical flask and add 10 ml of distilled 6 *M* hydrochloric acid. Heat the solution to boiling and add drop by drop about 10 ml of 30% hydrogen peroxide to complete dissolution of the sample. Continue heating until the excess of hydrogen peroxide decomposes and the volume of the solution reduces to about 5 ml by evaporation. Add 5 ml of concentrated hydrochloric acid to make the hydrochloric acid concentration about 9 *M*.

Pass the resulting solution through the ion-exchange column at a flow rate of 1.5 ml per min. Elute the column with 60 ml of 9 *M* hydrochloric acid maintaining at the same flow rate and collect the eluate in a 200-ml beaker. Evaporate the eluate to dryness and add 5 ml of the supporting electrolyte, 1 *M* potassium hydroxide–0.1 *M* potassium cyanide.

Transfer this solution to the polarograph cell, deaerate for 5 min with a stream of pure nitrogen and record the polarogram at an applied D.C. potential between –0.6 and –1.6 V vs. S. C. E. Measure the peak height of the lead wave at the potential of –0.76 V vs. S. C. E. and that of the nickel wave at –1.38 V vs. S. C. E. Obtain the concentration by comparison of the peak height with calibration curves.

In order to determine the blank, carry 10 ml of 9 *M* hydrochloric acid through the entire procedure. The blank is subtracted from the found value and the impurity content of the sample is obtained.

#### *Preparation of the calibration curves*

Using the standard solutions of lead and nickel, transfer known quantities of lead and nickel to a series of 100-ml beakers. Evaporate each solution to dryness and add 5 ml of 1 *M* potassium hydroxide–0.1 *M* potassium cyanide to dissolve the residue. Record the polarogram at the several instrument sensitivities and plot the peak heights against the quantities of lead and nickel.

### RESULTS AND DISCUSSION

#### *Ion-exchange separation*

KRAUS AND NELSON<sup>11</sup> studied in detail the anion-exchange adsorption of numerous transition elements from hydrochloric acid solutions. It was shown that, at higher concentrations in hydrochloric acid, the distribution coefficient of uranium(VI) is very large, whereas those of lead(II) and nickel(II) are low, so that a quantitative separation of lead and nickel from uranium can be effected.

As was previously found satisfactory for the separation of manganese<sup>2</sup>, 9 *M* hydrochloric acid solution was again employed as an eluant. A synthetic solution which contained 1 g of uranium, 26  $\mu\text{g}$  of lead and 29  $\mu\text{g}$  of nickel in 10 ml of 9 *M* hydrochloric acid was prepared and introduced into the ion-exchange column. The column was then eluted with 9 *M* hydrochloric acid at a flow rate of 1.5 ml per min. The effluent from the column was fractionated every 2 min. Lead and nickel in each fraction were measured by square-wave polarography. The elution curves obtained are shown in Fig. 1, which indicates that both lead and nickel are easily separated from large amounts of uranium during the elution with 9 *M* hydrochloric acid. Lead(II) and nickel(II) are eluted completely by the passage of about 60 ml of the eluant. Uranium(VI) remains strongly adsorbed in the resin bed and does not appear in the eluate.

#### *Supporting electrolyte*

Lead(II) gives well-defined waves corresponding to reversible reductions in many different supporting electrolytes. Since nickel(II) is reduced irreversibly from non-complexing supporting electrolytes, the square-wave polarographic wave is drawn out and not suitable for sensitive determination. HUME AND KOLTHOFF<sup>12</sup> have studied the D.C. polarographic behavior of the nickel cyanide complex and showed that

nickel(II) gives an irreversible but well-defined wave in the presence of a large excess of cyanide. FERRETT AND MILNER<sup>13</sup> employed alkaline cyanide solution as a supporting electrolyte for the square-wave polarographic determination of nickel in aluminum alloy.

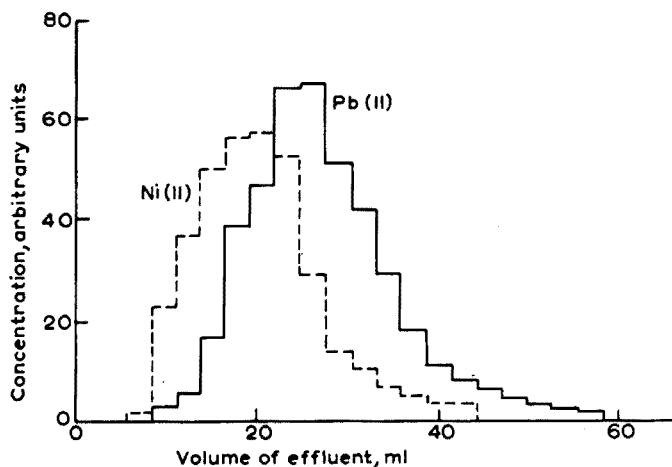


Fig. 1. Elution curves for lead(II) (solid line) and nickel(II) (dotted line) with 9 *M* hydrochloric acid.

TABLE I  
EFFECT OF CYANIDE CONCENTRATION

Cyanide concentration ( <i>M</i> )	Lead(II)		Nickel(II)	
	Potential <sup>a</sup>	Height <sup>b</sup>	Potential	Height
0.01	-0.76	42	-1.38	21
0.05	-0.75	46	-1.35	24
0.1	-0.76	44	-1.38	25
0.2	-0.76	43	-1.38	24
0.3	-0.76	42	-1.38	24

<sup>a</sup> Peak potential in V vs. S. C. E.

<sup>b</sup> Peak height for  $1 \cdot 10^{-4}$  *M* Pb(II) and  $2 \cdot 10^{-4}$  *M* Ni(II) at 1/256 of maximum sensitivity.

To make possible a simultaneous and sensitive determination of lead and nickel, 1 *M* potassium hydroxide-potassium cyanide solutions were studied with different cyanide concentrations. The results obtained are shown in Table I. Lead(II) and nickel (II) gave sharp peaks at -0.76 and -1.38 V vs. S. C. E., respectively, which were independent of cyanide concentration. The lead peak was much higher than that of nickel. The peak height of nickel(II) from the 1 *M* potassium hydroxide-0.01 *M* potassium cyanide was less reproducible. For the present procedure, the 1 *M* potassium hydroxide-0.1 *M* potassium cyanide was chosen. With this supporting electrolyte, calibration curves were prepared at several instrument sensitivities. A linear relation was obtained between the concentration and the peak height. An example of the polarogram of lead(II) and nickel(II) in the 1 *M* potassium hydroxide-0.1 *M* potassium cyanide solution is shown in Fig. 2.

As mentioned by FERRETT AND MILNER<sup>13</sup>, manganese(II) in the alkaline cyanide solution is unstable and rapidly oxidized to manganese dioxide by dissolved and atmospheric oxygen. This oxidation and precipitation of manganese prevents formation of the polarographic peak. Therefore, nickel and lead can be determined without interference from manganese, which accompanies the other metals in the ion-exchange

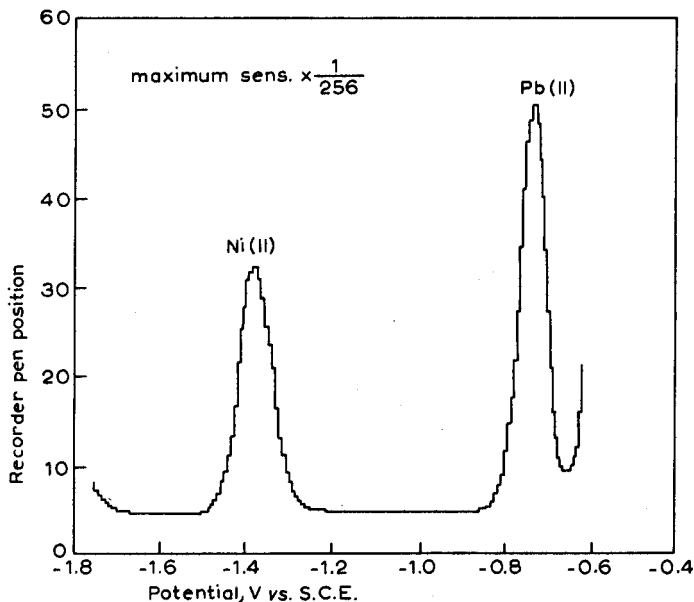


Fig. 2. Square-wave polarogram for  $1 \cdot 10^{-4}$  M Pb(II) and  $2 \cdot 10^{-4}$  M Ni(II) in 1 M KOH-0.1 M KCN.

separation step. Complete removal of oxygen is necessary to prevent the oxidation. By passing purified nitrogen and adding saturated sodium sulfite to the supporting electrolyte, the precipitation was prevented and a wave was observed at about  $-1.5$  V vs. S. C. E. The wave, however, was not suitable for the sensitive determination of manganese, because its peak was rather diffuse. The simultaneous determination of manganese is, therefore, not proposed in the present procedure.

#### Analytical results

Synthetic samples were analyzed in order to evaluate the present method. Known amounts of lead and nickel added to the purified uranium solution were determined as described in the recommended procedure. The results are shown in Tables II and III. If the blank value is subtracted, the found values agree well with the added ones. This agreement confirms that lead and nickel are separated quantitatively by the ion-exchange procedure and that the present method provides an accurate method for the determination of lead and nickel in uranium.

The present method has been applied to reactor-grade uranium dioxides. Lead and nickel in uranium or its compounds can be determined simultaneously by this

TABLE II  
DETERMINATION OF LEAD IN SYNTHETIC SAMPLES

<i>Pb added</i> (p.p.m.)	<i>Pb found</i> (p.p.m.)	<i>Mean of Pb</i> <i>found</i> (p.p.m.)	<i>Deviation</i> (p.p.m.)
2.1	3.4 3.9 2.9	3.6	+1.5
4.1	5.6 5.8 5.8	5.7	+1.6
6.2	9.2 6.7 8.0	7.7	+1.7
10.4	10.8 11.7 12.4	11.6	+1.2
Blank	1.4 1.9 1.6	1.7	

TABLE III  
DETERMINATION OF NICKEL IN SYNTHETIC SAMPLES

<i>Ni added</i> (p.p.m.)	<i>Ni found</i> (p.p.m.)	<i>Mean of Ni</i> <i>found</i> (p.p.m.)	<i>Deviation</i> (p.p.m.)
5.9	7.6 7.6 7.3	7.5	+1.6
23.5	24.0 24.9 24.2	24.4	+0.9
29.4	30.2 31.2 30.6	30.7	+1.3
82.2	87.0 81.6 82.6	83.5	+1.2
Blank	0.9 1.5 1.0	1.1	

method down to 1 p.p.m. and there is no interference from the other impurities usually contained in uranium.

The author wishes to express his sincere thanks to Dr. K. SAKAI for his helpful discussions, and to Dr. T. NAKATOGAWA and Dr. N. KAWASHIMA for their kind guidance throughout the experiments.

## SUMMARY

A sensitive method for the simultaneous determination of trace lead and nickel in uranium is described. These elements are separated from uranium by anion exchange and then determined by square-wave polarography using the alkaline cyanide solution as supporting electrolyte. The procedure is applicable to uranium metal and its compounds containing as little as 1 p.p.m. of lead and nickel.

## RÉSUMÉ

Une méthode est décrite pour le dosage simultané de traces de plomb et de nickel dans l'uranium; elle est basée sur une séparation au moyen d'un échangeur d'anions. Le dosage se fait par polarographie à ondes carrées, en utilisant un cyanure alcalin comme électrolyte de base. Il est possible de doser ainsi des teneurs en plomb et en nickel de 1 p.p.m. dans l'uranium et ses composés.

## ZUSAMMENFASSUNG

Es wird eine Methode zur gleichzeitigen Bestimmung von Spuren Blei und Nickel im Uran beschrieben. Sie beruht auf der Trennung dieser Elemente vom Uran mit Hilfe eines Anionen-Austauschers und anschließender Bestimmung mit der Squarewave-Polarographie, unter Anwendung von alkalischer Zyanidlösung als Grundlösung. Nach dieser Methode können noch 1 p.p.m. Blei und Nickel im Uran und seinen Verbindungen bestimmt werden.

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## SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM(III) WITH COMPLEXANS

G. DEN BOEF AND B. C. POEDER

*Laboratory for Analytical Chemistry, University of Amsterdam, Amsterdam (The Netherlands)*

(Received August 20th, 1963)

PŘIBIL AND KLUBALOVA mentioned the spectrophotometric determination of chromium(III) with EDTA<sup>1</sup>. In a previous paper<sup>2</sup> we described a method for the selective spectrophotometric determination of chromium(III) with EDTA, without the separation of interfering elements as iron, cobalt, nickel and copper. The method was based on the different rates of formation of the complexes of EDTA with chromium(III) (very slow formation) and with the interfering metals (instantaneous formation). Two aliquots of the unknown chromium(III) solution were treated with excess of EDTA; one of the aliquots was heated and the other was kept at room temperature. In the heated solution all metals were then present as their EDTA complexes, but in the unheated solution all metal ions but chromium(III) were complexed. The difference in extinction,  $\Delta E$ , of these two solutions at any wavelength was therefore equal to  $\Delta \epsilon cd$ , where  $\Delta \epsilon$  is the difference in the molar absorptivity of the chromium(III) complex and of the uncomplexed chromium(III) solution\* at the wavelength selected for the determination. The unknown chromium(III) concentration,  $c$ , could therefore be determined in this way. In general, the proper choice of the wavelength for this kind of determination is a maximum in the  $\Delta \epsilon$ -wavelength plot. Good results for the determination of chromium(III) in the presence of normally interfering elements were found<sup>2</sup>; of the metals taken into consideration, only cobalt appeared to interfere.

Since the publication of this paper, we have continued our investigations on this subject; attempts were made to eliminate the interference of cobalt and improvements were sought by means of the use of other complexans. During the investigation it was noticed that the method of preparation of the original solution influenced the extinction of the unheated solution, which could be a source of error. It was also noticed that anions had some effect on the extinction of the chromium(III) chelates.

The results of these observations are mentioned in the present paper.

## EXPERIMENTAL

All chemicals used were of analytical grade. Interfering metals were added as nitrates, chlorides and sulphates. Extinction measurements were carried out on a Unicam SP 500 spectrophotometer.

\* Of course, *uncomplexed* is used here instead of aqueous or mixed aquo-anion complexes.



## RESULTS

*The uncomplexed chromium(III) solution*

The absorptivity curves of the chromium(III) complexes with EDTA and most other complexans have, in the pH region 1 to 5, a maximum in the wavelength region 545 – 555  $m\mu$ , which is suitable for analytical purposes. The molar absorptivity at the maxima is between 100 and 200 for the various complexes. The corresponding maximum in the  $\Delta\epsilon$ -wavelength curve, which is practically always selected as the wavelength for the determinations, is almost at the same wavelength as that of the complex in all cases (see Fig. 1). At this wavelength the molar absorptivity of chromium(III) in

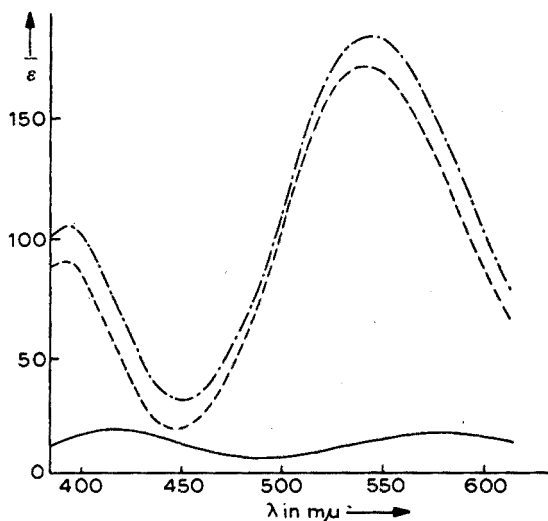


Fig. 1. —,  $\epsilon$ -curve Cr(III) sulphate (pH = 3.5); ---,  $\epsilon$ -curve Cr(III)-EDTA (pH = 3.5); - · -  $\Delta\epsilon$ -curve Cr(III)-EDTA, Cr(III).

nitrate, chloride or sulphate medium at pH 2–5 varies from 8 to 15, depending on the anions present, the time elapsed from the preparation of the solution, and other experimental conditions. These variations cause fluctuations in the value of  $\Delta\epsilon$  and therefore result in errors in the determinations of chromium(III), which may be as much as 4%, when the molar absorptivity of the complex is only 100. An attempt was therefore made to find conditions under which the value of  $\Delta\epsilon$  would be subject to such small fluctuations that negligible errors would arise.

The results of these investigations may briefly be summarized as follows.

(1) Although the molar absorptivity of the uncomplexed solution at 550  $m\mu$  may vary under the experimental conditions from 8 to 15, the general aspect of the absorption curves is always the same.

(2) When uncomplexed solutions of chromium(III) nitrate, chloride or sulphate are treated with enough sulphuric acid, sodium sulphate or a mixture of these compounds to give a sulphate concentration of about 0.1 *M*, the fluctuations mentioned above diminish to 12–14 in the same pH region. The errors mentioned would therefore, under these conditions, always be less than 1%.

(3) The influence of acetate and acetic acid was considered, because in those cases where the experiments must be carried out at pH values of 4 or higher, the pH is adjusted with an acetic acid-acetate buffer solution. Acetate in some cases has a considerable effect on the extinction of the uncomplexed solution, because of the formation of chromium(III)-acetate complexes, which are quite stable and are not quantitatively decomposed by EDTA and other complexans.

When the uncomplexed solution is treated with sulphate as mentioned under (2), the effect of acetate buffer on the extinction is negligible at room temperature within the first hour.

(4) It is necessary that the extinction of the uncomplexed solution does not change by complex formation in the time between the addition of the complexan and the extinction measurement. In some cases this lapse of time may not exceed 5 min, which however suffices for the preparation of the uncomplexed solution and the extinction measurement.

#### *The complexed chromium(III) solution*

The absorption curves of the complexes of chromium(III) with complexans are very similar. The complexes are influenced by the pH, owing to protolysis of the complex. In general there are for each complex two regions in which the absorptivity curve is constant, one in acid medium somewhere between pH 1 and 5 and one in alkaline solution at a pH larger than 9. The acid form of the complex is generally best suited for analysis. The molar absorptivity curve of this form is given in Fig. 1 for EDTA, together with that of the uncomplexed chromium(III) in the sulphate form and that of the difference curve ( $\Delta\epsilon$ ).

The preparation of the chromium(III) complexes with complexans can always be carried out by simply heating a weakly acidic solution of the two compounds for ca. 30 min in a boiling water bath. Except in the case of DTPA and EDTA, the absorptivity curves of the complexes are independent of the fact whether chlorides, sulphates or nitrates are used. Because acetate complexes of chromium(III) cannot be quantitatively decomposed by complexans, it is necessary, when an acetate buffer has to be used to adjust the pH of the solution to be measured, to carry out this adjustment after the formation of the complex. Once the complex has been established, acetate generally has no effect on the extinction, except in the case of EDTA.

#### DETERMINATIONS

Determinations of chromium(III) with complexans, based on the principles developed above, have been carried out in detail with EDTA and NTA (nitrilotriacetic acid). For other complexans only a few determinations were carried out. Experimental details of these determinations will be given separately.

#### *Determination of chromium(III) with EDTA*

The chromium(III)-EDTA complex has a constant absorptivity curve in acidic solution in the pH region 3 to 4. The maximum in the curve is at 545 m $\mu$ , but the molar absorptivity at this maximum depends on the anions present. Chromium(III) nitrate and chromium(III) chloride lead to an  $\epsilon$ -value of 202, but the sulphate gives a value of 183. When sulphate is added to a chromium(III) chloride or nitrate solution before the establishment of the complex, the  $\epsilon$ -value of the complex is 183; but once

the complex has been established, sulphate does not lower the extinction of the complex formed from chloride or nitrate solution. Excess of sulphate is not necessary, since a chromium(III) sulphate solution to which excess of chloride is added also leads to  $\epsilon=183$  for the complex. The  $\epsilon$ -value of the other maximum at  $395 \text{ m}\mu$  is 106.

The addition of sulphate to the original solution in which chromium(III) has to be determined, which is necessary in order to avoid fluctuations in the extinction of the uncomplexed solution, therefore also leads to reliable extinctions for the complexed solution. Under these conditions the value of  $\Delta\epsilon$  is 170. Beer's law appears to be valid, as the  $\Delta\epsilon$ -concentration curve in this pH region is a straight line.

Acetate ions decrease the absorptivity mentioned for the chromium(III)-EDTA complex. However, the addition of acetate buffer was not necessary in this case and therefore was avoided.

The observations mentioned so far lead to the following procedure for the determination of chromium(III) with EDTA in the presence of other metals.

*Recommended procedure.* A sample containing 0.4 to 10 mg of chromium(III) is dissolved in such a way that 20 ml of solution at pH 2 to 3 results. When necessary, treat the solution with sodium sulphate to give a sulphate concentration of about 0.1 M after making up to the mark in a 25-ml measuring flask.

Transfer a 10-ml aliquot of the resulting 25-ml solution to another 25-ml measuring flask (flask A). Transfer another 10-ml aliquot to a 25-ml tube. To the tube, add enough EDTA solution (use a 0.35 M solution prepared by dissolution of the required

TABLE I  
DETERMINATION OF CHROMIUM WITH EDTA IN THE PRESENCE OF OTHER METALS

Number of the experiment	Amount of other metals (mg)							Amount of Cr (mg)		Error (%)	
	Cu	Ni	Al	Mn	Zn	Co	Fe(II)	Fe(III)	Present		Found
1	115								0.750	0.754	+ 0.5
2		115							0.750	0.758	+ 1.1
3			115						0.750	0.742	- 1.1
4				115					0.750	0.746	- 0.5
5					115				0.750	0.750	0
6						20			0.750	0.790	+ 5
7 <sup>a</sup>						20			0.750	0.750	0
8 <sup>a</sup>						40			0.750	0.864	+ 15
9							10		0.750	0.758	+ 1.1
10							60		0.750	0.834	+ 11
11								115	0.750	0.750	0
12 <sup>a</sup>	20					10			0.750	1.500	+ 100
13 <sup>a</sup>		20				10			0.750	1.500	+ 100
14 <sup>a</sup>			20			10			0.750	1.300	+ 75
15 <sup>a</sup>				20		10			0.750	1.100	+ 50
16 <sup>a</sup>					20	10			0.750	1.300	+ 75
17 <sup>a</sup>						10		20	0.750	2.300	+ 200
18	20	20	20	20	20			20	0.750	0.750	0
19	20	20	20	20	20			20	0.250	0.250	0

<sup>a</sup> Heating and cooling under nitrogen (see note 2).

amount of the disodium salt of EDTA) to ensure that a ten-fold amount with respect to chromium(III) is present, along with twice the amount necessary to complex the other metal ions present. Add diluted sodium hydroxide solution or diluted sulphuric acid to make the pH slightly more than 3. Then heat the tube for 30 min in a boiling water bath. Cool the solution and transfer it to a 25-ml measuring flask (flask B). Make up to the mark and fill a cell of the spectrophotometer (1-cm or 4-cm cell, depending on the amount of chromium present) with the solution. Add to flask A the same amounts of EDTA and sodium hydroxide or sulphuric acid as were added for the preparation of the solution in flask B. Make up to the mark immediately, fill a cell of the spectrophotometer with this solution and measure the difference in extinction  $\Delta E$  of the two solutions in flasks B and A within 5 min of the addition of EDTA to flask A. Calculate the unknown amount of chromium(III) from a calibration curve.

The results of some determinations of chromium(III) in the presence of other metals are mentioned in Table I. Only experiments with large amounts of other elements present are included (for alloys see Table III).

*Notes.* (1) When samples with small chromium contents have to be analyzed, it is necessary to take an amount of the sample corresponding to 0.4 to 1.0 mg Cr in order to avoid the addition of such large amounts of EDTA that precipitation of the reagent would occur. The same holds for the analysis of chromium with the other complexans.

(2) The extinction of a cobalt(II)-EDTA solution increases when the solution is heated, causing positive errors for chromium (experiment 6). However, when the heating needed to establish the chromium complex and the cooling are carried out in a nitrogen atmosphere, a 25-fold amount of cobalt does not interfere (experiment 7). In all experiments marked with \* this part of the procedure was carried out in a nitrogen atmosphere. Experiments 12 to 17 show that the combined presence of cobalt and other metals in large amounts always leads to large positive errors, even when a nitrogen atmosphere is applied. The positive errors obviously result from oxidation of cobalt(II)-EDTA to cobalt(III)-EDTA.

(3) Large amounts of iron(II) have to be oxidized to iron(III) in the original solution. In experiments 9 and 10 no oxidation was carried out. It has been mentioned in the literature that in solutions containing iron(II) and EDTA a decomposition of the organic molecule may occur. This decomposition probably causes errors such as that in experiment 10.

(4) When the reproducibility required for the determinations can be over  $\pm 1\%$ , smaller amounts of chromium can be determined. In experiment 19 the value of  $\Delta E$  was 0.050 using 4-cm cells.

#### *Determination of chromium(III) with NTA*

The complex of chromium(III) with NTA has a constant molar absorptivity in the pH region 2 to 4. However, after the heating period needed for complex formation, the solution of the complex must be kept at room temperature for a short time before the extinction becomes constant. In the pH region 2.6 to 3.0 which was selected for the determinations, this time is about 20 min. At higher pH values more time is necessary; at lower pH values, less than 20 min is required, but such low pH values are less suitable for the determinations, because of the decreased solubility of NTA.

The extinction of the chromium(III)-NTA complex is the same when chlorides,

nitrates and sulphates are used. The maximum of the absorptivity curve in the pH region 2 to 4 is at  $555 \text{ m}\mu$  ( $\epsilon = 106$ ). Another maximum for chromium(III) complexes with complexans is always found at a wavelength of about  $400 \text{ m}\mu$  (see Fig. 1). In general this maximum has no analytical significance, but in the case of NTA, where it occurs at  $405 \text{ m}\mu$  ( $\epsilon = 110$ ) it has advantages over the other maximum in some cases.

The  $\Delta\epsilon$ -values are about 95 under these conditions for both maxima and Beer's law is followed at both wavelengths.

*Recommended procedure.* The procedure for the determination of chromium(III) with NTA is the same as that for EDTA, but for a few alterations. The sample contains 0.8–20 mg of chromium(III). The pH of the final solutions in flasks A and B is 2.6–3.0. The extinction is measured not earlier than 20 min after flask A has been made up to the mark. The NTA solution used is 0.4 M. It is prepared by dissolution of 7.64 g NTA and 3 g sodium hydroxide in water and dilution to 100 ml.

Some results are given in Table II. The results of the determination of chromium in some standard alloys are given in Table III.

*Notes.* (1) For the same reason as mentioned in note 2 on the results of the determinations with EDTA, it is necessary to work in a nitrogen atmosphere during heating and cooling of the mixtures of cobalt(II) and the complexan (see experiments 6 and 7). Contrary to the determinations with EDTA, in the case of NTA the combined presence of 20-fold amounts of cobalt and other metals caused no errors.

(2) When apart from chromium(III), only cobalt(II) is present, the extinction meas-

TABLE II  
DETERMINATION OF CHROMIUM WITH NTA IN THE PRESENCE OF OTHER METALS

Number of the experiment	Amount of other metals (mg)							Amount of Cr (mg)		Error (%)	
	Cu	Ni	Al	Mn	Zn	Co	Fe(II)	Fe(III)	Present		Found
1	150								1.50	1.50	0
2		150							1.50	1.51	+ 0.7
3			150						1.50	1.50	0
4 <sup>a</sup>				75					1.50	1.50	0
5					150				1.50	1.50	0
6						20			1.50	1.58	+ 5
7 <sup>a</sup>						40			1.50	1.54	+ 2.6
8 <sup>a</sup>						60			1.50	1.74	+ 16
9							75		1.50	1.54	+ 2.6
10 <sup>a</sup>							75		1.50	1.63	+ 9
11								75	1.50	1.54	+ 2.6
12 <sup>a</sup>							30	30	1.50	1.50	0
13 <sup>a</sup>						30	30		1.50	1.50	0
14 <sup>a</sup>						45		45	1.50	1.47	- 2
15 <sup>a</sup>	30	30	30	30	30	30		30	1.50	1.51	+ 0.7
16 <sup>a</sup>	15	15	15	15	15	15		15	1.50	1.52	+ 1.3
17 <sup>a</sup>	20	20	20	20	20	20	20		1.50	1.49	- 0.7
18 <sup>a</sup>	20	20	20	20	20	20		20	1.50	1.51	+ 0.7
19	40	40	40	40	40				1.50	1.50	0

<sup>a</sup> See note 1.

TABLE III

DETERMINATION OF CHROMIUM IN SOME STANDARD ALLOYS WITH EDTA AND NTA

Approximate composition	Complexing agent	% Chromium		Relative deviation (%)
		Stated	Found	
93% Al, 4% Cu, 1.5% Mg, 0.6% Mn, 0.2% Fe, traces Si, Ni, Zn, Ti, Pb, Ga and V (N.B.S. 85 b)	EDTA	0.211	0.216	+ 2.4
	NTA		0.216	+ 2.4
72% Fe, 13% Ni, 5% Cu, 3% C, 2% Si, 1% Mn, traces P and S (B.C.S. 173)	EDTA	3.97	3.99	+ 0.5
	NTA		3.99	+ 0.5
97.5% Fe, 1% C, 0.4% Mn, 0.3% Si, traces P and S (French standard alloy)	EDTA	1.21	1.20	- 1
	NTA		1.19	- 1.6
	NTA		1.24	+ 2.5
	NTA		1.21	0

urement can better be carried out at 405  $m\mu$ . In experiments 6, 7 and 8 this resulted in errors of 2.5, 1.0 and 5%. The changes in extinction by the oxidation of cobalt(II) obviously are smaller at 405  $m\mu$  than at 555  $m\mu$ .

#### *Determination of chromium(III) with other complexans*

Four other complexans were considered in this investigation, *viz.* EGTA (ethylene-glycol-bis- $\beta$ -aminoethylether-tetraacetic acid), HEDTA (N-hydroxyethylenediamine-triacetic acid), DTPA (diethylenetriaminepentaacetic acid) and DCTA (1,2-diamino-cyclohexanetetraacetic acid).

EGTA appeared to be of no practical importance. The heating time needed for complex formation of chromium(III) and EGTA was more than 1 h, the extinction values were variable, Beer's law was not followed and the molar absorptivity did not exceed a value of 45 in the visible region.

The other three complexans, HEDTA, DTPA and DCTA, were all suitable for the determination of chromium(III) according to the procedure given for EDTA, with modifications for the pH and the quantity of chromium to be taken in the sample. The complexes could be formed by heating a weakly acidic solution of the two compounds for 30 min. The 3 complexes all had molar absorptivity curves with maxima at 390  $m\mu$  and 545  $m\mu$ . For HEDTA the  $\epsilon$ -values were 122 and 153 respectively, and for DCTA 98 and 204, irrespective of whether chlorides, nitrates or sulphates were used. For DTPA these 3 anions had an effect similar to that observed in the case of EDTA. In sulphate medium the  $\epsilon$ -values were 84 and 107 at the two maxima, but in nitrate and chloride solutions these values were a few per cent higher. The chromium-(III)-DTPA complex had a constant extinction in the pH region 2.2-5. For the HEDTA complex this pH region was 2.1-3.3 and for the DCTA complex 3.6-5.6.

So far only a few determinations for chromium(III) with DTPA, HEDTA and DCTA have been carried out, in the presence of the ten-fold amounts of iron(III), copper, nickel and cobalt. Copper and nickel did not interfere at all. In the case of DTPA cobalt did not interfere, and with HEDTA iron did not interfere. None of the experi-

ments was carried out in a nitrogen atmosphere. If it is later found that better results can be obtained with these complexans than with EDTA or NTA, such results will be published in a short communication. The determination of chromium(III) with DCTA has already been described by SELMER-OLSEN<sup>3</sup> and KHALIFA *et al.*<sup>4</sup>.

#### *Determination of chromium(III) with other complexing agents*

A few other complexing agents for the determination of chromium(III) have been mentioned in the literature. Ferricyanide and oxalic acid did not lead to good results in our procedure. However, pyridine-2,6-dicarboxylic acid, first proposed by HARTKAMP<sup>5</sup> and later by MORIMOTO AND TANAKA<sup>6</sup>, gave excellent results<sup>7</sup>.

Our thanks are due to Mrs. A. GIJZEN, Mrs. S. WESTRA and Mr. G. FEENSTRA for experimental assistance.

#### SUMMARY

Selective spectrophotometric determinations of milligram amounts of chromium(III) with complexans are described, based on the fact that the chromium(III) complexes are formed rapidly at boiling temperatures, but very slowly at room temperature, while the formation of some interfering complexes takes place instantaneously. Determinations with EDTA are more sensitive, but the combined presence of cobalt and other metals still interferes; there is no interference with the less sensitive NTA. The combined presence of a 100-fold amount of copper, nickel, cobalt and iron generally has no effect on the results. The use of DCTA, DTPA and HEDTA is discussed

#### RÉSUMÉ

Une méthode est proposée pour le dosage spectrophotométrique du chrome(III) au moyen de divers complexants: EDTA, NTA, HEDTA, DTPA et DCTA, sans qu'il soit nécessaire de séparer le nickel, le fer, le cobalt et le cuivre.

#### ZUSAMMENFASSUNG

Es wird eine spektralphotometrische Methode zur Bestimmung von Chrom(III) mit Hilfe von EDTA, NTA, HEDTA, DTPA und DCTA ohne Abtrennung von Nickel, Eisen, Kobalt und Kupfer beschrieben.

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## *n*-PENTYL-2-PYRIDYL KETOXIME AS A SELECTIVE COLORIMETRIC REAGENT FOR COPPER

FRED TRUSELL AND KENNETH LIEBERMAN

*Department of Chemistry, Texas Technological College,  
Lubbock, Texas (U.S.A.)*

(Received August 18th, 1963)

Several pyridine-2-oximes have found application as colorimetric reagents for copper and iron. Examples include pyridine-2-aldoxime<sup>1,2</sup>, 6-methylpyridine-2-aldoxime<sup>3</sup>, methyl-2-pyridyl ketoxime<sup>4</sup>, and phenyl-2-pyridyl ketoxime<sup>5</sup>. In most of the foregoing cases the determinations are subject to interference from a fairly large number of commonly occurring ions. In the present work *n*-pentyl-2-pyridyl ketoxime has been shown to have a sensitivity for copper which is lower than that of the aforementioned reagents, but to possess a much higher degree of selectivity toward this element.

### EXPERIMENTAL

#### *Materials and equipment*

*Standard copper solution.* A 0.01 *M* solution was prepared by dissolving 0.6354 g of electrolytic copper (Matheson, Coleman and Bell, Norwood, Ohio) in 10 ml of concentrated nitric acid and diluting with water to the mark in a 1-l volumetric flask.

*Hydroxylammonium chloride.* A 10% solution was prepared by dissolving 100 g of hydroxylammonium chloride in 900 ml of water.

*n-Pentyl-2-pyridyl ketoxime hydrochloride.* The corresponding ketone was prepared from 1-bromopentane and 2-cyanopyridine and was oximated with hydroxylammonium chloride.

Fifty ml of anhydrous ether, 6.76 g (0.28 moles) of magnesium metal and a few crystals of iodine were introduced into a 1-l, 3-neck round-bottom flask fitted with a stirrer and a condenser. Fifteen ml of a solution of 31.4 ml of 1-bromopentane in 50 ml of anhydrous ether were introduced into the flask, and when the reaction started the remainder of the 1-bromopentane was added dropwise with constant stirring at a rate sufficient to keep the reaction at reflux temperature. An ice bath was used to help control the temperature. When the addition of 1-bromopentane was complete the reaction mixture was stirred for one hour while cooling to room temperature. A solution of 24.5 ml (0.25 moles) of 2-cyanopyridine in 200 ml of anhydrous ether was dropped into the cooled Grignard reagent with constant stirring over a 2-h period and the reaction mixture was stirred for 8 h at room temperature. A cold solution of 50 g of ammonium chloride in 200 ml of water and 50 ml of concentrated hydrochloric acid was added to the reaction, and the mixture was stirred for 5 h. The ether layer



was separated and retained. The aqueous layer was refluxed for 2 h, cooled, made just alkaline with sodium hydroxide, and extracted with 4 150-ml portions of ether. All of the ether fractions were combined and distilled. The colorless fraction distilling at 118–119° at a pressure of 11 mm Hg was collected. The *n*-pentyl-2-pyridyl ketone becomes yellow when exposed to light, and must be stored in a dark bottle.

Two ml of *n*-pentyl-2-pyridyl ketone, 6 ml of 5 *M* hydroxylammonium chloride, and 6 ml of 5 *M* sodium acetate were combined with 10 ml of 95% ethanol and heated gently for 2 h. The *n*-pentyl-2-pyridyl ketoxime floated to the surface of the mixture, a red color indicating that it was contaminated with iron. The reaction mixture was extracted once with 20 ml of ether. The ether layer was retained and dried over anhydrous magnesium sulfate. The magnesium sulfate was separated by filtration and a steady stream of dry hydrogen chloride was bubbled through the ether solution precipitating *n*-pentyl-2-pyridyl ketoxime hydrochloride. The crude product was dried under vacuum and then shaken with 20 ml of ether saturated with hydrogen chloride. The precipitate was filtered off and dried at room temperature under vacuum. Melting point: 149–151°.

A 0.01 *M* solution of *n*-pentyl-2-pyridyl ketoxime hydrochloride was prepared by dissolving 0.573 g in 250 ml of water.

All spectrophotometric data were obtained on a Beckman Model DU spectrophotometer using matched 1-cm silica cells.

All pH measurements were made on a Beckman Model 76 pH meter.

#### *Preliminary investigations*

*n*-Pentyl-2-pyridyl ketoxime hydrochloride is a white crystalline solid, soluble in water and insoluble in ether, carbon tetrachloride, and benzene. It is hygroscopic and must be stored in a desiccator. Aqueous solutions are colorless and are stable under ordinary laboratory conditions for at least a month.

The reactions of *n*-pentyl-2-pyridyl ketoxime with metal ions are very similar to those of the lower homologues of the series. These reactions are summarized in Table I.

TABLE I  
REACTIONS OF *n*-PENTYL-2-PYRIDYL KETOXIME WITH VARIOUS CATIONS

<i>Cation</i>	<i>Color</i>	
	<i>pH</i> 2.0–6.0	<i>pH</i> 6.0–10.0
Iron(II)	Orange	Purple-red
Iron(III)	Pale orange	Pale red
Copper(I)	Pale green <sup>a</sup>	Yellow-green <sup>b</sup>
Copper(II)	Green	Green
Cobalt(II)	Yellow <sup>a</sup>	Yellow
Manganese(II)	Pale yellow	Pale yellow

<sup>a</sup> Solid forms

<sup>b</sup> Hydroxide forms at approximately pH 7

#### *Reaction with copper*

When a 5-fold excess of *n*-pentyl-2-pyridyl ketoxime is added to a solution containing copper(I) a soluble green product is formed. On standing for a few minutes a

green precipitate settles out. This material was separated, dried at 110°, and analyzed. Calculated for  $\text{Cu}(\text{C}_{11}\text{H}_{16}\text{N}_2\text{O})\text{Cl} \cdot 1/2 \text{H}_2\text{O}$ : C = 43.98%, H = 5.71%, Cl = 11.82%. Found: C = 43.87%, H = 5.77%, Cl = 12.01%. The copper compound precipitates from aqueous solutions above pH 1.5. At about pH 7 the compound decomposes, leaving a residue of hydrous copper oxide. The copper(I)-oxime compound is soluble in chloroform and in isoamyl alcohol and can be extracted into these solvents from aqueous suspensions. This extractability is exploited in the spectrophotometric procedure for copper described below. In isoamyl alcohol the copper(I)-oxime compound conforms to Beer's law in concentrations up to  $5.6 \cdot 10^{-4} M$  and has a molar absorptivity of 2650 at 360  $m\mu$ .

#### Procedure

Weigh out a sample containing less than 1 mg of copper and dissolve in nitric or sulfuric acid or in aqua regia. By the addition of sodium hydroxide adjust the pH to between 2.5 and 3.0. Add 20 ml of 10% hydroxylammonium chloride, 5 ml of 0.01 M oxime, and extract once with 15 ml of isoamyl alcohol. Allow the layers to separate and reject the aqueous phase. Transfer the organic layer to a 25-ml volumetric flask and dilute to the mark with isoamyl alcohol. At the end of 1 h, determine the absorbance of the solution at 360  $m\mu$ .

#### Influence of foreign ions

The effect of foreign ions on the determination of copper by the foregoing method was examined. The metals chosen were those which form colored complexes with the ligand and those usually associated with copper. The results are summarized in Table II. Cobalt(II) forms a solid yellow compound with the ligand which is also extracted into isoamyl alcohol and interferes with the determination of copper by this method.

TABLE II  
EFFECT OF FOREIGN IONS ON THE DETERMINATION OF  
COPPER WITH n-PENTYL-2-PYRIDYL KETOXIME

Foreign ion	Mole ratio foreign ion to copper	mg Copper	
		Added	Found
Iron(II)	4 : 1	0.635	0.635
Arsenic(III)	5 : 1	0.635	0.635
Cobalt(II)	5 : 1	0.635	<sup>a</sup>
Nickel(II)	4 : 1	0.635	0.634
Antimony(III)	5 : 1	0.635	0.641

<sup>a</sup> Complete interference

#### RESULTS AND DISCUSSION

To test the reliability of this method a copper determination was run on National Bureau of Standards Sample No. 53d, a lead-base bearing metal. In addition to lead and copper it contained antimony, arsenic, tin, bismuth, and nickel. Samples weighing 0.2 g were weighed into 150-ml beakers, treated with 15 ml of concentrated sulfuric acid, and heated for 1.5 h. The mixture was cooled, diluted with 50 ml of water and

the resulting lead sulfate was filtered off using a porous bottom crucible. The above procedure was then followed. The results of the analyses are given in Table III.

TABLE III

DETERMINATION OF COPPER IN NATIONAL BUREAU OF STANDARDS SAMPLE NO. 53d

Sample weight (g)	Weight copper (mg)	Per cent copper
0.2002	0.533	0.266
0.1434	0.381	0.266
0.2258	0.600	0.266
	Average	0.266
	NBS value	0.268

This work was carried out under Grant D-094 from The Robert A. Welch Foundation, Houston, Texas.

## SUMMARY

*n*-Pentyl-2-pyridyl ketoxime hydrochloride has been prepared and examined as a colorimetric reagent for copper. It is less sensitive than some reagents, but shows a remarkable selectivity toward copper. The copper(I)-oxime compound can be extracted into isoamyl alcohol or into chloroform. In isoamyl alcohol the colored compound conforms to Beer's law in concentrations up to  $5.6 \cdot 10^{-4} M$  and has a molar absorptivity of 2650 at  $360 \mu$ . A procedure for the colorimetric determination of copper is given and its reliability is shown.

## RÉSUMÉ

Les auteurs ont effectué une étude sur la préparation et l'utilisation du chlorhydrate de *n*-pentyl-2-pyridylcétoxime, comme réactif colorimétrique du cuivre. Sa sensibilité est inférieure à celle de certains réactifs, mais sa sélectivité est remarquable. Le composé obtenu peut être extrait dans l'alcool isoamylique ou dans le chloroforme. Une méthode est proposée pour le dosage colorimétrique du cuivre.

## ZUSAMMENFASSUNG

*n*-Pentyl-2-pyridylketoxim-hydrochlorid wurde hergestellt und als kolorimetrisches Reagens auf Kupfer geprüft. Es erwies sich als unempfindlicher, aber selektiver als andere Reagentien. Die Kupfer(I)-Oxim-Verbindung kann mit Isoamylalkohol oder Chloroform extrahiert werden. Für die gefärbte Verbindung ist in Isoamylalkohol das Beersche-Gesetz bis zu einer Konzentration von  $5.6 \cdot 10^{-4} M$  gültig. Die molare Absorption beträgt 2650 bei  $360 \mu$ .

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## SEPARATION DES ALCALINO-TERREUX PAR L'EDTA SUR RESINE ECHANGEUSE D'IONS

J. J. BOUQUIAUX ET J. H. C. GILLARD

*Institut d'Hygiène et d'Epidémiologie, Ministère de la Santé Publique et de la Famille, Bruxelles (Belgique)*

(Reçu le 12 Septembre, 1963)

FOUARGE ET FUGER<sup>1</sup> et BOVY ET DUYNCKAERTS<sup>2</sup> utilisent la différence de stabilité entre les complexes formés avec l'EDTA pour séparer sur colonne de résine échangeuse d'ions des quantités des alcalino-terreux de l'ordre de quelques milligrammes.

DAVIS<sup>3</sup> signale qu'en solution EDTA, à pH 5.25, le strontium est quantitativement retenu sur une colonne de Zeocarb, alors que le calcium est complexé et filtré; à pH plus bas, le calcium est partiellement retenu.

WADE ET SEIM<sup>4</sup> dissolvent du calcium et du strontium dans l'EDTA et font passer cette solution, à pH 4.8, sur colonne de Dowex. A ce pH se fixe seulement une partie du calcium, que ces auteurs éluent ensuite à l'aide d'EDTA à pH 5.3, sans entraîner le strontium (celui-ci est élué à l'aide d'HCl). Cette technique permet la séparation de quantités très importantes de calcium de petites quantités de strontium.

La première partie de la présente étude montre la possibilité, dans la technique de WADE ET SEIM, de déceler avec précision la fin de l'éluion du calcium par la surveillance du pH de l'éluat.

La deuxième partie est relative à l'éluion du calcium, du strontium et du baryum par l'EDTA et est basée sur l'augmentation de la stabilité des complexes EDTA-alcalino-terreux en fonction du pH. L'élévation du pH de l'éluant EDTA après l'éluion de chacun des alcalino-terreux permet en effet le "décrochage" immédiat de l'alcalino-terreux suivant et la suppression du battement important habituellement inévitable entre les pics d'éluion.

## PARTIE EXPÉRIMENTALE

*Appareillage et réactifs*

Tous les essais sont effectués sur résine cationique Dowex 50W  $\times$  8, 200-400 mesh, traitée par lévigation pour en éliminer les particules les plus fines. Avant toute expérience, la résine est amenée sous forme ammoniacale à l'aide d'EDTA 0.01 M ajusté à pH 9.0 au moyen d'ammoniaque, et rincée à l'eau distillée.

La hauteur de la couche de résine, fixée après quelques essais d'orientation, est de 25 cm pour toutes les colonnes.

Le débit est invariablement de 1 ml par min par cm<sup>2</sup> de section de colonne.

La section de la colonne, déterminée expérimentalement de manière à être aussi réduite que possible tout en assurant une bonne séparation, est de 2 cm<sup>2</sup> pour les expériences décrites ici. Une colonne de section plus petite ne permet pas la fixation, par le mode opératoire proposé, des 20 mg de strontium généralement mis en oeuvre. Par contre des colonnes de section supérieure à 2 cm<sup>2</sup> permettent d'augmenter la quantité de calcium jusqu'à plusieurs grammes.

L'éluat des colonnes est recueilli par fractions de 7.5 ml par cm<sup>2</sup> de section de colonne.

Les concentrations en calcium, strontium et baryum dans les fractions d'éluat sont mesurées par spectrophotométrie de flamme aux longueurs d'onde suivantes: Ca, 422.7 m $\mu$ ; Sr, 460.7 m $\mu$ ; Ba, 493.4 m $\mu$ . Le dosage n'est pas toujours quantitatif, notamment aux fortes concentrations en calcium, mais les courbes obtenues sont toujours suffisamment suggestives pour indiquer si la séparation est complète ou non.

Le réactif d'éluat est une solution 0.1 M d'acide éthylène-diamine-tétraacétique (EDTA), amenée aux différents pH requis à l'aide d'NH<sub>4</sub>OH 1 M. Une solution 0.01 M suffit cependant pour l'éluat du baryum et le reconditionnement de la résine.

### Expérimentation

#### 1ère partie

Cette première partie de l'expérimentation est conditionnée par la nécessité d'éluer rapidement le calcium tout en assurant la détection nette et aisée des variations de pH de l'éluat qui permettent de suivre cette éluat.

(1) *Dissolution et fixation des alcalino-terreux sur la colonne.* Afin de standardiser la solution de départ, les alcalino-terreux sont amenés sous forme de précipité de carbonate avant d'être dissous dans une quantité stoechiométrique d'EDTA 0.1 M à pH 5.25 (1 molécule d'EDTA par atome d'alcalino-terreux).

La solution est amenée au pH requis à l'aide d'HCl 1 M ou d'NH<sub>4</sub>OH 1 M avant fixation sur la colonne.

(2) *Influence de l'ajustement du pH avant la fixation.* L'ajustement précis du pH de la solution des alcalino-terreux dans l'EDTA avant fixation sur la colonne présente une grande importance. Les résultats des essais effectués à ce sujet sont consignés dans la Fig. 1, le 5e essai ayant été réalisé sans ajustement préalable de pH. Le calcium est élué dans chaque cas à pH 5.25.

On peut constater que le calcium retenu par la colonne est d'autant moins abondant que le pH est élevé. A pH 5.8, le calcium n'est pratiquement plus retenu. De même, à ce pH, le strontium ne se fixe plus que partiellement.

(3) *Recherche du pH d'éluat optimum du calcium.* Les essais d'éluat du calcium à différents pH sont repris dans la Fig. 2, la fixation des éléments sur la colonne ayant été faite dans chaque cas à pH 4.8.

Comme on peut le constater, le pH 5.5 "décroche" le strontium avant la fin de l'éluat du calcium. Le pH 5.0 fournit une très bonne séparation Ca-Sr, mais l'étalement du calcium est important (48 fractions). Par contre, le pH 5.25 assure un étalement acceptable du calcium (27 fractions) et un battement entre le calcium et le strontium satisfaisant (56 fractions).

(4) *pH de l'éluat au cours de l'éluat.* Les variations du pH de l'éluat peuvent

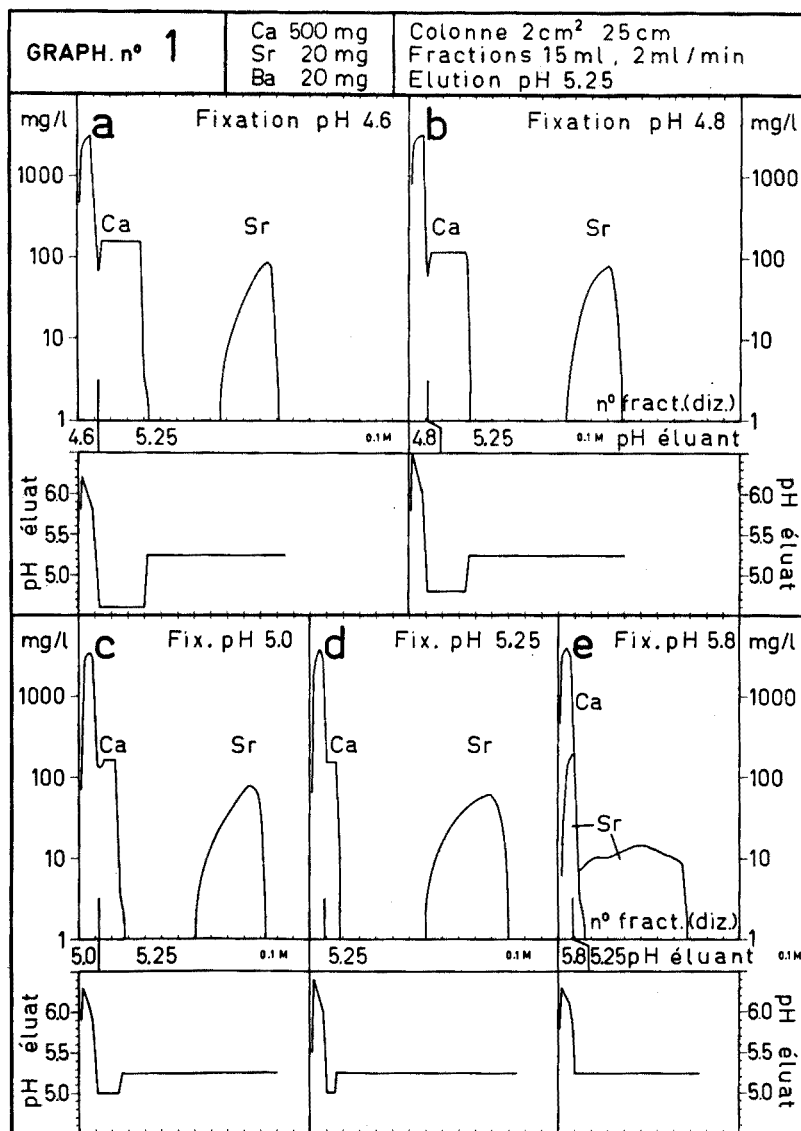


Fig. 1. Ajustement du pH de fixation: influence sur la fixation du calcium et sur le pH de l'éluat.

indiquer les différentes phases de la séparation. En particulier un saut de pH se produit à la fin de l'éluat du calcium.

On observe successivement (Figs. 1 et 2): (a) pendant la fixation des éléments sur la colonne, une élévation du pH de l'éluat jusqu'à 6.3 ou 6.5 dans les 2 ou 3 premières fractions, suivie d'une chute progressive du pH. Cette chute atteint le pH de la solution de fixation utilisée lorsque cette fixation s'effectue à pH 4.6, 4.8 ou 5.0 (Fig. 1); (b) pendant l'éluat du calcium, une stabilisation du pH; (c) à la fin de l'éluat du

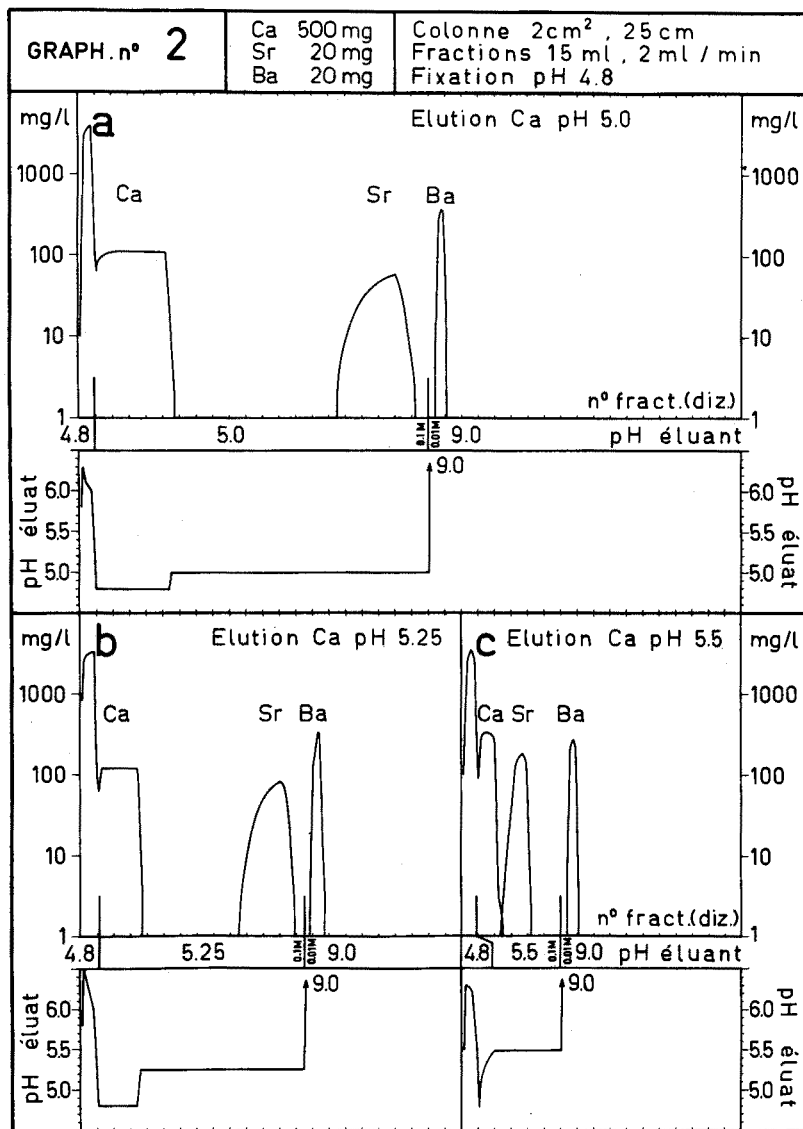


Fig. 2. pH d'éluion optimum du calcium.

calcium, un saut brusque du pH (en 2 ou 3 fractions). Celui-ci se stabilise cette fois au pH de l'éluant utilisé (Fig. 2).

La comparaison des Figs. 1 et 2 indique que la fixation des alcalino-terreux à pH 4.8 suivie de l'éluion du calcium à pH 5.25 conduit à l'éluion rapide du calcium et à un battement important entre le calcium et le strontium, tout en permettant la détection aisée du saut de pH (de 4.8 à 5.25).

Assez remarquablement, ces conditions élaborées sous l'angle de la détection nette et précise de la fin de l'éluion du calcium par la variation du pH de l'éluant, rejoignent

celles mises au point par WADE ET SEIM sur la base du rendement de la séparation.

La Fig. 4 montre que le saut de pH est parfaitement net et qu'il indique avec précision la fin de l'élution du calcium, pour des quantités de calcium très variées.

### 2e partie

Dans tous les essais de cette 2e partie, les alcalino-terreux en solution dans l'EDTA 0.1 M sont fixés sur la colonne à pH 4.8 et le calcium est élué à pH 5.25, selon la technique mise au point dans la 1ère partie.

Les expériences visent à séparer calcium, strontium et baryum par l'EDTA en réduisant au minimum le battement entre les pics d'élution.

(1) *Influence de la quantité de calcium sur la séparation Ca-Sr.* Des essais effectués avec des quantités de calcium variant de 20 à 1000 mg en présence de 20 mg de strontium et 20 mg de baryum indiquent que la modification du pic du calcium est plus sensible en hauteur (de 400 à 4000 mg/l) qu'en largeur (de 11 à 54 fractions). (Des observations similaires se dégagent de la Fig. 4.)

Ces essais montrent que, quelle que soit la quantité de calcium, et si l'élution est poursuivie à pH 5.25, le strontium apparaît aux environs de la 90e fraction (comme dans la Fig. 2b), et son élution s'étale sur 30 à 40 fractions. Le battement entre le calcium et le strontium est encore d'une quarantaine de fractions pour 1000 mg de calcium, mais n'est que de quelques fractions pour 2000 mg de calcium.

(2) *Recherche du pH d'élution optimum du strontium.* En augmentant la stabilité du complexe EDTA-strontium par élévation du pH de l'éluant, un décrochage plus rapide du strontium peut être obtenu. La Fig. 3 rend compte des essais effectués dans ce sens, le calcium ayant été élué au préalable à pH 5.25.

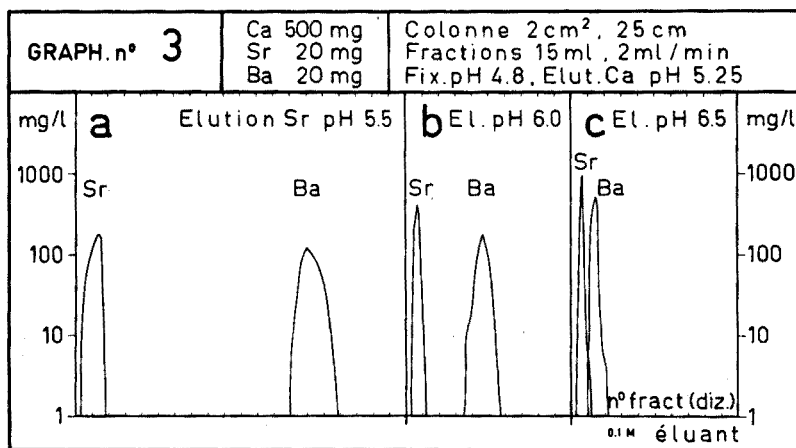


Fig. 3. pH d'élution optimum du strontium.

L'élévation du pH assure l'élution pratiquement immédiate du strontium. A pH 5.5 cependant, le strontium reste fort étalé, et à pH 6.5 le baryum décroche trop rapidement. Le pH 6.0 par contre donne pleine satisfaction: le strontium se retrouve



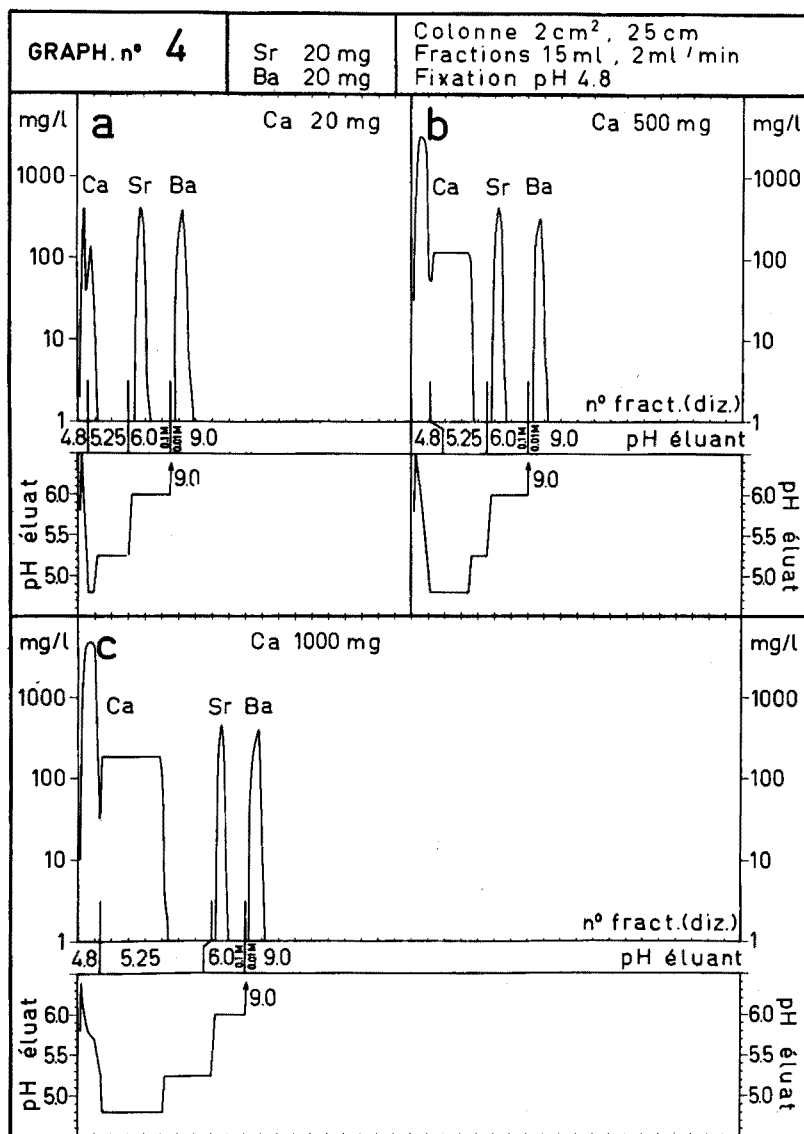


Fig. 4. Séparation des alcalino-terreux par variation du pH de l'éluant, pour différentes quantités de calcium.

dans une dizaine de fractions, et le baryum n'apparaît qu'une vingtaine de fractions après le strontium.

D'autres expériences montrent que la quantité de calcium n'affecte en rien cette séparation Sr-Ba.

Il est donc possible, par élution à pH 6.0, de recueillir immédiatement les 20 mg de strontium mis en oeuvre dans une douzaine de fractions (180 ml), sans contrôle analytique de la fin de l'élution du strontium ni de l'apparition du baryum.

Au cours de l'élution à pH 6.0, le pH de l'éluat ne manifeste aucune particularité et reste fixé à 6.0.

(3) *pH d'élution du baryum. Régénération de la colonne.* Dès la fin de l'élution du strontium, une nouvelle élévation du pH de l'éluant assure l'élution du baryum. L'EDTA 0.1 M à pH 7.0 ou 7.5 suffirait. Cependant, à pH 9.0, une solution dix fois plus diluée (0.01 M) assure l'élimination des 20 mg de baryum en une douzaine de fractions (Fig. 4). L'EDTA 0.01 M à pH 9.0 ramène de plus la résine à la forme ammoniacale de départ.

#### RÉSUMÉ

Les auteurs décrivent une méthode permettant de séparer quantitativement quelques mg Sr et Ba de plusieurs g Ca. Les carbonates alcalino-terreux sont dissous dans de l'EDTA 0.1 M, et après fixation à pH 4.8, sur colonne de Dowex ammoniacal, sont élués, également à l'aide d'EDTA 0.1 M, le calcium à pH 5.25, le strontium à pH 6.0, le baryum à pH 9.0. Ils mettent en évidence la possibilité de déceler avec précision la fin de l'élution du calcium, indiquée par un saut brusque du pH de l'éluat (de 4.8 à 5.25).

#### SUMMARY

The quantitative separation of a few mg of strontium and barium from several g of calcium is described. The alkaline earth carbonates are dissolved in 0.1 M EDTA, fixed at pH 4.8 on an ammoniacal Dowex column, and eluted, also with 0.1 M EDTA, calcium at pH 5.25, strontium at pH 6.0, barium at pH 9.0. The end of the calcium elution can be followed accurately by a sudden pH increase in the eluate (from 4.8 up to 5.25).

#### ZUSAMMENFASSUNG

Die quantitative Trennung weniger Milligramme Strontium und Barium von einigen Grammen Calcium wird beschrieben. Die Erdalkalicarbonate werden in 0.1 M EDTA gelöst und mit einem pH-Wert 4.8 auf eine Kolonne mit ammoniakalischem Dowex gegeben. Die Elution erfolgt ebenfalls mit 0.1 M EDTA. Der pH-Wert der Lösung beträgt beim Calcium 5.25, beim Strontium 6.0 und beim Barium 9.0. Das Ende der Calcium-Elution erkennt man am plötzlichen Anstieg des pH-Wertes von 4.8 auf 5.25 im Eluat.

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## THEORY OF TITRATION CURVES

## V. LOCATIONS OF EXTREMA ON CONDUCTOMETRIC, AMPEROMETRIC, SPECTROPHOTOMETRIC, AND OTHER LINEAR ("SEGMENTED") TITRATION CURVES

JAMES A. GOLDMAN AND LOUIS MEITES

*Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, N.Y. (U.S.A.)*

(Received July 29th, 1963)

The preceding papers of this series<sup>1-4</sup> have described the conclusions obtained from rigorous and extensive investigations of the properties of several different types of potentiometric titration curves.

Another general class of titration curves is obtained in conductometric, amperometric, spectrophotometric, and other titrations. Except in the vicinity of the equivalence point, these curves are composed of segments that are linear when appropriate corrections are applied for dilution, in contrast to the familiar sigmoidal shape of a potentiometric titration curve. The intersection of these line segments is considered to correspond to the end-point.

The common characteristic of the methods used to obtain such titration curves is that the property measured is directly proportional to a summation of contributions from all or some of the species present. It may be proportional to the concentration of a single species, as in many amperometric and spectrophotometric titrations; it may be proportional to a linear combination of the concentrations of two or more species, as in other titrations of the same types; or it may be proportional to a summation of contributions from all of the ionic species present, as is always true in conductometric titrations.

This paper deals with the locations of maxima and minima on titration curves of the linear type. We shall consider only single-step ion-combination reactions in which the product makes no contribution to the property measured. These include many acid-base, precipitation, complexation, and redox titrations. In general, linear titration curves may have either maxima or minima. In conductometric and spectrophotometric titration curves of the type discussed here, however, only minima are possible.

Heretofore there has been no rigorous discussion of the locations of these extrema. BRITTON<sup>5</sup> examined the conductometric titration curve for the neutralization of a strong acid by a strong base and concluded that the minimum occurs slightly beyond the equivalence point, but his treatment neglects both the effect of dilution and the contributions of the cation of the base and the anion of the acid. KOLTHOFF AND LINGANE<sup>6</sup> discussed the maximum or minimum that is obtained in an amperometric

precipitation titration in which both of the ions of the precipitate are electro-oxidizable or electro-reducible, and concluded that the extremum coincides with the equivalence point only when the precipitate is isovalent and when the diffusion current constants of its ions are identical. They asserted that the extremum does not coincide with the equivalence point "if the latter condition is not fulfilled, or when the precipitate is of unsymmetrical valence type". Their treatment ignores the effect of dilution.

#### THE GENERAL EQUATION OF THE TITRATION CURVE

In the titrations under consideration, the measured property  $P$  is the summation of the individual contributions  $p_i$ , and each  $p_i$  is directly proportional to the molar concentration  $C_i$  of the corresponding species at equilibrium. It is assumed that equilibrium has been attained before  $P$  is measured. We may accordingly write

$$P = \sum_i p_i = \sum_i k_i C_i \quad (1)$$

where  $k_i$  is the appropriate proportionality constant for the  $i$ 'th species, and is assumed to remain constant throughout the titration. Although in general one has  $k_i = p_i/C_i$ , the form of  $k_i$  depends on the property that is measured.

In conductometric titrations  $k_i$  is given by

$$k_i = |z_i| \lambda_i / 10^3 \theta \quad (2)$$

where  $|z_i|$  is the absolute value of the charge of the  $i$ 'th ion,  $\lambda_i$  is its equivalent conductance (in mho-cm<sup>2</sup>/equivalent), and  $\theta$  is the cell constant (in cm<sup>-1</sup>). The value of  $\lambda_i$  is generally equated with that of  $\lambda_i^0$ , the ionic equivalent conductance at infinite dilution. In these titrations  $P$  is the conductance  $\kappa/R$  (in mhos).

In amperometric titrations with a dropping mercury electrode  $P$  is the diffusion current  $i_d$ , and  $k_i$  is given by

$$k_i = I_i m^{2/3} t^{1/6} \quad (3)$$

where  $I_i$  is the diffusion current constant of the  $i$ 'th ion, equal to  $607 n_i D_i^{1/2}$  at 25° if  $i_d$  is the average diffusion current in  $\mu\text{A}$ ;  $n_i$  is the number of electrons consumed in the half-reaction that involves the  $i$ 'th ion;  $D_i$  is the diffusion coefficient of that ion (in cm<sup>2</sup>/sec); and  $m$  (in mg/sec) and  $t$  (in sec) are the capillary characteristics. For an anodic process  $I_i$ ,  $n_i$ ,  $k_i$ , and the diffusion current are all negative; for a cathodic one they are all positive. If a rotated platinum electrode is used instead of a dropping electrode,

$$k_i = n_i D_i F A / \delta \quad (3a)$$

where  $F$  is the faraday,  $A$  the area of the electrode, and  $\delta$  the thickness of the hypothetical Nernst diffusion layer; again  $k_i$  may be either positive or negative, depending on the ion involved and the conditions under which the titration is performed.

In spectrophotometric titrations  $k_i$  is given by

$$k_i = \varepsilon_i b \quad (4)$$

where  $\varepsilon_i$  is the molar absorptivity (in l/mole-cm or for all practical purposes, cm<sup>2</sup>/mmole) and  $b$  is the thickness of the cell (in cm), while  $P$  is the absorbance  $A$ .

In conductometric titrations *all* ionic species have values of  $k_i$  that are both finite and positive. In amperometric titrations  $k_i$  may be zero for some species under the conditions employed; if it is not zero it may be either positive or negative. In spectrophotometric titrations  $k_i$  may be either zero or positive, but cannot be negative.

We shall consider the general ion-combination reaction



whose equilibrium constant may be written

$$K = [B^{m+}]^n [A^{n-}]^m \quad (6)$$

It is assumed that the product  $B_nA_m$  is present at the start of the titration. The unusual form taken by eqn. (6) when  $m = n \neq 1$  has been discussed previously<sup>2</sup>.

For the titration of  $V_B^0$  ml of  $C_B^0$   $F$   $BX_m$  with  $C_T F Y_n A$  the electroneutrality equation becomes, after simplification<sup>2</sup>,

$$[B^{m+}] = \alpha + \frac{zK^{1/m}}{[B^{m+}]^z} \quad (7)$$

where<sup>2</sup>

$$z = n/m \quad (8)$$

$$\alpha = zC_B^0(1-f)/(z+rf) \quad (9)$$

$$f = zV_T C_T / V_B^0 C_B^0 \quad (10)$$

and

$$r = C_B^0 / C_T \quad (11)$$

so that

$$[Y^+] = nC_B^0 f / (z + rf) \quad (12a)$$

and

$$[X^-] = nC_B^0 / (z + rf) \quad (12b)$$

In general, therefore,

$$P = \frac{k_A K^{1/m}}{[B^{m+}]^z} + k_B [B^{m+}] + \frac{nC_B^0 (k_X + k_Y) f}{z + rf} \quad (13)$$

It is assumed that  $k_{B_n A_m} = 0$ , so that the product of the reaction makes no contribution to  $P$ .

Prior to the equivalence point, in the region where the reaction is driven essentially to completion by the excess of  $B^{m+}$  remaining, the concentration of  $A^{n-}$  is negligible and

$$P' = P(z + rf)/z = C_B^0 (k_B + mk_X) + C_B^0 f (mk_Y - k_B) \quad (14)$$

whereas after the equivalence point, in the region where the reaction is driven essentially to completion by the excess of  $A^{n-}$  present, the concentration of  $B^{m+}$  is negligible and

$$P' = P(z + rf)/z = C_B^0 (mk_X - k_A) + C_B^0 f (mk_Y + k_A) \quad (15)$$

In these equations  $P'$  represents the quantity that is actually plotted in constructing the titration curve; the factor  $(z + rf)/z$  is equal to  $(V_B^0 + V_T)/V_B^0$ , which is the more usual form of the dilution correction. According to these equations, the titration curve (which is a plot of  $P'$  vs.  $f$ ) consists of two straight lines intersecting at  $f = 1$ , which corresponds to the equivalence point. In practice, of course, there is always some curvature around the equivalence point because the incompleteness of the reaction is appreciable there.

The only requirement for the existence of an extremum is that the slopes,  $dP'/df$ , of the lines for  $f < 1$  and  $f > 1$  must have opposite signs. There will be a minimum if

$$mk_Y - k_B < 0 \quad \text{and} \quad mk_Y + k_A > 0 \quad (16)$$

whereas the requirement for the existence of a maximum is

$$mk_Y - k_B > 0 \quad \text{and} \quad mk_Y + k_A < 0 \quad (17)$$

It is interesting to note that these conditions do not involve  $z$ , but rather only the valence of the cation initially present; of course, this is partly due to the assumption that Y and X are monovalent.

If  $k_A$ ,  $k_B$ , and  $k_Y$  are all positive, the necessary and sufficient condition for the occurrence of a minimum is simply  $k_B > mk_Y$ . In this case the other general requirement,  $mk_Y > -k_A$ , is trivial because  $m$  is always positive by definition. If  $k_A$ ,  $k_B$ , and  $k_Y$  are all negative, the necessary and sufficient condition for the occurrence of a maximum is that  $mk_Y > k_B$ ; here the general requirement  $mk_Y < -k_A$  is trivial.

If either  $m = k_B/k_Y$  or  $m = -k_A/k_Y$ , neither a maximum nor a minimum can exist.

If  $k_Y = 0$ , there will be a minimum only if both  $k_A$  and  $k_B$  are positive, and there will be a maximum only if both  $k_A$  and  $k_B$  are negative.

If either  $k_A$  or  $k_B$  is equal to zero, eqns. (16) and (17) will define the conditions under which extrema can exist. There can be no extremum if two of the three  $k$ 's appearing in these equations are equal to zero.

In most common situations, there can be an extremum only if all of the  $k$ 's that are not equal to zero are either positive or negative.

#### GENERAL EQUATIONS FOR THE LOCATIONS OF THE EXTREMA

Because the quantity  $P'$  that is plotted is related to the quantity  $P$  that is measured in the manner described by the equation

$$P' = P \left( 1 + \frac{rf}{z} \right) \quad (18)$$

it is readily apparent that

$$\frac{dP'}{df} = \left( 1 + \frac{rf}{z} \right) \frac{dP}{df} + \frac{r}{z} P \quad (19)$$

At an extremum in the titration curve  $dP'/df = 0$ , and therefore

$$\frac{dP}{df} = - \frac{rP}{z + rf} \quad (20)$$

Let us consider the case in which a minimum is possible. If both  $k_A$  and  $k_B$  are

positive while  $k_Y \geq 0$ , two different situations may be discerned. When  $P$  (and therefore also  $P'$ ) is positive in the region of the minimum, the minimum in  $P'$  will precede that in  $P$  because, according to eqn. (19),  $dP'/df$  will already be positive when  $dP/df = 0$ . The two minima can coincide only in the hypothetical case in which the reagent is infinitely concentrated (so that  $r = 0$ ). On the other hand, if  $P$  (and likewise  $P'$ ) is negative in the region of the minimum, the minimum in  $P'$  will follow that in  $P$  in any real titration ( $r > 0$ ), for  $dP'/df$  will still be negative when  $dP/df = 0$ . This situation arises whenever  $k_X$  is sufficiently negative ( $k_X < -k_Y$ ). Here again the two minima can coincide only in the hypothetical case in which  $r = 0$ . It is also clear that the two minima will always coincide if  $P = 0$  at the minima.

Analogously, if both  $k_A$  and  $k_B$  are negative while  $k_Y \leq 0$ , there are two situations in which a maximum can occur. When  $P$  and  $P'$  are negative in the region of the maximum,  $dP'/df$  will already be negative when  $dP/df = 0$ , so that the maximum in  $P'$  will precede that in  $P$ . But if  $P$  and  $P'$  are positive in the region of the maximum,  $dP'/df$  will still be positive when  $dP/df = 0$ , and the maximum in  $P'$  will follow that in  $P$ . The first situation arises when  $k_X \leq 0$ ; the second arises when  $k_X$  is positive and sufficiently large ( $k_X > -k_Y$ ). As above, the minima can coincide only if  $P = 0$  or in the hypothetical case in which  $r = 0$ . All these cases are summarized for convenience in Table I.

TABLE I  
CHARACTERIZATION OF EXTREMA IN LINEAR TITRATION CURVES FOR  
SINGLE-STEP ION-COMBINATION REACTIONS

(The first column gives the nature of the extremum and the conditions required for its existence. The second gives the sign of the values of  $P$  and  $P'$  in the region of the extremum. The third gives the sign of  $dP/df$  at the extremum in the titration curve, where  $dP'/df = 0$ . The fourth gives the sign of the quantity  $(f_{dP'/df=0} - f_{dP/df=0})$ ; if this is positive, the extremum in  $P'$  follows that in  $P$ ; if it is negative, the extremum in  $P'$  precedes that in  $P$ ; if it is zero, the two extrema coincide. The last column gives the conditions under which  $P$  and  $P'$  will have the sign given in the second column)

Type of extremum and conditions for existence	Sign of $P$ and $P'$ at extremum	Sign of $dP/df$	Relation between extrema in $P$ and $P'$	Conditions
Minimum ( $k_A > 0$ , $k_B > 0$ , $k_Y \geq 0$ )	$> 0$	$\leq 0^a$	$\leq 0^c$	$k_X \geq 0$
	$< 0$	$\geq 0^b$	$\geq 0^c$	$k_X < -k_Y$
Maximum ( $k_A < 0$ , $k_B < 0$ , $k_Y \leq 0$ )	$< 0$	$\geq 0^a$	$\leq 0^c$	$k_X \leq 0$
	$> 0$	$\leq 0^b$	$\geq 0^c$	$k_X > -k_Y$

<sup>a</sup> The equalities are possible only if  $r = 0$ .

<sup>b</sup> The equalities are possible only if  $r = 0$  or if  $P = P' = 0$  at the extremum.

<sup>c</sup> The equalities are possible only if the extrema in  $P$  and  $P'$  coincide.

Unfortunately, eqn. (20) cannot be solved explicitly for  $[B^{m+}]$  or  $f$  at the minimum except in the isovalent case ( $m = n$ ). In general, therefore, we must proceed in the following fashion. Consider the minimum at which  $P$  and  $P'$  are positive, which is the ordinary case in which a minimum is observed. According to Table I, the minimum in  $P'$  occurs when  $dP/df \leq 0$  (the equality being valid only if  $r = 0$ ); according to eqn. (13), it occurs when

$$\frac{d[B^{m+}]}{df} \leq - \frac{nC_B^0 (zk_Y - rk_X)}{\{k_B - (zk_A K^{1/m} / [B^{m+}]^{(z+1)})\} (z + rf)^2} \quad (21)$$

As usual, the equality is possible only if  $r = 0$ . Equation (21) is valid at the extremum; from eqn. (7) one can obtain

$$\frac{d[B^{m+}]}{df} = \frac{[B^{m+}](d\alpha/df)}{(z+1)[B^{m+}] - \alpha z} = - \frac{zC_{B^0}(z+r)[B^{m+}]}{\{(z+1)[B^{m+}] - \alpha z\}(z+rf)^2} \quad (22)$$

since

$$\frac{d\alpha}{df} = - \frac{zC_{B^0}(z+r)}{(z+rf)^2} \quad (23)$$

Comparing eqns. (21) and (22) gives, at the extremum,

$$k_B\{1 - (\alpha z K^{1/m}/[B^{m+}]^{(z+1)})\}(z+r) \geq m\{(z+1) - \alpha z/[B^{m+}]\}(zk_Y - rk_X) \quad (24)$$

where

$$\alpha = k_A/k_B \quad (25)$$

However, from eqn. (7),

$$\frac{\alpha}{[B^{m+}]} = 1 - \frac{zK^{1/m}}{[B^{m+}]^{(z+1)}} \quad (26)$$

so that eqn. (24) may be written

$$k_B\{1 - (\alpha z K^{1/m}/[B^{m+}]^{(z+1)})\}(z+r) \geq m\{1 + (z^2 K^{1/m}/[B^{m+}]^{(z+1)})\}(zk_Y - rk_X) \quad (27)$$

where the value of  $[B^{m+}]$  is understood to be that for which  $dP'/df = 0$ ; henceforth this will be designated  $[B^{m+}]_{\min}$ .

The solution of eqn. (27) is

$$[B^{m+}]_{\min} \geq [zK^{1/m}]^{1/(z+1)} \left\{ \frac{z(k_A + nk_Y) + r(k_A - nk_X)}{z(k_B - mk_Y) + r(k_B + mk_X)} \right\}^{1/(z+1)} \quad (28)$$

which may be written more concisely as

$$[B^{m+}]_{\min} \geq [zK^{1/m}]^{1/(z+1)} Q^{1/(z+1)} \quad (28a)$$

where  $Q$  represents the quantity enclosed between braces in eqn. (28). As usual, the equality is possible only if  $r = 0$ . Whereas eqns. (28) and (28a) give the concentration of  $B^{m+}$  at the minimum, its concentration at the equivalence point is given by

$$[B^{m+}]_{f=1} = [zK^{1/m}]^{1/(z+1)} \quad (29)$$

It may be noted that the value of  $Q$  — whose variation is responsible for any variation in the position of the minimum — depends on  $r$ ,  $z$ , and the  $k_i$ 's, but not on the concentration of  $B^{m+}$  in the solution titrated.

Combining eqns. (28a) and (7), solving for  $f_{\min}$  (defined as the value of  $f$  at which  $dP'/df = 0$ ), one obtains

$$f_{\min} \leq \frac{z\{C_{B^0} - (zK^{1/m})^{1/(z+1)}[(Q-1)/Q^{z/(z+1)}]\}}{zC_{B^0} + r(zK^{1/m})^{1/(z+1)}[(Q-1)/Q^{z/(z+1)}]} \quad (30)$$

If  $Q \geq 1$ , then  $f_{\min} \leq 1$ , and the minimum will precede the equivalence point in any real titration; even if  $Q = 1$  the minimum cannot coincide with the equivalence point unless in addition  $r = 0$ . On the other hand, for  $Q < 1$ , the minimum may follow,



coincide with, or precede the equivalence point, depending on the extent to which the value of  $[B^{m+}]_{\min}$  exceeds the value of the quantity on the right-hand side of eqn. (28a).

Because the equality in eqn. (30) is possible only if  $r = 0$ , all that can be calculated explicitly for a real titration of the type under consideration is an upper limit to the value of  $f_{\min}$ .

When  $P$  and  $P'$  are negative in the region of a maximum (which is the usual case in which a maximum is observed), Table I shows that the maximum in  $P'$  occurs when  $dP/df \geq 0$  (the equality again being possible only if  $r = 0$ ), while eqn. (13) shows that it occurs when

$$\frac{d[B^{m+}]}{df} \geq - \frac{nC_B^0(zk_Y - rk_X)}{\{k_B - (zk_A K^{1/m}/[B^{m+}]^{(z+1)})\}(z+rf)^2} \quad (31)$$

An expression giving the lower limit to the value of  $f_{\max}$  (the value of  $f$  at the maximum) may be obtained from this in the same way that eqn. (30) is obtained from eqn. (21); eqns. (22), (23), and (26) are applicable as they stand, and it is necessary only to reverse the directions of the inequalities in eqns. (24), (27), (28), and (28a). The result is

$$f_{\max} \geq \frac{z\{C_B^0 - (zK^{1/m})^{1/(z+1)}[(Q-1)/Q^{z/(z+1)}]\}}{zC_B^0 + r(zK^{1/m})^{1/(z+1)}[(Q-1)/Q^{z/(z+1)}]} \quad (32)$$

In this case, if  $Q \leq 1$ , then  $f_{\max} \geq 1$ , and the maximum will follow the equivalence point in any real titration; for the maximum to coincide with the equivalence point one must have both  $Q = 1$  and  $r = 0$ . If  $Q > 1$ , the maximum may precede, coincide with, or follow the equivalence point.

There are so many parameters included in  $Q$  that a discussion of the effect of each would be tedious and unrevealing, nor is there any *a priori* reason for selecting any of them as more important than any others. It seems more useful to consider the forms assumed by the general eqns. (30) and (32) for some important special cases of the titration methods of interest.

#### CONDUCTOMETRIC TITRATIONS

As was mentioned previously, only minima are possible in conductometric titrations based on single-step ion-combination reactions because all  $k_i$ 's are finite and positive.

One commonly considered titration of the type discussed here is that of a mono-basic strong acid with a monoacidic strong base. For the titration of hydrochloric acid with sodium hydroxide as a typical example, eqn. (28) becomes

$$[H^+]_{\min} \geq K_w^{1/2} \left[ \frac{(\lambda_{Na^+} + \lambda_{OH^-}) + r(\lambda_{OH^-} - \lambda_{Cl^-})}{(\lambda_{H^+} - \lambda_{Na^+}) + r(\lambda_{H^+} + \lambda_{Cl^-})} \right]^{1/2} \quad (33)$$

since  $z = 1 = n = m$ . Replacing each of the equivalent ionic conductances in eqn. (33) by its value at infinite dilution<sup>7</sup> gives

$$[H^+]_{\min} \geq K_w^{1/2} \left[ \frac{248.7 + 122.2 r}{299.7 + 426.2 r} \right]^{1/2} \quad (34)$$

whence, if  $r = 0$ ,  $[H^+]_{\min} = 0.911 K_w^{1/2}$ . This corresponds to  $f_{\min} = 1 + 0.187 K_w^{1/2}/C_B^0$ , where  $C_B^0$  is the initial concentration of the acid. For  $f_{\min}$  to equal unity

with an error of 0.1% or less,  $C_B^0$  must equal or exceed  $1.87 \cdot 10^{-5} F$  at  $25^\circ$ , where  $K_w^{1/2} = 1 \cdot 10^{-7}$ . This value of  $[H^+]_{\min}$  corresponds to  $pCH_{\min} = 7.04$ ; if  $C_B^0$  equals or exceeds the value just given one will have  $1 < f_{\min} \leq 1.001$ .

It may be mentioned in passing that for the reverse titration (of sodium hydroxide with hydrochloric acid), eqns. (33) and (34) become

$$[H^+]_{\min} \leq K_w^{1/2} \left[ \frac{(\lambda_{OH^-} - \lambda_{Cl^-}) + r(\lambda_{Na^+} + \lambda_{OH^-})}{(\lambda_{H^+} + \lambda_{Cl^-}) + r(\lambda_{H^+} - \lambda_{Na^+})} \right]^{1/2} = K_w^{1/2} \left[ \frac{122.2 + 248.7r}{426.2 + 299.7r} \right]^{1/2}$$

so that  $[H^+]_{\min}$  must always be smaller than  $K_w^{1/2}$  and the minimum must always precede the equivalence point.

Although  $r$  is usually small in practical titrations, it can never be equal to zero, and therefore eqn. (34) explicitly provides only a lower limit to the value of  $[H^+]_{\min}$  in the titration of hydrochloric acid with sodium hydroxide. This corresponds to an upper limit to the value of  $f_{\min}$ , which is described by

$$f_{\min} \leq \frac{1 - (K_w^{1/2}/C_B^0)[(Q - 1)/Q^{1/2}]}{1 + r(K_w^{1/2}/C_B^0)[(Q - 1)/Q^{1/2}]} \quad (35)$$

For any value of  $r$ , the value of the upper limit increases as the initial concentration  $C_B^0$  of the acid decreases. The actual value of  $f_{\min}$  approaches this upper limit more and more closely as  $r$  decreases and also as the values of  $P$  and  $P'$  at the minimum decrease.

In this titration,  $P'$  (which is the conductance of the solution after correction for dilution) may be expressed as

$$P' = \frac{1}{R} \frac{V_B^0 + V_T}{V_B^0} = \left\{ \frac{198.6 \cdot 10^{-14}}{[H^+]} + 349.82[H^+] \right\} (1 + rf) + C_B^0(76.40 + 50.11f)$$

while

$$f = \frac{C_B^0 + \{(K_w/[H^+]) - [H^+]\}}{C_B^0 - r\{(K_w/[H^+]) - [H^+]\}}$$

Provided that  $C_B^0 \gg r\{(K_w/[H^+]) - [H^+]\}$ , one may write

$$P' = \left\{ \frac{198.6 \cdot 10^{-14}}{[H^+]} + 349.82[H^+] \right\} (1 + r) + 126.5C_B^0 + 50.11\{(K_w/[H^+]) - [H^+]\}(1 + r) \quad (36)$$

As the value of  $\{(K_w/[H^+]) - [H^+]\}$  is usually about  $2 \cdot 10^{-8}$  at and very near the minimum, it is only necessary that  $C_B^0 \geq 2 \cdot 10^{-5} r$  for eqn. (36) to be in error by 0.1% or less. By successive approximations it is then possible to calculate the value of  $[H^+]_{\min}$ . For each of a number of values of  $r$ , Table II lists both the actual value of  $[H^+]_{\min}$  thus evaluated and the lower limit to  $[H^+]_{\min}$  as given by eqn. (34).

Although the lower limit to  $[H^+]_{\min}$  decreases as  $r$  increases, the actual value of  $[H^+]_{\min}$  remains the same. As would be expected, therefore, the lower limit describes the actual value more and more closely as  $r$  decreases. Under any reasonable practical conditions the discrepancy between the minimum and the equivalence point is negligible.

TABLE II

LOCATIONS OF MINIMA IN CONDUCTOMETRIC TITRATIONS OF SODIUM HYDROXIDE WITH HYDROCHLORIC ACID

(The first column gives the value of  $r$ . The second gives the lower limit to the value of  $[H^+]_{\min}/K_w^{1/2}$ , as calculated from eqn. (34). The third gives the actual value of  $[H^+]_{\min}/K_w^{1/2}$ , as obtained from eqn. (36) by successive approximations. The fourth gives the value of  $(P' - 126.5 C_B^0)$  at the minimum, also calculated from eqn. (36). Each number in the fourth column contains more digits than are justified by the accuracies of the values of  $\lambda_i^0$ ; this is because the quantity tabulated here varies only in the fourth decimal place as  $[H^+]/K_w^{1/2}$  deviates from its value at the minimum by  $\pm 0.002$  unit. To avoid misinterpretation of the constant values in the third column, we may emphasize that in general  $[B^{m+}]_{\text{ext}}$  is *not* necessarily independent of  $r$ ; titrations can be devised in which it *must* vary with  $r$ )

$r$	$[H^+]_{\min}/K_w^{1/2}$		Minimum value of ( $P' - 126.5 C_B^0$ )
	Lower limit	Actual value	
0	0.911	0.911	54.6044
0.05	0.891	0.911	57.3345
0.1	0.873	0.911	60.0648
1	0.715	0.911	109.2087

BRITTON<sup>5</sup> obtained an explicit equation for  $[H^+]_{\min}$  by neglecting dilution, which causes the minima in  $P$  and  $P'$  to coincide. As may be seen from eqn. (33), for  $r = 0$  one has

$$[H^+]_{\min} = K_w^{1/2} \left[ \frac{\lambda_{Na^+} + \lambda_{OH^-}}{\lambda_{H^+} - \lambda_{Na^+}} \right]^{1/2}$$

so that obviously  $[H^+]_{\min}$  could only equal  $K_w^{1/2}$  if  $\lambda_{H^+} - \lambda_{OH^-} = 2\lambda_{Na^+}$ . BRITTON neglected the contributions of both sodium and chloride ions to the conductance; this is unjustifiable because, although the contribution of chloride ion does vanish from eqn. (33) if  $r = 0$ , that of sodium ion does not. BRITTON's criterion for coincidence of the minimum with the equivalence point, which was  $\lambda_{H^+} - \lambda_{OH^-} = 0$ , is therefore incorrect, and so is his value for  $[H^+]_{\min}$ , which was  $0.753 K_w^{1/2}$ , corresponding to  $pCH_{\min} = 7.12$  at  $25^\circ$ .

Precipitation titrations in which  $z = 1 = n = m$  are also described by the above equations; it is only necessary to replace  $K_w$  wherever it occurs by the solubility product of the precipitate formed. But because the differences among the equivalent conductances of the ions involved are generally much smaller than in titrations of strong acids with strong bases, use of the rigorous equations is much more imperative. As illustrations we shall consider the titrations of solutions of silver nitrate with solutions of potassium chloride or sodium chloride. When potassium chloride is used as the titrant,

$$[Ag^+]_{\min} \geq K_{AgCl}^{1/2} \left[ \frac{(\lambda_{K^+} + \lambda_{Cl^-}) + r(\lambda_{Cl^-} - \lambda_{NO_3^-})}{(\lambda_{Ag^+} - \lambda_{K^+}) + r(\lambda_{Ag^+} + \lambda_{NO_3^-})} \right]^{1/2} \quad (37)$$

or, with the values of the limiting ionic equivalent conductances<sup>7</sup>,

$$[Ag^+]_{\min} \geq K_{AgCl}^{1/2} \left[ \frac{149.8 + 4.9r}{-11.6 + 133.6r} \right]^{1/2} \quad (38)$$

This is obviously meaningless unless its right-hand side has a real value, which will be

the case only if  $r \geq 0.0868$ . If, however, sodium chloride is used as the titrant,

$$[\text{Ag}^+]_{\min} \geq K_{\text{AgCl}}^{1/2} \left[ \frac{(\lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-}) + r(\lambda_{\text{Cl}^-} - \lambda_{\text{NO}_3^-})}{(\lambda_{\text{Ag}^+} - \lambda_{\text{Na}^+}) + r(\lambda_{\text{Ag}^+} + \lambda_{\text{NO}_3^-})} \right]^{1/2} \quad (39)$$

or

$$[\text{Ag}^+]_{\min} \geq K_{\text{AgCl}}^{1/2} \left[ \frac{126.4 + 4.9r}{11.8 + 133.6r} \right]^{1/2} \quad (40)$$

whose right-hand side is real for all values of  $r$ .

This situation arises because the minimum in the titration curve (where  $dP/df = 0$ ) is a point at which  $dP/df < 0$ . As may be seen from eqn. (19), however, one may also have  $dP/df < 0$  even though  $dP'/df > 0$ . In effect this means that a plot of  $P$  vs.  $f$  may have a minimum even though one of  $P'$  vs.  $f$  does not\*. If, in the titration with potassium chloride,  $r$  is zero or very small,  $P$  (which here is the measured conductance) will increase slowly up to the equivalence point and more rapidly thereafter; there will be no minimum in  $P$  (nor, of course, will there be one in  $P'$ ). But if  $r$  is made to exceed a certain value by diluting the titrant, the dilution resulting from the addition of reagent will be large enough to overcome the small increase of  $P$  that would otherwise occur up to the equivalence point, while still being insufficient to overcome the much more rapid increase of  $P$  at points beyond the equivalence point. In this way an artificial minimum in  $P$  may arise, but this disappears when the correction for dilution is applied and so cannot represent a meaningful solution of eqn. (38). When sodium chloride is used as the titrant, the conductance must decrease up to the equivalence point regardless of the value of  $r$ , and so in this case there is a minimum in  $P$  no matter how small  $r$  may be; and this minimum in  $P$  reflects the existence of a minimum in  $P'$ . We may summarize this by saying that *if  $r$  has a finite lower limit no minimum in  $P'$  is possible*.

If, but only if, the conductance of the reagent is smaller than that of the solution at the equivalence point, the measured conductance can be made to decrease throughout the titration, even beyond the equivalence point, by increasing  $r$  sufficiently. The conductance of the reagent is proportional to  $(C_{\text{B}^0}/r)\Lambda_{\text{YA}}$  (where  $\Lambda_{\text{YA}}$  is the equivalent conductance of the salt YA), while that of the solution at the equivalence point is proportional to  $[C_{\text{B}^0}/(1+r)]\Lambda_{\text{YX}}$ . Since  $C_{\text{B}^0}/(1+r)$  can never exceed  $C_{\text{B}^0}/r$ , the reagent can have the smaller conductance only if  $\Lambda_{\text{YA}} < \Lambda_{\text{YX}}$  (i.e., if  $\lambda_{\text{A}} < \lambda_{\text{X}}$ ). This is not the case in either of the titrations just discussed, because the equivalent conductance of chloride ion (= A) is larger than that of nitrate ion (= X), and so in these titrations the measured conductance must increase beyond the equivalence point no matter how large  $r$  may be.

However, it would be the case if a solution of silver nitrate were titrated with one of sodium tetraphenylborate. Then eqn. (39) would be applicable if the equivalent

\* Note that in eqns. (37) and (39) the first term in the denominator is proportional to the slope of the idealized titration curve (i.e., the plot of  $P'$  vs.  $f$  that would be obtained if the solubility of the precipitate were negligible) prior to the equivalence point but has the opposite sign, while the first term in the numerator is proportional to, and also has the same sign as, the slope of the titration curve beyond the equivalence point. Consequently, if potassium chloride is used as the titrant the slope of the titration curve is positive both before and after the equivalence point, and there is no minimum in  $P'$ . But if sodium chloride is used the slope of the titration curve is negative before the equivalence point and positive after it.

conductance of chloride ion were replaced by that of tetraphenylborate ion, and eqn. (40) would accordingly become

$$[\text{Ag}^+]_{\text{min}} \geq K_{\text{AgB}(\text{C}_6\text{H}_5)_4}^{1/2} \left[ \frac{68.11 - 53.42r}{11.8 + 133.6r} \right]^{1/2}$$

which is meaningless for  $r > 1.275$ . It can be shown that if  $r = 1.275$  the solution of sodium tetraphenylborate being added will have a conductance just equal to that of the sodium nitrate solution at the equivalence point, so that there will be no further change of conductance as excess reagent is added; there will be no minimum in  $P$ . If  $r$  exceeds this value, obviously, the conductance will actually decrease beyond the equivalence point. This may be summarized by saying that *if  $r$  exceeds its upper limit no minimum in  $P$  is possible.*

For the heterovalent precipitation titrations

$$[\text{B}^{m+}]_{\text{min}} \geq (zK_{\text{B}_n\text{A}_m}^{1/m})^{1/(z+1)} \left\{ \frac{z(m\lambda_{\text{A}} + n\lambda_{\text{Y}}) + r(m\lambda_{\text{A}} - n\lambda_{\text{X}})}{z(n\lambda_{\text{B}} - m\lambda_{\text{Y}}) + r(n\lambda_{\text{B}} + m\lambda_{\text{X}})} \right\}^{1/(z+1)} \quad (41)$$

from which the lower limit of  $[\text{B}^{m+}]_{\text{min}}$  (and thence, by eqns. (7) and (9), the upper limit of  $f_{\text{min}}$ ) may be evaluated under any desired conditions. One must demand that both the numerator and denominator of  $Q$  (the term within braces) be positive; if either a lower or an upper limit to  $r$  is needed to satisfy this demand, it has the same significance as in the cases discussed above.

In our general derivation we have assumed that the "specific conductance of a solution of [an] electrolyte is a linear function of the [equilibrium] concentrations of the various species in solution"<sup>8</sup>. This is "true only over certain ranges of concentration", so that, for example, Job's method of continuous variations may lead to invalid conclusions when applied to conductometric data<sup>8</sup>. In conductometric titrations, however, the only species whose concentrations vary appreciably in the neighborhood of the equivalence point are those whose contributions to the total conductance are small, and therefore no great error is made by assuming all the ionic equivalent conductances to be independent of dilution over the narrow region that is of interest. A more significant criticism of the above treatment would be directed at the use of the limiting ionic equivalent conductances instead of the values pertinent to the region of the equivalence point. To a first approximation, however, the equivalent conductances of the various ions will be affected similarly by the presence of the finite concentration of electrolyte, and as only ratios of equivalent conductances are involved the error may confidently taken to be quite small. No doubt it would be undetectable experimentally; the deviations of the equivalent conductances from the limiting values will increase with increasing  $C_{\text{B}}^0$ , but this also has the effect of bringing  $f_{\text{min}}$  closer and closer to unity.

#### AMPEROMETRIC TITRATIONS

These differ from conductometric titrations in that some ionic species may have  $k_i (= I_i m^{2/3} t^{1/6}) = 0$  at the potential selected for the titration. One common type of amperometric titration is that in which both  $k_{\text{X}}$  and  $k_{\text{Y}}$  are zero; for this case eqn. (28) becomes

$$[\text{B}^{m+}]_{\text{min}} \geq (zK^{1/m})^{1/(z+1)} \quad (42)$$

As usual, the equality applies if  $r = 0$ . Here, however, the right-hand side is invariant with  $r$ , and so if the equality applies at  $r = 0$  it must apply at all other values of  $r$ . We may therefore write

$$[B^{m+}]_{\min} = (z\kappa K^{1/m})^{1/(z+1)} \quad (43)$$

It can also be shown that the concentration of  $B^{m+}$  is also described by eqn. (43) at the maximum of the curve obtained when both  $k_A$  and  $k_B$  are negative.

It is clear from eqn. (43) that the extremum coincides with the equivalence point if  $\kappa = 1$  regardless of whether the precipitate is isovalent or heterovalent. This contradicts the conclusion of KOLTHOFF AND LINGANE<sup>9</sup>. But their conclusion was only an expression of opinion, not the result of an investigation of what they described as the "rather complex algebra" of the situation.

By combining eqn. (43) with eqns. (7) and (9) one may obtain

$$f_{\text{ext}} = \frac{1 - [(\kappa - 1)/C_B^0] [zK^{1/m}/\kappa z]^{1/(z+1)}}{1 + r[(\kappa - 1)/C_B^0] [K^{1/m}/(z\kappa) z]^{1/(z+1)}} \quad (44)$$

where  $f_{\text{ext}}$  is the value of the extremum whether this be a maximum or a minimum. It is evident that the condition  $\kappa = 1$  is not only necessary but also sufficient for coincidence of the extremum and the equivalence point. If  $\kappa > 1$ , the extremum will precede the equivalence point; if  $\kappa < 1$ , it will follow the equivalence point. For eqn. (44) to have physical significance it is necessary that  $\kappa > 0$ , which means that the diffusion current constants of A and B must have the same sign; no extremum is possible if they have opposite signs. The value of  $\kappa$  for any particular titration can be calculated from literature values of the appropriate diffusion current constants<sup>10</sup>; where these are not available, it can be crudely approximated by  $n_A/n_B$ .

The diffusion current at the extremum is given by combining eqns. (43) and (13) as

$$i_{a_{\text{ext}}} = (z + 1) (\kappa K)^{1/(z+1)} k_B / z^{z/(z+1)} \quad (45)$$

which may of course be used, if  $\kappa$  is known, to evaluate  $K$  from the measured value of  $i_{a_{\text{ext}}}$ .

#### SPECTROPHOTOMETRIC TITRATIONS

In spectrophotometric titrations of the type considered in this paper, only minima are possible because any  $k_t$  that is not zero must be positive\*. Titrations performed in the presence of added indicators are outside the scope of this discussion; only "self-indicator systems"<sup>11</sup> are considered.

As in amperometric titrations, minima are most commonly observed when only A and B absorb at the wavelength selected and thus contribute to the measured values of  $P$ . Regardless of whether the ion-combination reaction is of the isovalent or heterovalent type, the minimum may precede, coincide with, or follow the equivalence

\* Maxima are, of course, possible in other types of spectrophotometric titrations, and one example is cited by HEADRIDGE<sup>11</sup>: the "heterometric" titration of aqueous lead nitrate with sodium citrate in 50% ethanol<sup>12</sup>. This differs from the titrations considered here in two ways: it is not a single-step reaction (a precipitate formed in the first step is redissolved in the second), and  $k_t$  for the product of the ion-combination reaction is not zero. Another kind of titration in which a maximum would be observed, but which also does not come within the scope of the present discussion, is that of the dibasic acid  $H_2Z$  with a base at a wavelength where  $HZ^-$  alone has a finite absorptivity.

point, depending solely on whether  $\kappa$  (which in this case is the ratio of the molar absorptivities of A and B) is greater than, equal to, or less than 1, respectively. The treatment is completely analogous to that of amperometric titrations above and need not be described in detail.

#### SUMMARY

For both isovalent and heterovalent single-step ion-combination reactions whose products do not make any contributions to the property measured, this paper presents the results of a rigorous investigation of the conditions required for the existence of extrema on linear titration curves and their locations. These results are applied to various conductometric, amperometric, and spectrophotometric titrations.

#### RÉSUMÉ

Les auteurs ont effectué une étude rigoureuse sur la recherche des conditions, nécessaires à l'obtention d'"extrêmes" sur des courbes de titrage linéaires, et leur localisation. Ces résultats sont appliqués à divers titrages conductométriques, ampérométriques et spectrophotométriques.

#### ZUSAMMENFASSUNG

Es werden mit Hilfe mathematischer Methoden die Bedingungen abgeleitet, die für die Existenz eines "Maximums" erforderlich sind, wie es bei linearen Titrationskurven (Konduktometrie, Amperometrie, Spektrophotometrie, usw.) auftritt. Die Lage des Maximums wird diskutiert.

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## ELEKTRODEN-PROBLEME IN DER POTENTIOMETRIE

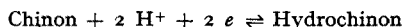
F. L. HAHN

*Angel Urraza 718-303, Mexico, D.F. (Mexico)*

(Eingegangen den 9. August, 1963)

## HAT DIE ART DER ELEKTRODE EINFLUSS AUF DEN POTENTIALGANG?

Grundannahmen der potentiometrischen Analyse sind, dass je nach der Art der Bestimmung ein Metall in der Lösung eines seiner Salze sein Potential proportional dem Logarithmus der Salzkonzentration ändert, oder aber dass eine nicht angreifbare "Ableitungs-Elektrode" auf eine (oder beide) der Komponenten eines Redox-Systems mit einer Potentialänderung anspricht, die dem Logarithmus des Konzentrationsquotienten Oxydans zu Reduktor proportional ist. Ein klassisches Beispiel dafür, dass man eine unbequeme "Metall"-Elektrode durch ein geeignetes Redox-System ersetzen kann, haben wir in der Chinhydron-Elektrode, die auf das Gleichgewicht



anspricht. Wie eben angedeutet, ist elektrochemisch der Wasserstoff als Metall anzusehen, und somit kann eine korrekt arbeitende Metallelektrode in wässriger Lösung nur dann möglich sein, wenn das Metall edler ist als der Wasserstoff oder/und die Konzentration seiner Ionen beträchtlich grösser. Ferner aber passivieren sich manche Metalle, so dass sie selbst auf kräftige Konzentrationsänderungen ihrer Ionen kaum noch mit einer Potentialänderung ansprechen. Leichtes Amalgamieren kann diese Schwierigkeit mildern, aber das Messen von Konzentrationsänderungen in Blei- oder Zinklösungen an den entsprechenden Metallelektroden bleibt immer noch problematisch.

Hier könnte nun die Redox-Elektrode einspringen, da Hexacyanoferrat(II) diese Metalle fällt, während die entsprechenden Hexacyanoferrate(III) löslich sind. Man kann also die Konzentration an Oxydans (praktisch) konstant halten, während beim Durchschreiten des Äquivalenzpunktes die Konzentration des als Fällungsreagens dienenden Reduktors sprunghaft ansteigt. MÜLLER<sup>1</sup> erörterte das für eine Fällung von  $\text{K}_2 \text{Zn}_3 [\text{Fe}(\text{CN})_6]_2$ ; dabei ist ihm das Versehen unterlaufen (gelegentlich soll selbst der gute Homer geschlummert haben) anzunehmen, man habe an dieser Redox-Elektrode einen dreimal so grossen "Sprung" zu erwarten wie an der Metallelektrode (falls diese korrekt ansprechen würde); das ist gleichwertig der Behauptung, bei trigonometrischer und barometrischer Messung einer Bergeshöhe könnten Zahlenwerte im Verhältnis eins zu drei gefunden werden! Was errechnet wurde ist die Steilheit des Potentialganges vor dem Endpunkt, also bei Zinküberschuss, für die Zinkelektrode, und nach dem Endpunkt, bei Reduktor-Überschuss, für die Redox-Elektrode, also — um bei unserem Vergleich zu bleiben — die Steilheit des



Nord- bzw. Südhangs unseres Berges, nicht aber seine Höhe. KOLTHOFF UND FURMAN<sup>2a</sup> haben den Denkfehler übernommen, ihn aber auf eine Fällung von  $\text{Ag}_4[\text{Fe}(\text{CN})_6]$  übertragen, in der nun — theoretisch — beide Elektroden brauchbar sein sollten, so dass ein Versuch den Fehlschluss erwiesen haben würde; dieser Versuch fehlt aber. Führt man ihn durch, so findet man erstens, dass im Gebiet kleinster Reaktortüberschüsse beide Elektroden sehr schlecht ansprechen, so dass mit beiden die Fällung analytisch kaum von Wert sein dürfte; zweitens, dass in der Grösse der mit Schwierigkeiten zu messenden Sprünge kein Unterschied besteht.

#### WECHSELNDES POTENTIAL BEI WECHSELNDER RÜHRGESCHWINDIGKEIT

In einer kurzen Mitteilung<sup>3</sup> habe ich angegeben, dass bei Silberhalogenid-Fällungen das messbare Potential beträchtlich von der Geschwindigkeit abhängen kann, mit der die Lösung gerührt wird, und dass der Grund hierfür sicher in der Phasengrenzschicht an der Elektrode und nicht im Adsorptionsgleichgewicht am Niederschlag zu suchen ist. Inzwischen sind mir die Arbeiten von LANGE<sup>4</sup> (mit SCHWARTZ und mit BERGER) zugänglich geworden, die ich damals nach den Angaben von KOLTHOFF UND FURMAN<sup>2b</sup> zitiert hatte; auch dort ist — was KOLTHOFF UND FURMAN übersehen haben — mit aller Deutlichkeit ausgesprochen, dass es sich um einen Effekt an der Elektroden-Oberfläche handeln müsse: "Dann liegt im Grunde derselbe Fall wie bei einer Hg-Tropfelektrode vor: Die Phasengrenzfläche wird dauernd vergrössert, es müssen sich deshalb immer neue Oberflächenteile in das Adsorptionsgleichgewicht einstellen". Bei den Versuchen von LANGE UND BERGER lag ein Gummischaber mit regelbarem Druck an einem Silberzylinder an, der mit regelbarer Geschwindigkeit rotierte; hier hängt das Elektrodenpotential merkbar davon ab, wie schnell der Zylinder rotiert, das bedeutet, wie oft in der Zeiteinheit das Phasengleichgewicht an der Elektrodenoberfläche sich neu einstellen muss.

Wenn es sich aber um einen Einfluss der Elektroden-Oberfläche handelt, dann sollten Elektroden verschiedener Grösse und Oberflächenbeschaffenheit in sehr verdünnten Silber- bzw. Halogenidlösungen geprüft werden; dies Programm ist schon (ohne Kenntnis der LANGESchen Arbeiten) in der anfangs erwähnten Mitteilung gegeben worden. Um nun auch niederschlagsfreie Chlorid-Lösungen beobachten zu können, wurde die Silberelektrode durch sekundenlanges anodisches Polarisieren in einer KCl-Lösung mit einer hauchdünnen AgCl-Schicht bedeckt; das Potential dieser Elektrode blieb bei starkem Wechsel der Rührgeschwindigkeit (vier zu eins) völlig konstant, in Chlorid- wie in Silberlösungen. Ebenso wirksam ist kurzes Eintauchen der Elektrode in eine zehntelnormale Jodlösung; die gut abgespülte Elektrode hat einen gelben Schimmer und wird, unter destilliertem Wasser am Licht aufbewahrt, allmählich bräunlich oder auch tiefschwarz. Wir arbeiten jetzt seit Monaten mit solchen Elektroden, haben nie auch nur die geringsten Schwierigkeiten mit der Potentialeinstellung gehabt und konnten Jodidmengen von weniger als 1 Microval mit guter Genauigkeit messen, am besten in etwa zehntelnormaler Morpholin-Lösung, wo die so störende, minutenlange Wartezeit bis zum Erreichen eines festen Potentials völlig verschwindet<sup>4</sup>; das gleiche gilt für Bromid-Bestimmungen. Eine einleuchtende Erklärung drängt sich auf: Diese Elektroden haben eine rauhe, etwas poröse Oberfläche, und in diesen Poren bildet sich das potentialbestimmende Phasengleichgewicht in einer ruhenden Flüssigkeitsschicht aus, an der die bewegte Lösung ohne merklichen Effekt vorbeigeleitet. Damit wäre das Problem praktisch und theore-

tisch gelöst, wenn es uns nur gelungen wäre, an glatten Silberelektroden den Einfluss wechselnder Rührgeschwindigkeit wieder zu erhalten; aber auch an diesen ist er bis auf weiteres verschwunden; grosse und kleine Elektroden, Blech oder Draht, blank oder leicht amalgamiert: Wir konnten in den letzten Monaten an keiner einen messbaren Einfluss der Rührgeschwindigkeit auf das Potential wiederfinden. Dass dieser auch bei analytischen Arbeiten sich nur *gelegentlich* in störendem Ausmass bemerkbar macht, wurde anfangs gesagt; sollte das "Jodieren" der Elektrode ein Mittel sein, ihn *immer* zu vermeiden? Diese Frage wage ich nicht zu bejahen, bis es uns gelingt, in ein und derselben Lösung die Störung wiederholt an einer blanken Elektrode zu beobachten, während an der jodierten Elektrode das Potential unabhängig von der Rührgeschwindigkeit bleibt. Eines jedoch scheint schon jetzt festzustehen, nämlich, dass die jodierte Silberelektrode in Silber- wie in Halogenidlösungen, sauer, neutral oder mit  $\text{NH}_3$  oder Morpholin versetzt, rasch zu ausgezeichnet reproduzierbaren Potentialeinstellungen führt. Das Titrieren in ammoniakalischer (Jodid) oder morpholinhaltiger (Jodid oder Bromid) Lösung ist so viel rascher und sicherer, dass es selbst dann empfohlen werden kann, wenn es sich nicht um Bestimmungen eines schwerer löslichen Halogenids neben einem leichter löslichen handelt.

#### EINE NEUE UND ZWECKMÄSSIGE BEZUGSELEKTRODE

Für die Bestimmung physikochemischer Daten — und dazu ist auch die routinemässige Messung von pH-Werten zu rechnen — bietet die Kalomel-Elektrode den Vorteil eines bekannten und völlig konstanten Potentials. Für potentiometrische Titrationsen aber brauchen wir das gar nicht: Ein ungefähr bekanntes und stabiles Potential ist völlig ausreichend. Wenn eine chloridfreie Bezugslektrode hergestellt werden kann, die dieser Forderung genügt und die ohne die lästige Zwischenlösung bei argentometrischen Titrationsen verwendbar ist, so bedeutet das eine schätzenswerte Vereinfachung der Arbeitstechnik. Metallisches Kupfer (das aufgefasernde Ende eines dünnen Plastik-Kabels) in einem Gemisch von käuflichem, basischem Kupfercarbonat mit Natriumsulfat und mit gesättigter Natriumsulfatlösung bedeckt, hat sich vorzüglich bewährt; die Elektrode ist um etwa 20 mV edler als die Kalomel-Elektrode. Wir haben sie aus einem Plastik-Fläschchen hergestellt (100 ml), das seitlich oben zwei gegenüberliegende Durchbohrungen hat, durch die — dicht anliegend — das Elektrodenkabel und der Flüssigkeitsheber gesteckt wurden; dieser kann — bei Verwendung eines statischen Potentiometers — am äusseren Ende sogar durch eine Zellophan-Membran verschlossen sein (in siedendem Wasser erweicht, angelegt und dann ein Stückchen eng anliegenden Schlauches übergezogen). Die Elektrode wird einfach neben den Titrierbecher gestellt statt über ihm angeklammert; das Arbeiten mit ihr ist sicher und angenehm.

Meiner Assistentin, Fr. GUILLERMINA SALAZAR V. habe ich für Hilfe bei der Durchführung der Versuche zu danken.

#### ZUSAMMENFASSUNG

Der Potentialgang im Verlauf einer potentiometrischen Titration ist unabhängig von der verwendeten Messelektrode. Der Einfluss wechselnder Rührgeschwindigkeit auf das Elektrodenpotential wurde an Silberelektroden verschiedenster Grösse und Oberflächenbeschaffenheit studiert. Eine halogenidfreie Bezugslektrode wird als wertvolle Vereinfachung für argentometrische Titrationsen beschrieben.

## SUMMARY

The variations of the potential, calculated and observed during a potentiometric titration, are independent of the nature of the electrode used. The influence of changing the rate of agitation upon the potential of silver electrodes of different surfaces is studied. A halide-free reference electrode is described as a suitable simplification in argentometric titrations.

## RÉSUMÉ

Les variations de potentiel observées au cours d'un titrage potentiométrique, sont indépendantes de la nature de l'électrode active utilisée. On a étudié l'influence de la vitesse d'agitation variée sur des électrodes d'argent à surfaces différentes. On décrit une électrode de référence libre d'haloïdes, très utile dans les titrages argentométriques.

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## SELECTIVE HYDROXYL GROUP DETERMINATION BY DIRECT TITRATION WITH LITHIUM ALUMINUM AMIDE

DONALD E. JORDAN

*Research and Development Department, Continental Oil Company, Ponca City, Oklahoma (U.S.A.)*

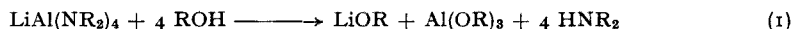
(Received July 15th, 1963)

Lithium aluminum hydride as a reagent for easily reducible functional groups, such as carbonyls, carboxyls and esters, is widely recognized. The determination of compounds containing active hydrogen with lithium aluminum hydride solutions has also been demonstrated. The quantitative procedure is a modified Zerewitinoff method requiring elaborate gasometric apparatus in which the liberated hydrogen gas is measured under given conditions.

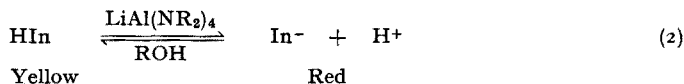
LINTNER, SCHLEIF AND HIGUCHI<sup>1</sup> described a titration procedure in which excess lithium aluminum hydride solution was added to an air-free ether system containing compounds with organic functional groups. After a specified time, the excess reagent was titrated with a standard solution of alcohol in benzene solvent, and the hydride consumed by the sample was calculated. Because of the great basicity of the hydride, no specific functional group reaction was possible. Air and water also interfered, and elaborate steps were carried out to exclude them. HIGUCHI AND ZUCK<sup>2</sup> extended the procedure to include a visual end-point. They also described several indicator compounds that may be applicable.

Less basic lithium aluminum amides prepared from lithium aluminum hydride and primary and secondary amines should afford better selectivity in determining specific organic functional groups in the presence of other organic functional groups. HIGUCHI, CONCHA AND KURAMOTO<sup>3</sup> used these amides to determine functional groups by a procedure similar to that described for lithium aluminum hydride; and in mixtures of functional groups, no selectivity was observed. In contrast, the present work describes a procedure whereby organic hydroxyl groups are quantitatively determined in the presence of carbonyls, esters, amines, alkoxides and complex hydrocarbon mixtures by direct titration with lithium aluminum amide. The analysis is rapid, accurate, and relatively easy to carry out. The end-point is determined visually using *N*-phenyl-*p*-aminoazobenzene as an indicator. Interfering impurities found in alcohols or complex alcohol systems consist of water, molecular oxygen and organic acids. However, the concentrations of organic acids and molecular oxygen usually found in alcohols do not interfere, while water interference is corrected by a Karl Fischer titration. Amines do not interfere, since the amine formed is the conjugate acid of the reaction and a much less dissociated acid than the alcohol. SMALL<sup>4</sup> recently described a procedure in which he selectively titrated hydroxyl groups in ethanolamines with lithium aluminum amide. He also observed no interference from the amine.

In the work described here, a lithium aluminum amide is used in preference to the strong reducing and unselective lithium aluminum hydride reagent. The amide is relatively selective for functional group determination, as well as being much easier to handle and store than the hydride. In this work, the end-point reaction can be pictured as a neutralization reaction of a relatively strong Brønsted base and a weak acid, alcohol.



In order to determine the proper end-point visually, it is obvious that a suitable chemical indicator must be a very weak acid. The reversible indicator reaction can also be loosely pictured according to the equation:



The  $pK_a$  values of commonly available alcohols range in the order of 16 to 17. In the complex systems and the high molecular weight alcohols also described in this work, the  $pK_a$  can be estimated to be in the order of 18–19. Since the primary function of a chemical indicator is to bring about a color change at the stoichiometric end-point, one must be used that has a  $pK_i$  of 22 or greater. At the same time, the  $pK_i$  must not be so large that excessive reagent is used after the weak acid alcohol is titrated in order to obtain a characteristic color change. Of the several indicator compounds investigated, N-phenyl-*p*-aminoazobenzene described by HIGUCHI AND ZUCK<sup>2</sup> was the most applicable.

In the titration of weak acid alcohols with lithium aluminum amide, the equilibrium lies far to the right because of the greater electron affinity of the metals for the alkoxide moiety. At the same time, the amide ion has greater proton affinity for the hydrogen ion forming the very weak conjugate acids, amines.

The structure of lithium aluminum hydride is well known; however, neither the type of bonding nor the actual structure of the lithium aluminum amide molecule has been fully determined. It is reasonable to assume that the structure will be similar to that of the hydride with the nitrogen-aluminum bonds displaying more covalent character than the hydrogen-aluminum bonds of the hydride. On this basis and on the experimental evidence of greater selectivity for determination of functional groups, it is apparent that the amide will display less protophilic strength than the hydride.

#### EXPERIMENTAL

##### Reagents

*Lithium aluminum hydride* (95%). Metal Hydrides, Inc., Beverly, Massachusetts.

*1,2-Dimethoxyethane*. Matheson, Coleman and Bell, No. DX 1530.

*Tetrahydrofuran*. Matheson, Coleman and Bell, No. TX 280.

*Dibutylamine*. Matheson, Coleman and Bell, No. DX 545.

*Indicator solution*. An 0.05 % (w/v) solution of N-phenyl-*p*-aminoazobenzene in benzene was used.

*n-Octanol* through *n-eicosanol*.

##### Procedure

Place 750 ml of 1,2-dimethoxyethane (dried over molecular sieve 4 A or 5 A or

freshly distilled from lithium aluminum hydride) in a 1-l, 2-necked flask fitted with ground glass joints and vertical condenser. Add 2-3 drops of indicator solution and just enough lithium aluminum hydride to change the solution color from yellow to red; then add an additional 1.5 g of lithium aluminum hydride to the solution and reflux for 25 min. Add in increments 31 ml of dibutylamine slowly through the condenser, allowing the reaction for hydrogen gas formation and evolution to subside between increments. Continue to reflux for an additional 10-15 min and then remove the condenser; blanket the reagent with nitrogen, stopper, and allow to cool. (Solids will settle in approximately 1 h.) Displace the air in a 10-ml automatic gravity filling buret with a Teflon stopcock (Fischer and Porter Co., Hatboro, Pennsylvania) with dry nitrogen and filter the clear solution through a glass wool plug into the reservoir. Stopper the reservoir and maintain a slight flow of nitrogen through it.

Place 50-75 ml of tetrahydrofuran and a Teflon stirring bar in a 200-ml 50/50 standard taper beaker with a 50/50 standard taper top with 5 septum-covered ports for nitrogen inlet and outlet, sample addition, and buret tip. Add 5 drops of indicator solution, cover the beaker with the top containing 5 ports, and start the magnetic stirrer. Insert the buret tip and the nitrogen inlet and outlet tubes into the appropriate ports by means of hypodermic needles (Yale B. D. 20 gauge), purge the system with nitrogen for 10 min, and then titrate from yellow to the reproducible red end-point. Weigh the sample which is placed in a Yale hypodermic syringe equipped with a silicone gum rubber plug capped needle. Uncap the needle and insert it through a port. Inject the sample directly onto the tetrahydrofuran solvent. Withdraw the syringe barrel so that none of the sample remains on the tip of the needle; then withdraw the syringe assembly from the septum, recap the needle, and reweigh. Determine the sample weight by difference. Solid alcohols are melted and then added by means of a dropping bottle. Titrate immediately to the reproducible red end-point originally used. Calculate the per cent hydroxyl or hydroxyl number.

The solution is standardized daily or as required by titrating alcohols of known purity. In this work, secondary standards of commercial alcohols were prepared by comparison against pure alcohols. The secondary standards then were used for solution standardization.

#### DISCUSSION

All pure alcohols used were prepared in our distillation laboratory and the purity determined by gas-liquid chromatography.

Although 1,2-dimethoxyethane was used to prepare lithium aluminum amide solution, other ethers can be as readily used. Tetrahydrofuran and 1,2-dimethoxyethane usually contain excessive reactive impurities. Addition of molecular sieve to each of them normally results in an acceptably dry product, although over a period of time a minor amount of peroxide formation may occur. Occasionally, some batches of dimethoxyethane and tetrahydrofuran are quite impure and must be distilled from lithium aluminum hydride before use.

The lithium aluminum amide is prepared so that the stoichiometric concentration plus a slight excess of amine is present. Excess lithium aluminum hydride will result in a reaction between it and any trace ester or carbonyl impurities present in complex alcohol mixtures. It is therefore important that only small increments of lithium

aluminum hydride be used to finish drying the 1,2-dimethoxyethane just prior to preparation of the amide.

Occasionally, an extended settling time is required to obtain a clear amide solution. This usually is due to the use of impure hydride or an excessive refluxing time during solution preparation. Such a solution is also difficult to transfer free of the finely divided sludge particles.

Transfer of the solution free from solids is quite difficult. It is transferred in a closed system using nitrogen gas pressure by fitting a glass wool mat into an appropriate glass tube in such a way that the glass wool remains in place while the liquid is forced through the tube into the reservoir of the buret. The buret is designed so that nitrogen flow through it will be uninterrupted.

Tetrahydrofuran is used as a titration solvent; but other ethers, for example dimethoxyethane, can be as easily used. The indicator color change is extremely sharp and distinct. The color fades back to yellow within a short time; but since this is a titration from a given color back to the same color, no error is observed as long as the colors are the same. About 10 samples can be titrated before the end-point becomes inconsistent because of the precipitates of lithium and aluminum alkoxide salts.

High molecular weight solid samples are melted and the melt added directly to the titration solvent. Solution is instantaneous, and titration proceeds immediately. If solid samples are placed in the titration solvent, solution is quite slow and offers little advantage over other methods.

#### RESULTS

Data in Table I show the results obtained with pure alcohols. The agreement between the observed and theoretical values is excellent. The accuracy of the method is in all cases better than  $\pm 1\%$  of the true value. These results were determined over a period of several months using numerous preparations of titrant.

TABLE I  
ACCURACY STUDY OF HYDROXYL GROUP ANALYSIS BY DIRECT TITRATION

Sample	% Hydroxyl		% Error
	Found	Theory	
Octanol	13.00	13.06	0.45
	13.13		0.54
	13.15		0.69
	13.13		0.54
	13.17		0.90
Decanol	10.67	10.75	0.75
Tetradecanol	7.87	7.93	0.76
Hexadecanol	7.03	7.02	0.14
	7.01		0.14
	7.02		0.00
	6.97		0.72
Eicosanol	5.73	5.70	0.58
	5.68		0.38
	5.69		0.19

Table II summarizes a study of the precision of the method. The study was conducted on several samples of both known and unknown compositions. The samples

TABLE II  
PRECISION OF THE PROCEDURE

Sample	No. of replicate determinations	% Hydroxyl		Coefficient of variation (%)
		Range	Average	
Octanol	6	13.00-13.17	13.12	0.45
Sample A <sup>a</sup>	9	12.37-12.64	12.51	0.93
Sample B <sup>a</sup>	10	10.38-10.46	10.43	0.52
Sample C <sup>a</sup>	8	10.24-10.41	10.33	0.90
Hexadecanol	4	6.97- 7.03	7.01	0.43

<sup>a</sup> Mixture of commercial "ALFOL" alcohols.

with unknown composition contained other oxygenated impurities, such as ethers and carbonyls, in low concentrations. For each sample, the coefficient of variation is less than  $\pm 1\%$  of the true value of known samples and the assumed value for the mixtures. It is quite reasonable to assume that higher molecular weight alcohols and alcohol mixtures containing no other active hydrogen groups will have the same precision and accuracy described by Tables I and II.

Results in Table III summarize hydroxyl group determination by direct titration and classical base-catalyzed acetylation procedures. From the data, either procedure is applicable: however, the time required for analysis varies from 0.5 to 4 h for acetylation, while an analysis by direct titration requires only 5 to 6 min.

TABLE III  
HYDROXYL CONTENT OF COMMERCIAL ALCOHOLS AND COMPLEX MIXTURES BY DIRECT TITRATION AND ACETYLATION PROCEDURE

Sample	Direct titration	Classical acetylation
1	12.51	12.39
2	12.91	12.75
3	9.09	9.06
4	6.60	6.86
5	7.56	7.50
6 <sup>a</sup>	7.01	6.95
7 <sup>a</sup>	5.81	5.85
8 <sup>a</sup>	8.05	8.19
9 <sup>a</sup>	9.82	9.74
10 <sup>a</sup>	9.34	9.46

<sup>a</sup> Complex organic mixtures containing alcohol ranging from butanol to tetracontanol.

The results described in Table IV show the effect of various functional groups on the analysis for hydroxyl groups. As expected, only organic functional groups with active hydrogen interfere in the titration. Amines do not interfere even though they do have active hydrogen, since they, in general, are very weak acids and in actual practice form the conjugate acid of the titrating amide.

Inorganic acids, water and molecular oxygen all interfere. The stoichiometry of



TABLE IV

INTERFERENCE IN HYDROXYL ANALYSIS BY 5 MMOLE ADDITIONS OF VARIOUS FUNCTIONAL GROUPS

<i>Functional group</i>	<i>Interference</i>
Esters	—
Carbonyl	—
Ether	—
Amines	—
Carboxylic acids	+
Inorganic acids (anhydrous)	+
Water	+
Air (oxygen)	+

these, as well as carboxylic acids, is currently under investigation. It is expected that the stoichiometry will be fully elucidated and reported in the very near future.

## SUMMARY

The selective determination of hydroxyl groups in most complex alcohol systems by direct titration with standard lithium aluminum amide solution is described. The titration is carried out in ether solvent under nitrogen with N-phenyl-*p*-aminoazobenzene as reversible indicator. The accuracy is better than  $\pm 1\%$ ; less than 6 min are required for a complete determination of alcohols up to triacontanol. Aldehydes, ketones, esters, amines and alkoxy groups do not interfere, but organic and inorganic acids, and water and molecular oxygen, interfere. Water and acid interferences can be corrected for after a Karl Fischer titration and neutralization reactions respectively.

## RÉSUMÉ

Une méthode est décrite pour le dosage sélectif des groupements hydroxyles, dans la plupart des systèmes alcools complexes, par titrage direct au moyen d'une solution étalon de  $\text{LiAl}(\text{NR}_2)_4$ . Le dosage est effectué dans l'éther, sous azote et en présence de N-phénol-*p*-aminoazobenzène, comme indicateur réversible. Ce procédé est rapide et d'une précision supérieure à  $\pm 1\%$ . Les aldéhydes, cétones, esters, amines et groupements alcoyles ne gênent pas; mais les acides organiques et inorganiques, l'eau et l'oxygène moléculaire gênent. Les interférences de l'eau peuvent être corrigées après titrage selon Karl Fischer et celles des acides après neutralisation.

## ZUSAMMENFASSUNG

Die selektive Bestimmung von Hydroxylgruppen in den meisten komplexen Alkohol-Systemen durch direkte Titration mit Lithiumaluminiumamid wird beschrieben. Die Titration wird in Äther unter Stickstoff mit N-Phenyl-*p*-aminoazobenzol als reversibler Indikator durchgeführt. Die Genauigkeit ist besser als  $1\%$ . Das Verfahren benötigt weniger als 6 Min. zur Bestimmung der Alkohole. Aldehyde, Ketone, Ester, Amine und Alkoxygruppen stören nicht. Organische und anorganische Säuren, Wasser und molekularer Sauerstoff stören. Die Störungen durch Wasser und Säuren können durch die Karl-Fischer-Titration und Neutralisations-Reaktionen beseitigt werden.

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## APPLICATIONS OF INFRARED SPECTROSCOPY

PART XIII<sup>1</sup>. THE DETERMINATION OF SMALL AMOUNTS OF ALCOHOLS  
IN AQUEOUS SOLUTION

D. M. W. ANDERSON AND S. S. H. ZAIDI

*Department of Chemistry, The University, Edinburgh 9 (Great Britain)*

(Received August 20th, 1963)

A simple method was required for the identification and determination of small concentrations (*ca.* 0.05%) of lower alcohols in aqueous solution. Since simple mixtures of alcohols were liable to be present, many of the standard methods of analysis were inapplicable.

A literature survey indicated that methanol and ethanol are still most frequently determined by distillation or diffusion<sup>2</sup>, followed by oxidation with permanganate<sup>3</sup> or dichromate<sup>4</sup>. Although such methods can be extended to butan-1-ol<sup>5</sup> and to secondary alcohols<sup>6,7</sup>, errors are liable to occur through incomplete reaction or over-oxidation<sup>8</sup>. Some investigators prefer to determine the aldehydic or acidic oxidation products<sup>4,6,9</sup>; others determine the excess dichromate electrometrically<sup>10</sup> or spectroscopically<sup>8</sup>.

Considerable attention has been devoted in recent years to the development of new methods of analysis, including those based on the use of acetylation<sup>11</sup>, colorimetry<sup>12,13</sup>, chemiluminescence<sup>14</sup>, reaction with vinyl cyanide<sup>15</sup>, conversion to nitrite<sup>16</sup>, formation of vanadium-oxinate complexes<sup>17,18</sup>, and gas-liquid chromatography<sup>19-21</sup>.

For mixtures of alcohols, differential rates of reaction can be used<sup>22</sup>, but gas-liquid chromatography<sup>23</sup> undoubtedly provides an extremely sensitive method (a detection limit<sup>24</sup> of 0.1% in water for a 5- $\mu$ l sample). For positive identification of the chromatographic peaks, a non-aqueous solvent extraction method<sup>25</sup> and a combined infrared-GLC technique<sup>26</sup> have been described.

When only a small number of determinations are required, however, it is not always economic in time and cost to prepare a special gas chromatography column and to carry out the modifications necessary for the analysis of aqueous solutions. This paper describes a simple modification of the Zeisel reaction which has been found to give satisfactory results for the analysis of aqueous solutions containing low concentrations of alcohols.

## EXPERIMENTAL AND RESULTS

*Compounds*

For development of the method, dilute solutions (1 ml of alcohol per l of distilled water, *i.e.* *ca.* 0.079%, w/v) were prepared from methanol and ethanol (B.D.H. Ltd.; "special for spectroscopy"). In later work, similar dilutions of the propanols and butanols were prepared from reagent-grade samples after redistillation. Finally,

independent test solutions were prepared both on a weight/volume and volume/volume basis, the concentration being calculated from the density of the alcohol used.

#### *Zeisel apparatus and reagents*

These have been described<sup>27</sup>, together with details of the technique for trapping volatile reaction products and of the infrared vapour-phase method for their subsequent identification and determination.

#### *Procedure for determinations as iodides*

An aliquot (1.00 ml) of the sample solution is pipetted into the reaction flask of the micro Zeisel apparatus. A few crystals of phenol (about 25 mg) are added, followed by 3 ml of hydriodic acid (AnalaR, about 66%, sp. gr. 1.94). The reaction flask consequently contains the unknown amount of alcohol(s) dissolved in 4 ml of hydriodic acid of specific gravity 1.70, *i.e.* closely approximating to the constant-boiling azeotrope. Small differences from the azeotropic composition are not critical when the liberated alkyl iodides are determined spectroscopically; in determinations where a volumetric or gravimetric finish is used, the specific gravity must not exceed 1.70, so that water, and not hydriodic acid, distils with the volatile reaction products. (In this connection it has been found advisable to determine the density of the commercial acid, since this is frequently lower than 1.94.)

The reflux periods required are: methanol and ethanol, 1 h; *n*-propanol and *n*-butanol, 3 h. If the alcohol(s) present are not known, a preliminary qualitative analysis should be based on the products from a 3-h reaction.

The sensitivity depends on the gas-cell used<sup>28</sup>. The procedure described here can be carried out adequately with the aid of the less expensive, bench-type spectrometers now available commercially. Such instruments can usually accommodate a gas-cell of about 10 cm length. With a simple, conventional cell of this length, 1–5 mg of methyl iodide can be determined to within  $\pm 1\%$ . Because of the very favourable factor incurred through conversion to the iodide, methanol concentrations within the range 0.2–1.1 g/l can be determined. The ranges for ethanol, propanols and butanols are slightly less sensitive, since the conversion factors are progressively less favourable (4.4 for methanol, 2.5 for butanols).

#### *Limitations on determinations as iodides*

When determined as iodides, *tert.*-butanol<sup>29</sup> and isopropanol<sup>1</sup> give low results as a result of olefine formation. Determinations as bromides overcome this difficulty<sup>1,29</sup>. Any of the lower alcohols can, of course, be determined as bromides, although some loss of sensitivity results. This is because (a) the conversion factor for bromides is less favourable than for iodides, and (b) the intensity of absorption is less for alkyl bromides than for iodides. Thus 2–6 mg of methyl bromide, for example, can be determined in a 10-cm gas-cell; taking 1-ml aliquots, methanol concentrations in the range 0.5–2 g/l can therefore be determined.

#### *Procedure using hydrobromic acid*

The procedure using hydrobromic acid is similar to that described for hydriodic acid, except that 4 ml of hydrobromic acid (66%, sp. gr. 1.70) is added to a 1-ml

aliquot of the unknown aqueous solution. This gives a reaction mixture (5 ml) which is virtually azeotropic in composition (sp. gr. 1.48).

The possible binary mixtures of the C<sub>1</sub>-C<sub>4</sub> alcohols are shown in Table I: in only a few mixtures is a component not determinable.

TABLE I  
DETERMINACY OF BINARY COMBINATIONS OF THE LOWER ALCOHOLS AS BROMIDES\*

Mixture of alcohols	Bromides liberated							
	Methyl	Ethyl	n-Propyl	Isopropyl	n-Butyl	Isobutyl	sec.-Butyl	tert.-Butyl
Me/Et	D	D						
Me/n-Pr	D		D					
Me/iPr	D			D				
Me/n-Bu	D				D			
Me/iBu	D					D		
Me/s-Bu	D						D	
Me/t-Bu	D							D
Et/n-Pr		ND	D(MP)					
Et/iPr		D(CF)		D(MP)				
Et/n-Bu		ND			ND			
Et/iBu		D(CF)				D(MP)		
Et/s-Bu		ND					D	
Et/t-Bu		D						D
n-Pr/iPr			D(MP)	D(MP)				
n-Pr/n-Bu			D(MP)		D(MP)			
n-Pr/iBu			D(MP)			D(MP)		
n-Pr/s-Bu			D(MP)				D(MP)	
n-Pr/t-Bu			D					D
iPr/n-Bu				D	D(MP)			
iPr/iBu				D(MP)		D(MP)		
iPr/s-Bu				D(MP)			D(MP)	
iPr/t-Bu				D				ND
n-Bu/iBu					D	D(MP)		
n-Bu/s-Bu					D(MP)		D	
n-Bu/t-Bu					D			D
iBu/s-Bu						D	D	
iBu/t-Bu						D(MP)		ND
s-Bu/t-Bu							D	ND

\* D: Determinable.

ND: Not determinable.

D(CF): Determinable using correction factor } see ref. 27.

D(MP): Determinable using minor peak

#### DISCUSSION

The simple modifications described allow the Zeisel reaction to be applied to the analysis of dilute aqueous solutions of the lower alcohols. Results accurate to within  $\pm 1\%$  were obtained for test solutions. Analyses of solutions containing only one component can, of course, be made using any of the conventional finishes to the Zeisel reaction; for mixtures of alcohols, the spectroscopic method undoubtedly offers great advantages. Determination as iodides is not satisfactory for isopropanol and

*tert.*-butanol, which require the use of hydrobromic acid.

Concentrations greater than about 0.1% can readily be determined by making an appropriate dilution; concentrations greater than about 10% can be found by normal Zeisel determinations. Concentrations less than about 0.02% can be analysed (1) by using longer conventional gas-cells, minimum volume gas-cells, or scale-expansion devices, etc., (2) by taking larger aliquots and scaling up the volumes of reactants proportionately, using a larger reaction-vessel, (3) by adding a known weight of the alcohol under test to the unknown solution, subsequently calculating the weight present in the unknown solution from the total weight recovered<sup>30</sup>. Concentrations down to about 0.002% can be determined by careful choice of the weight of alcohol added so that the most sensitive portion of the calibration curve for the gas-cell is involved.

The method is limited to systems known to contain alcohols only. At the low concentrations involved, ethers, esters and acetals may be sufficiently water-soluble to interfere. Ethylene glycol and its derivatives also interfere, but their presence is revealed by the formation of ethylene on reaction<sup>31</sup> with hydriodic acid.

We thank Professor E. L. HIRST for his interest in these studies, and the P.C.S.I.R., Karachi, for granting study leave and financial support (to S.S.H.Z.).

#### SUMMARY

Recent developments in methods of analysing dilute solutions of alcohols are briefly reviewed, and a simple modification to the Zeisel reaction is described. This permits the analysis, on a 1-ml aliquot, of dilute aqueous solutions of alcohols alone or in admixture.

#### RÉSUMÉ

Les auteurs passent en revue les récents développements dans les méthodes d'analyse de solutions diluées d'alcools. Ils décrivent une modification simple de la réaction de Zeisel; le dosage peut se faire sur une prise de 1 ml.

#### ZUSAMMENFASSUNG

Über die neueren Entwicklungen zur Analyse von verdünnten Alkohollösungen wird kurz berichtet und eine einfache Modifikation der Zeisel-Reaktion beschrieben. Sie ermöglicht die Analyse von 1-ml verdünnten wässrigen Alkohollösungen.

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## Short Communications

### A simple method for the dissolution of platinum metals

Dissolution of the platinum metals and their alloys is frequently a difficult operation. Although platinum and palladium yield to aqua regia, rhodium presents more difficulty and ruthenium and iridium are quite intractable. GILCHRIST<sup>1</sup> has reviewed the commonly used methods. The traditional approach which involves extraction of platinum and palladium with aqua regia, followed by repeated oxidative alkaline fusions, is tedious and unsatisfactory. The method developed by WICHERS, SCHLECHT AND GORDON<sup>2</sup> is effective but involves heating aqueous hydrochloric acid solutions to temperatures up to 300° in sealed glass tubes. Incidental to a study of the spectrophotometric characteristics of the platinum metal elements in molten salt media, we have observed molten potassium pyrosulfate containing potassium chloride to be an excellent medium for attacking the metals and their alloys. Although the method was not studied extensively, it proved so useful that it was felt worthwhile to describe it briefly in order that others with similar problems might have the opportunity to adapt and apply it to their own needs.

The oxidizing strength of fused potassium pyrosulfate increases with increasing temperature, and at 600° chloride ion appears to be oxidized slowly to chlorine. When the platinum metals are fused with a mixture of potassium chloride and pyrosulfate, they dissolve rapidly. Presumably the chlorine formed acts on the metals directly, and the presence of chloride ion removes and stabilizes the products as chloride complexes.

#### *Experimental*

Dry potassium pyrosulfate was prepared by heating the commercial product in a Pyrex flask at about 600–700° until cessation of active bubbling indicated that the water had been driven off. The melt was then poured out into the depressions on a porcelain spot plate which gave, on cooling, a supply of pellets of convenient size. The samples in the form of foil, powder, or fine granules were sealed in small Vycor tubes together with approximately 5-g portions of the dried pyrosulfate and 0.5-g portions of dried potassium chloride. The tubes were conveniently fabricated in the shape of small test tubes, about 10 cm long, from standard Vycor 13 mm o.d. tubing having a wall thickness of approximately 1.2 mm, and should have a volume about three times that of the melt. The Vycor tubing is easily worked with an oxyhydrogen torch. The sealed tubes were placed in a standard crucible furnace, electrically heated and maintained at approximately 600° by a thermocouple-activated temperature controller. At this temperature, about 10 mg of sheet iridium could be dissolved in about 15 min; rhodium was acted upon with similar speed. Compact samples reacted more slowly, and it was found convenient to leave the tubes in the furnace for several hours to ensure complete solution. Platinum and palladium dissolve very rapidly; in fact, palladium may be dissolved without the addition of potassium chloride.

The behavior of ruthenium metal is somewhat more complex. In the absence of

chloride, ruthenium is attacked by potassium pyrosulfate only at temperatures above 600°, whereupon it is converted partially to volatile ruthenium tetroxide and partially to a mixture of black substance believed to be ruthenium dioxide, insoluble in the melt and in water, together with a soluble species of unknown oxidation state. When chloride ion is present, ruthenium dissolves rapidly in the melt but the reaction products depend upon the temperature. At 600° in a sealed tube, a mixture of pyrosulfate and chloride converts the metal to a mixture of products including a brown solution probably containing ruthenium(IV), a black precipitate which is probably ruthenium dioxide, and traces of ruthenium tetroxide. At 500° under the same conditions, ruthenium dissolves rapidly and completely to form what is probably ruthenium(IV).

Gold metal is not attacked by potassium pyrosulfate alone. Gold salts decompose to metallic gold when fused with potassium pyrosulfate. In the presence of potassium chloride, however, gold metal is dissolved to give a yellow solution which is stable in the sealed tube. If a melt containing gold and chloride ion is allowed to stand open to the air, gold metal will precipitate after the chloride has volatilized.

### Discussion

The new method of dissolution is advantageous in several respects. In comparison with other methods, the rate of attack is very high. Although only the pure platinum metals and a platinum-10% iridium alloy were examined, it is expected that no alloy will be resistant to attack. The products of the fusion are readily soluble in water. The principal disadvantage of the method is that large amounts of potassium are introduced into the sample. It is of interest to compare the mechanical aspects of the dissolution method of WICHERS *et al.*<sup>2</sup> with the one developed in this work. In the former, pressures as high as 4000 p.s.i. are developed in the reaction tubes at the operating temperature of 300°. Generation of chlorine during the reaction also causes pressure to build up and the tubes must be cooled in solid carbon dioxide before they are opened. In the present method, the pressures developed are probably no higher than 30-40 p.s.i. and have never been great enough to break the standard wall 13 mm Vycor tubes that were used. The room temperature pressure, even after 15 h of heating, was always slightly below atmospheric. The method has been used mainly for the dissolution of amounts of metals in the 1 to 20 mg range. However, scaling up to gram quantities should introduce no serious difficulty.

This work was supported, in part, by the United States Atomic Energy Commission under Contract AT(30-1)-905.

*Department of Chemistry and Laboratory for Nuclear Science  
Massachusetts Institute of Technology  
Cambridge 39, Massachusetts (U.S.A.)*

DAVID R. GABBE  
DAVID N. HUME

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(Received September 5th, 1963)



### Paper chromatographic separation of silver(I), lead(II), mercury(II) and thallium(I) with solvents containing chloroform

Some of the possibilities of using chloroform and chloroform mixtures for inorganic paper chromatography have been described previously<sup>1</sup>. In the present work, similar ion migration studies and measurements of  $R_F$  values for silver, lead, mercury(II) and thallium(I) were carried out with twenty different solvent mixtures each containing chloroform.

#### Reagents

Silver(I), lead(II), mercury(II) and thallium(I) solutions were prepared from the analytical reagent-grade nitrates. All organic solvents used were twice-distilled and their mixtures were prepared on a volume-volume basis with the exception of phenol solutions. Pure concentrated nitric acid and glacial acetic acid (E. Merck) were used to acidify certain solvent mixtures.

#### Procedure

All studies were performed on 3 mm Whatman paper (11 cm diameter) which was cut with wicks of 3-4 cm as described previously<sup>1,2</sup>.

For measurement of  $R_F$  values of individual ions, the paper discs were spotted at the centre with the solution containing 10-15  $\mu\text{g}$  of cation per drop of 0.02 ml using a micropipette. The wet spots were outlined with pencil and the discs were dried at room temperature (*ca.* 25°). These were developed to obtain adequate migration of the particular ion. The solvent fronts were marked again and the discs were dried. A spray of yellow ammonium sulphide was used to detect the rings ( $\text{Ag}^+$ , grey;  $\text{Pb}^{2+}$ , dark brown;  $\text{Hg}^{2+}$ , black; and  $\text{Tl}^+$ , reddish brown, which faded gradually owing to oxidation of thallos sulphide to white sulphate). All  $R_F$  measurements were made with respect to inner ( $R_{F(i)}$ ), as well as outer ( $R_{F(o)}$ ) edges of the rings and the values in Table I are the mean of several measurements at different points on a particular ring.

Separations were carried out similarly with more concentrated solutions of the ions (40 to 50  $\mu\text{g}$  per drop) mixed in equal volumes and then spotting with one drop of the mixture. Successful separations were obtained for the 4 ions studied with solvents 2, 8, 12, and 18 (see Table I for solvent composition). Good separations were obtained for Hg, Ag and Tl with solvents 1, 4 and 14, for Hg, Pb and Tl with solvents 4 and 6, and for Ag, Hg and Pb with solvent 13.

#### Discussion

It was pointed out by BHATNAGAR AND POONIA<sup>1</sup> that absolute chloroform is not suitable for inorganic chromatography, but chloroform mixed with polar organic solvents allowed sufficient migration to give successful separations. LEDERER<sup>3</sup>, POLLARD *et al.*<sup>4</sup> and HARASAWA<sup>5</sup> have also emphasised the need for polar solvents for the effective separation of inorganic ions. The present studies with  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Tl}^+$  supports the use of mixed solvents containing chloroform for separation of inorganic species. The results in Table I show that the addition of polar solvents to

TABLE I

 $R_F$  VALUES FOR INDIVIDUAL CATIONS IN DIFFERENT SOLVENTS

(A = chloroform, B = methanol, C = ethanol, D = 2-propanol, E = butanol, F = amyl alcohol, G = acetone, H = 2-butanone, I = phenol, J = methyl acetate, K = ethyl acetate, L = concentrated nitric acid, M = glacial acetic acid)

No.	Solvent		Time of run (h)	$Pb^{2+}$		$Hg^{2+}$		$Ag^+$		$Tl^+$	
	ml A added	Composition Other additions		$R_F(\circ)$	$R_F(\circ)$	$R_F(\circ)$	$R_F(\circ)$	$R_F(\circ)$	$R_F(\circ)$	$R_F(\circ)$	$R_F(\circ)$
1	50	50 ml B	2	0.73	0.83	0.96	1.00	0.70	0.89	0.58	0.73
2	49	49 ml B, 2 ml L	2.5	0.32	0.45	0.85	0.96	0.21	0.33	0.28	0.42
3	50	50 ml C	2	0.62	0.77	0.51	0.99	0.63	0.85	0.43	0.74
4	49	49 ml C, 2 ml L	2.5	0.54	0.77	0.67	0.96	0.35	0.67	0.42	0.58
5	50	50 ml D	2	0.66	0.81	0.76	0.84	0.61	0.84	0.27	0.64
6	49	49 ml D, 2 ml L	4.5	0.62	0.77	0.83	0.97	0.35	0.64	0.46	0.61
7	50	50 ml E	5	0.00	0.00	0.00	0.00	0.00	0.09	0.00	0.08
8	49	49 ml E, 2 ml L	3	Diffusion	0.00	0.66	0.90	0.22	0.35	0.00	0.05
9	50	50 ml F	2	0.00	0.00	0.89	0.95	0.00	0.00	0.00	0.00
10	49	49 ml F, 2 ml L	2	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00
11	50	50 ml G	2.5	0.60	0.84	0.77	0.96	0.70	0.90	0.51	0.89
12	49	49 ml G, 2 ml L	3	0.61	0.81	0.72	0.96	0.12	0.25	0.36	0.60
13	50	50 ml H	3	0.61	0.73	0.58	0.79	0.69	0.95	0.53	0.69
14	49	49 ml H, 2 ml L	2	0.64	0.78	0.65	0.78	0.41	0.61	0.34	0.56
15	100	5 g I	2	0.11	0.16	0.18	0.25	0.11	0.14	Diffusion	
16	100	5 g I, 2 ml M	3.75	0.00	0.10	0.48	0.74	0.00	0.25	0.00	0.00
17	50	50 ml J	1.75	0.00	0.00	0.74	0.85	0.00	0.00	0.00	0.00
18	49	49 ml J, 2 ml L	3	0.15	0.26	0.82	0.89	0.00	0.07	0.28	0.56
19	50	50 ml K	1.5	0.00	0.00	0.89	1.00	0.00	0.00	0.00	0.00
20	49	49 ml K, 2 ml L	2.75	0.00	0.00	0.86	0.95	0.14	0.22	0.00	0.00

chloroform facilitates the movement and separation of ions.

In general, with solvent mixtures containing alcohols the  $R_F$  values of all the ions decreased with increase in the molecular weight of the alcohol added (Table I); this agrees with earlier findings<sup>1,6,7</sup>. In a chloroform–butanol system, silver and thallium(I) migrated only slightly; in a chloroform–amyl alcohol system, only mercury(II) migrated.

The ketonic systems gave good migration for all the ions studied, whereas the phenol–chloroform system proved to be of little use (contrary to its effect with the iron, cobalt, nickel and copper set<sup>1</sup>). In systems containing esters with chloroform, only mercury(II) migrated.

The desirability of the presence of an acid in inorganic chromatography has been emphasised by many workers<sup>7</sup>. Hydrochloric acid is normally used, but as the ions used in present work mostly had insoluble chlorides, nitric acid was preferred here. The presence of nitric acid modified the migration tendencies of the ions only for chloroform–ester systems; in other cases it had little effect on  $R_F$  values, or it decreased them (Table I). The  $R_F$  values for mercury(II) were the highest of the 4 ions in all the solvent systems (except in the case of the chloroform–2-butanone system, where the  $R_F$  value for silver was a little higher). The sequence of  $R_F$  values was generally Tl < Pb < Ag < Hg. In some cases (solvents 2, 3, 11 and 13) the values for lead and thallium(I) were nearly the same.

The separations of thallium, lead, silver and mercury from each other were satisfactory in acidic solvents containing chloroform and methanol, butanol, acetone or methyl acetate. Lead and thallium developed quite close to each other so that only qualitative results could be obtained. Separations of three of the metals from each other could be obtained with several solvents containing alcohols or ketones with chloroform. Several separations of any 3 of the above metals have been reported in the literature (see, e.g., refs. 7 and 8) with solvents not containing chloroform, but it seems that the separation of the 4 metals together has not previously been accomplished.

*Department of Chemistry,  
Government Science College,  
Gwalior (India)*

R. P. BHATNAGAR  
K. D. SHARMA

<sup>1</sup> R. P. BHATNAGAR AND N. S. POONIA, *Anal. Chem.*, 34 (1962) 1325; *Anal. Chim. Acta*, 30 (1964) 211.

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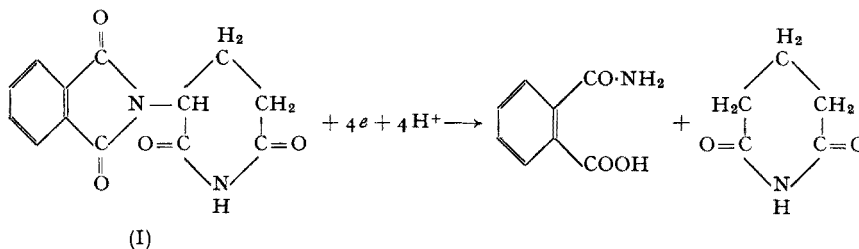
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(Received June 11th, 1963)

### Polarographic determination of N-phthalylglutamic acid imide (thalidomide)

A polarographic method for the determination of thalidomide is feasible because this substance can be reduced at the dropping mercury electrode; concentrations down to 2  $\mu\text{g/ml}$  can readily be determined with the conventional D.C. polarograph. The importance of the estimation of thalidomide is well known, and a polarographic method has not previously been described.

Thalidomide is sufficiently soluble (2 g/l) in 2 : 3 (v/v) tetrahydrofurfuryl alcohol-methanol, the solution being stable for months. The base electrolyte described below can also be used to dissolve thalidomide up to 200  $\mu\text{g/ml}$ , and the solutions are again very stable, even in contact with mercury; a solution containing 100  $\mu\text{g/ml}$  could be kept for 6 h in the cell without noticeable change in  $E_{\frac{1}{2}}$  or the wave height. In preliminary tests, the diffusion current for thalidomide was found to vary considerably with the pH. This indicates that hydrogen ions participate in the electrochemical reaction, and, assuming the formula (I) proposed for thalidomide by KUNZ, KELLER AND MÜCKTER<sup>1</sup>, it seems likely that the reaction proceeds as follows:



#### Apparatus

A Dr. A. KUNTZE pen recording polarograph was used, with the mercury pool as reference electrode and with cells of capacity 10 ml. The droptime at  $-1.0$  V was 3.0 sec with a mercury flow of 1.97 mg/sec. The temperature was 20°.

#### Reagents

All chemicals were of analytical grade. Tetrahydrofurfuryl alcohol (THFA), diethylbarbituric acid (sodium salt), veronal, were supplied by Dr. T. Schuchardt GmbH.

For the preparation of the stock solution of thalidomide, 0.500 g of thalidomide (high purity material from Chemie Grünenthal GmbH) was introduced into a dry 250-ml flask, 100 ml of THFA were added and the flask was shaken for a few sec; then 100 ml of methanol were added and the flask was immersed in hot water at 45° for 5 min. After cooling, the solution was made up to the mark with methanol.

Standard solutions of thalidomide containing 250, 500, 750, 1000, 1250, 1500  $\mu\text{g/ml}$  were prepared by diluting the stock solution with the base electrolyte.

For the base electrolyte, 10 g of veronal was mixed with 50 ml of *M* lithium chloride, 100 ml of deionized water and 200 ml of methanol, and stirred magnetically until a clear solution was obtained. The pH at this stage was approximately 10.4. Then 7 ml

of 50% (v/v) phosphoric acid was added, with constant stirring; a white precipitate was formed, which dissolved on addition of 140 ml of water. The pH value was then roughly 4 and was adjusted to 3.5 by dropwise addition of *M* phosphoric acid. Solutions in the pH range 1–8 were prepared by using the appropriate volumes of 50% phosphoric acid.

#### *Polarographic measurements*

One ml of each standard solution of thalidomide was introduced into a series of 10-ml volumetric flasks followed by 0.2 ml of a freshly prepared 0.5% gelatin solution. The solutions were diluted to the mark with the base electrolyte, pH 3.5. The flasks were stoppered and shaken a few times. The concentration of thalidomide in each flask was then 25, 50, 75, 100, 125 and 150  $\mu\text{g/ml}$ . Aliquots of 5 ml of each solution were introduced into the cell and deoxygenated for 5 min with purified nitrogen which had been presaturated with the base electrolyte. The polarograms were then recorded at applied potentials between  $-0.8$  V and  $-1.2$  V.

#### *Results and discussion*

Typical polarograms are shown in Fig. 1.

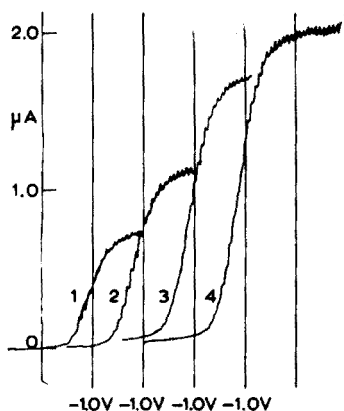


Fig. 1. 50, 75, 125, 150  $\mu\text{g/ml}$  of thalidomide; sensitivity 1/4

The heights of the reduction waves were proportional to the concentration of thalidomide over a wide range and the relationship is shown in Table I.

TABLE I  
WAVEHEIGHTS AND CURRENT QUOTIENTS FOR THALIDOMIDE

No.	Concn. ( $\mu\text{g}$ )	Waveheights (mm)	$i_d(\mu\text{A})$	$i_d/\text{mg}$
1	125	10	0.33	2.64
2	250	21	0.70	2.8
3	375	32	1.07	2.84
4	500	42	1.40	2.80
5	625	51	1.70	2.72
6	750	60	2.0	2.67

In the base electrolyte above pH 7.0, some decomposition of thalidomide was observed; at pH 8.0, a white precipitate formed immediately when a solution of thalidomide was added to the base electrolyte. At pH 7.0, 6.0 or 5.0, slow decomposition (decrease of the waveheights) was also observed. Variation in pH affected the half-wave potentials and the waveheights as shown in Table II. However, the shape of the waves was

TABLE II  
RELATION BETWEEN pH, HALF-WAVE POTENTIAL AND WAVEHEIGHT

pH	1	2	3	4	5	6	7
$-E_{1/2}$	0.84	0.90	0.96	1.02	1.08	1.14	1.2
Waveheight (mm)	42	46	50	54	58	62	66

not affected by pH changes or by the concentration of thalidomide. Easily measurable waves were obtained for concentrations down to 2  $\mu\text{g/ml}$ , which is an excellent sensitivity for the conventional polarograph, especially for organic substances. The replacement of methanol in the base electrolyte by ethanol had no effect on the  $E_{1/2}$  or on the shape of the waves.

Sulphate, nitrate, nitrite, ammonia salts, bromide and urea caused no interference. Of the metallic ions, zinc interfered owing to the formation of a wave at a slightly more negative potential than thalidomide.

The author thanks Dr. H. MÜCKTER of Chemie Grünenthal GmbH for his valuable help in providing the sample of high purity thalidomide and his interest in the work.

Dr. A. Kuntze *Electrochemical Laboratory*  
*Düsseldorf-Oberkassel*  
*(Federal Republic of Germany)*

J. S. HETMAN

<sup>1</sup> W. KUNZ, H. KELLER AND H. MÜCKTER, *Arzneimittel-Forsch.*, 6 (1956) 8.

(Received July 8th, 1963)

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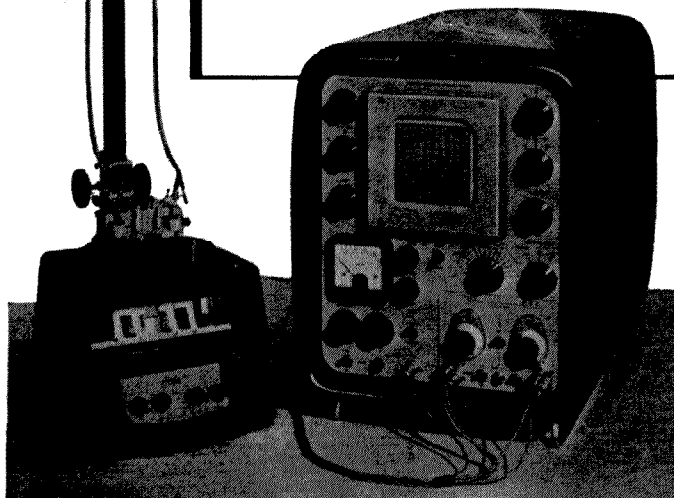
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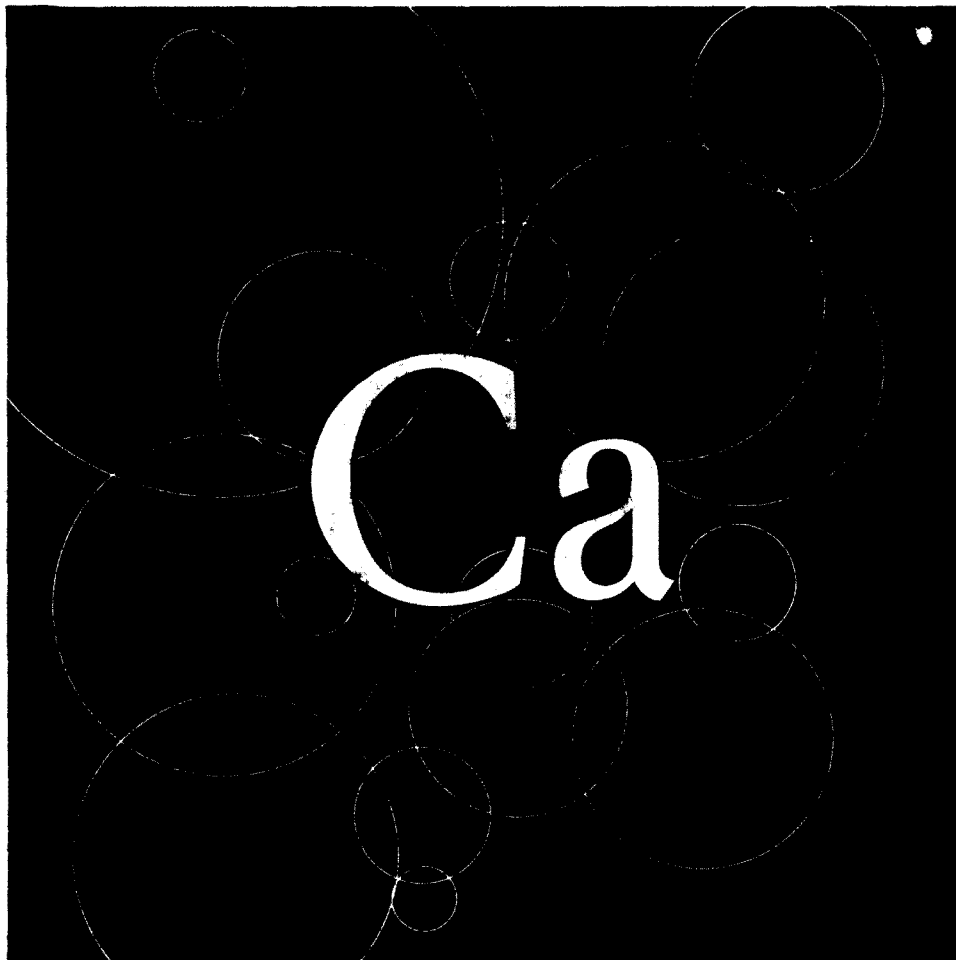
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