

An International Journal of Analytical Chemistry

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VOLUME 10

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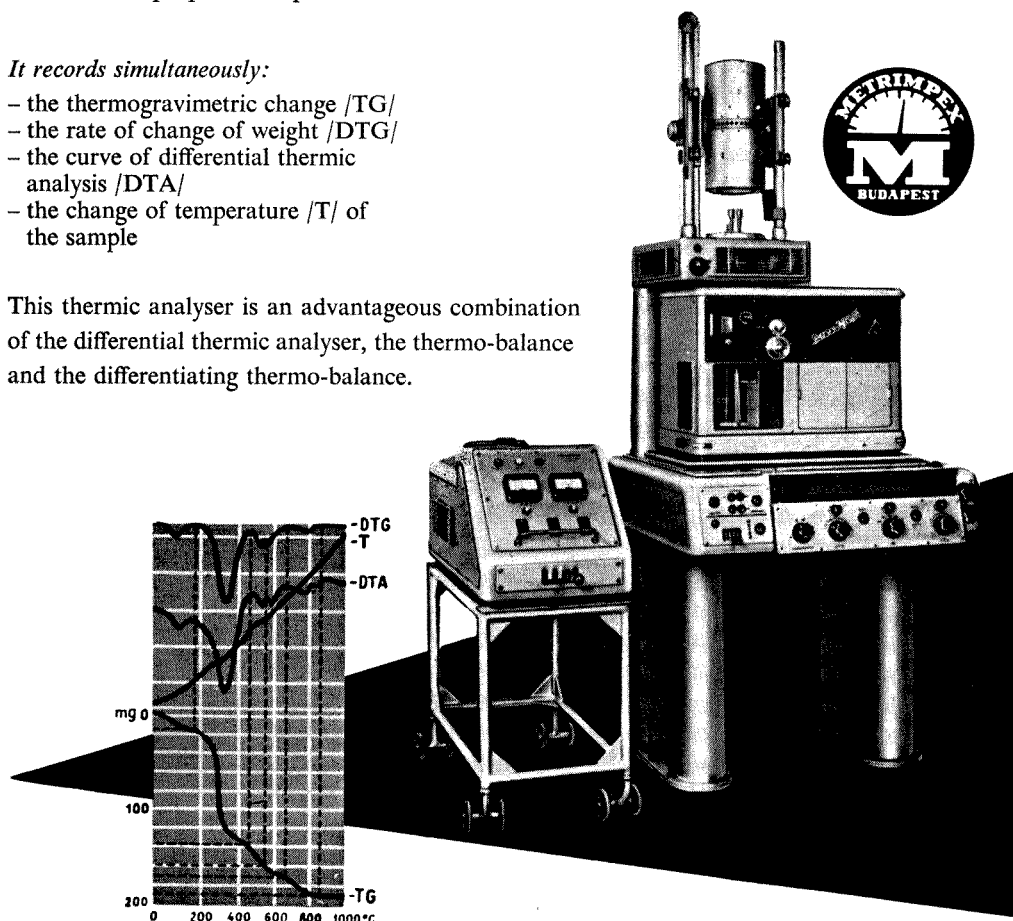
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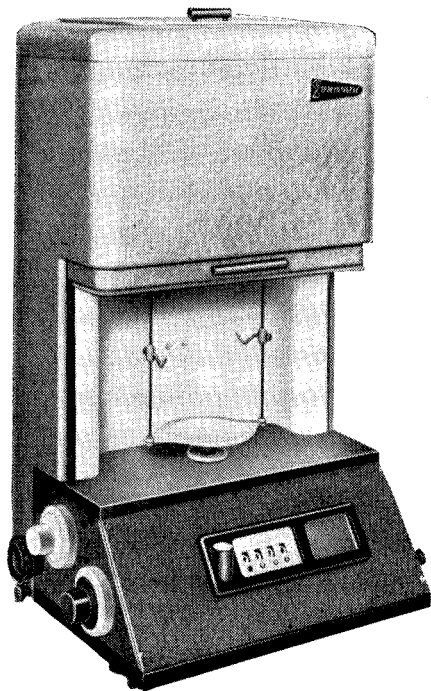
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## SUMMARIES FOR CARD INDEXES

**Indirect determination of hypochlorite and hypobromite by ascorbimetric titration of thallium<sup>III</sup> ions:** L. ERDEY and K. VIGH, *Talanta*, 1963, 10, 439.

**Summary**—An indirect determination of hypochlorite and hypobromite has been developed. To the hypochlorite or hypobromite solution an excess of thallium<sup>I</sup> sulphate solution is added, and thallium<sup>III</sup> ions, formed in equivalent amount, can be titrated with ascorbic acid in the presence of Variamine Blue as indicator.

**Investigation of the oxidation state of cerium in hot sulphuric acid solutions:** I. PAIS, E. SCHULEK and M. RÓZSAHEGYI, *Talanta*, 1963, 10, 445.

**Summary**—The reduction of cerium<sup>IV</sup> in hot concentrated sulphuric acid and in sulphuric acid hydrates, respectively, is investigated. It is found that on raising the concentration of sulphuric acid, the degree of reduction also increases. The degree of reduction depends to a great extent on the relative quantities of solid substance weighed and of sulphuric acid used for the boiling treatment. In contrast to other suggested mechanisms, no correlation is found to exist between the gaseous oxygen developed during reduction and the oxygen bound by sulphuric acid.

**Induced reactions in the peroxy compounds—IV: A study of the H<sub>2</sub>O<sub>2</sub>-OsO<sub>4</sub>-KMnO<sub>4</sub> [and -Ce(SO<sub>4</sub>)<sub>2</sub>] system:** L. J. CSÁNYI, S. KASZAI and I. MOLNÁR, *Talanta*, 1963, 10, 449.

**Summary**—It has been observed that the decomposition of hydrogen peroxide is induced if it is oxidised by 1-equivalent reagents (potassium permanganate or cerium<sup>IV</sup> sulphate). The main factors of this induced chain decomposition as well as the effects of foreign substances are described in detail.

**Titration of thallium<sup>I</sup> ions with a chemiluminescent end-point:** I. BUZÁS and L. ERDEY, *Talanta*, 1963, 10, 467.

**Summary**—Thallium<sup>I</sup> ions can be titrated accurately in a strong hydrochloric acid medium with potassium dichromate standard solution. The reaction was first examined by potentiometric titration. Siloxene proved to be suitable as a chemiluminescent indicator for detection of the end-point, emitting an orange-red chemiluminescence as soon as the titrant is present in excess.

**2-Hydroxy-4-amino-4'-methoxydiphenylamine: A new redox indicator:** L. ERDEY, I. KÁSA and T. MEISEL, *Talanta*, 1963, 10, 471.

**Summary**—2-Hydroxy-4-amino-4'-methoxydiphenylamine has been prepared and has been found useful for the detection of the end-point in the ascorbinometric titration of hexacyanoferrate(III) ions.

**Cacotheline as a redox indicator:** P. SZARVAS and J. LANTOS, *Talanta*, 1963, **10**, 477.

**Summary**—The authors have already shown that cacotheline is an excellent reversible redox indicator for most stannometric titrations. The potential-colour curves of the indicator have now been measured, and the formal potential and  $r_H$  values in acid medium. The mechanism of the reduction reaction has been studied.

**Indicator systems based on vanadiumcomplexone.** I. SAJÓ, *Talanta*, 1963, **10**, 493.

**Summary**—Quinquevalent vanadium is displaced from its EDTA complex by almost all ions which react with EDTA. The liberated vanadium can then give colour reactions with many dyes, and this can be used to indicate the end-point in a complexometric titration. Many indicator systems can be devised on this basis, and the present paper deals with systems containing vanadium<sup>V</sup>, EDTA and diphenylcarbazone, pyrocatechol violet, carminic acid or morin.

**Microdetermination of cyanide ion by radioactive precipitate-exchange:** É. BÁNYAI, F. SZABADVÁRY and L. ERDEY, *Talanta*, 1963, **10**, 499.

**Summary**—Small amounts of cyanide ion can be determined by radioactive precipitate-exchange, using mercury<sup>II</sup> iodate with tagged mercury. The accuracy of the method is  $\pm 5\%$ . Chloride and cyanide ions can also be determined in the presence of each other. The cyanide ion is expelled from an acidic solution by heating, or using the formaldehyde reaction.

**Non-aqueous titrations with a standard solution of amidazophene—I: Determination of carbonylic chlorides and their decomposition products:** L. BARCZA, *Talanta*, 1963, **10**, 503.

**Summary**—It is possible to determine directly the hydrochloric acid contamination of acid chlorides in a benzene solution by titration with a standard solution of amidazophene in benzene in the presence of dimethyl yellow. Subsequently, acid chloride is decomposed by methanol, and the equivalent amount of hydrochloric acid liberated by this reaction is measured similarly by titration with a benzene solution of amidazophene. On diluting the solution with methanol, the original content of organic acid in the sample can be measured by titration with methanolic potassium hydroxide in the presence of phenolphthalein. Thus, it is possible to assay a sample of acid chloride from only one weighing, very quickly and simply.

**Use of a plate electrode for the spectrochemical analysis of solutions:** T. KÁNTOR, *Talanta*, 1963, **10**, 507.

**Summary**—A carbon electrode, with three thin plates on one end, has been developed. With this "plate electrode," the ultramicro analysis of solutions can be carried out using d.c. arc excitation.

**The determination of manganese in aluminium alloys by difference in line intensities:** L. PÉTÉR, *Talanta*, 1963, 10, 513.

**Summary**—A new method is described for the analysis of Mn-Al alloys, based on the difference in line intensities. Feussner excitation is used with 15 kv kick voltage, 5000 pF, and 12.8 mH induction. Aluminium electrodes (99.99% pure) 4 mm apart are used. The spectrum is photographed on "Agfa blau extrahart" using a 20- $\mu$  slit width and 60 sec exposure time. The intensities of the pairs of manganese lines 3547.79–2798.27 and 3547.79–2576.10 are evaluated by Seidel's "W" transformation.

**Spectrographic investigation of Hungarian archeological finds from the Copper and Bronze Age:** Z. L. SZABÓ, O. SZAKÁCS and K. ZIMMER, *Talanta*, 1963, 10, 521.

**Summary**—A method has been evolved for the spectrographic investigation of copper-base archeological finds. Drillings from the specimens are placed in the cup of a carbon electrode and excited by an a.c. arc of anodic polarisation. The spectra are established using a special slit distributor with a two-step filter. Evaluation of spectra is carried out by visual comparison with spectra established with standards. The evolved method makes possible the classification of the archeological finds and, hence, conclusions to be drawn as regards their origin, age, etc.

**Spectrographic determination of 0.1–1.0% of copper in aluminium alloys:** T. TÖRÖK and A. PETHÖ, *Talanta*, 1963, 10, 527.

**Summary**—A method has been developed for the spectrographic determination of 0.1–1.0% copper in aluminium alloys. For this purpose, the lines of the spark spectrum of copper in the region below 2300 Å prove to be most suitable. Low-voltage spark excitation is applied. In establishing the spectra in the region of short wavelengths, spectral plates previously sensitised with an ethanolic solution of sodium salicylate are used. In the process of evaluation, P-transformation is applied. Because of the high  $\gamma$  values and the absence of self-absorption of the applied spectral lines, the analytical accuracy of the method markedly exceeds that obtained when using atomic lines.

**The accuracy of zinc determination by atomic absorption methods:** L. ERDEY, G. SVEHLA and L. KOLTAI, *Talanta*, 1963, 10, 531.

**Summary**—The best experimental conditions for zinc determinations by atomic absorption spectrophotometry, air pressure, slit width and concentration limits have been established. The precision of the method is calculated on the basis of error calculus of absorption measurements. If solutions containing 30–120 ppm of Zn<sup>2+</sup> are measured, the relative errors are lower than  $\pm 0.5\%$ . Interferences of anions and cations have been investigated, and found in most cases to be negligible.

**The role of rate of atomisation in flame photometry:** E. PUNGOR and M. MAHR, *Talanta*, 1963, **10**, 537.

**Summary**—It is established that if concentric atomisers are used, the surfacial pressure component of the pressure from Hagen-Poiseuille's law changes according to the grade of turbulency of the turbulent gas current. The amount of liquid passing through the capillary is influenced, therefore, by the viscosity of the solution, and more or less, as pointed out before, by the surfacial tension. If the atomiser is non-concentric, the surfacial tension has no influence on the rate of atomisation. In the case of concentric atomisers, the results can also be explained quantitatively.

**Photometric determination of molybdenum with Phenylhydrazine—I: The phenylhydrazine-molybdenum complex:** I. BOZSAI, *Talanta*, 1963, **10**, 543.

**Summary**—The properties, structure and conditions for the formation of the phenylhydrazine complex of molybdenum have been investigated, and also the composition of the solid complex. A structural model and an explanation of the reaction mechanism have been proposed.

**Derivatographic determination of the calcite content of bauxites:** F. PAULIK, G. LIPTAY and S. GÁL, *Talanta*, 1963, **10**, 551.

**Summary**—A derivatographic method has been developed for the determination of the calcite content of bauxites. The amount of calcite, calculated from the thermogravimetric curve, is in many cases higher than the true value. This positive error arises from the fact that a number of bauxite minerals only decompose completely above 650°, and therefore they overlap the thermal decomposition of calcite. A new graphic method is recommended for the estimation of this error.

**Application of the flask method to the analysis of highly halogenated organic materials:** L. MÁZOR, K. M. PÁPAY and P. KLATSMÁNYI, *Talanta*, 1963, **10**, 557.

**Summary**—The Mikl-Pech-Schöniger flask method has been used in the analysis of highly halogenated substances. Combustion is encouraged with powdered sugar, and the combustion products are absorbed in ammonia solution. In this way the time of shaking can be reduced. The halide ions can be titrated with silver nitrate in the presence of Variamine Blue redox indicator. If the excess of ammonia is removed after combustion, titration of the halogen can be carried out better in the salt-free solution.



**New methods for the determination of *p*-aminosalicylic acid:** E. SCHULEK, L. MAROS and I. PERL-MOLNÁR, *Talanta*, 1963, 10, 561.

**Summary**—In an acidic aqueous solution, *p*-aminosalicylic acid decarboxylates on boiling. The amount of carbon dioxide formed can be measured by using the simple distillation method earlier suggested by the authors. Decarboxylation also yields *m*-aminophenol and on brominating this product, tribromoresorcinol and ammonia are obtained. The quantity of ammonia formed can be measured by distillation, while the bromination reaction makes it possible to carry out a bromatometric measurement.

**Determination of *p*-aminobenzoic acid-*N,N*-diethyl-leucinol ester methane sulphonate and its decomposition products with tetrabutylammonium methoxide: Anwendung einer Multiplikationszahl bei der analytischen Berechnung von Gemischen:** L. GYENES and A. LASZLO, *Talanta*, 1963, 10, 567.

**Summary**—The impurities in *p*-aminobenzoic acid-*N,N*-diethyl-leucinol methane sulphonate [*p*-aminobenzoic acid (PAB) and *N,N*-diethyl-leucinol methane sulphonate] have been evaluated using a multiplication factor through a graphical procedure. The contents of methane sulphonate and of carboxylic groups have been determined in dimethylformamide medium with 0.05*N* tetrabutylammonium methoxide; the tertiary nitrogen atoms are titrated (after extraction with chloroform) in  $\text{CHCl}_3\text{-(CH}_3\text{CO)}_2\text{O}$  medium with 0.05*N* perchloric acid.

**Analytical control methods for polyvitamin preparations:** K. BURGER, *Talanta*, 1963, 10, 573.

**Summary**—Analytical control methods for determining the vitamin contents of polyvitamin preparations are studied. With the proposed methods it is possible to determine in a sample vitamins A, B<sub>2</sub>, B<sub>6</sub> and E spectrophotometrically, K vitamin polarographically, and nicotinamide in terms of ammonia after selective hydrolysis. The new methods make the separation of vitamins unnecessary before analysis of polyvitamin preparations.

**Argon ionisation detector in gas-liquid chromatography of organosilicon compounds:** G. GARZÓ and F. TILL, *Talanta*, 1963, 10, 583.

**Summary**—The feasibility and limits of applying gas-liquid chromatography to the qualitative and quantitative analysis of organosilicon compounds in a gas chromatograph equipped with an argon ionisation detector is demonstrated. Results obtained with methylchlorosilanes indicate that the instrument is unsuitable for the analysis of these compounds. However, the results permit some conclusions on the dissociation processes occurring in the ionisation space to be drawn. Relative retention data of some organosilicon compounds are established in a column containing Apiezon-M and silicone elastomer. The quantitative analysis of these compounds is feasible with the instrument. Reproducible pyrolysis chromatograms of high molecular linear and cross-linked siloxane polymers, obtained with a special pyrolysis chamber mounted on top of the column, are shown.

## Summaries for card indexes

**A general paper chromatographic method for orientative qualitative analysis:** A. SCHEER-ERDEY, *Talanta*, 1963, **10**, 591.

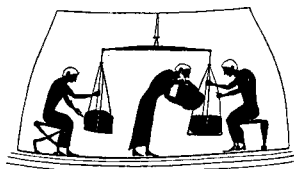
**Summary**—One drop of a solution of the unknown substance in hydrochloric acid is run by the ascending method on paper with ethanol-hydrochloric acid-water as solvent for about 20 hr at room temperature. Subsequently, the strip is sprayed with a 0.2% solution of morin in ethanol. The chromatogram is viewed after drying in this "acid" state and again after treatment with ammonia vapours, both in reflected and in transmitted sunlight and ultraviolet light. From the appearance, shade of colour, fluorescence and location of the spots visible under different circumstances, conclusions can be drawn as to the composition of the sample.

**Inorganic chromatographic investigations in a glacial acetic acid medium:** I. KRAUSZ, I. RÉTI-TAKÁCS and A. ENDRŐI-HAVAS, *Talanta*, 1963, **10**, 597.

**Summary**—The solubility of several salts in glacial acetic acid is determined. It has been found that on an alumina column, the glacial acetic acid sequence of chromatography, in order of increasing elution, is:  $\text{Pb}^{\text{II}}$ - $\text{Cd}^{\text{II}}$ - $\text{Cu}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Hg}^{\text{II}}$ - $\text{Ca}^{\text{II}}$ - $\text{Fe}^{\text{III}}$ ,  $\text{Zn}^{\text{II}}$ . Subsequent to chromatography, the iodometric determination of iron in the presence of copper has been carried out with a negative error not exceeding 3.5%.

# TALANTA

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

Because TALANTA is an international journal, contributions are expected to be of a very high standard. They should make a definite contribution to the subject. Papers submitted for publication should be new publications. The submission of a paper is held to imply that it has not previously been published in any major language (English, French, German, Russian), that it is not under consideration for publication elsewhere, and that, if accepted for publication, it will not be published elsewhere without the written consent of the Editor-in-Chief. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, **but should be critical**. The Editor-in-Chief will welcome correspondence on matters of interest to analytical chemists.

Original papers, short communications and reviews will be refereed (see *Talanta*, 1962, 9, 89). Referees will be encouraged to present critical and unbiased reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor-in-Chief, the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

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Preliminary communications should be limited to less than 1000 words in length and should not contain diagrams. If they do not fulfil these conditions they will be treated as short communications.

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

Because all material will be set directly in page proof, every attempt should be made to ensure that before being submitted, manuscripts are essentially in the final form desired by the authors, and that no alterations of moment will be required at the proof stage. Alterations suggested by the referee will be agreed with the authors at the manuscript stage. Authors whose native language is not English are advised that in submitting papers in English they should endeavour to have the paper thoroughly corrected before submitting for publication. If the manuscript requires considerable editing, it may have to be returned to the authors for retyping, resulting in a serious delay in publication.

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The preferred positions for all figures and tables should be indicated in the manuscript by the authors.

### References

References should be indicated in the text by consecutive superior numbers; and the full reference should be given in a list at the end of the paper in the following form:

<sup>1</sup> J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.

<sup>2</sup> S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.

<sup>3</sup> A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.

<sup>4</sup> W. Jones, *Brit. Pat.* 654321, 1959.

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

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## FOREWORD

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The Editorial Board and Publishers of TALANTA take great pleasure in marking the centenary of the birth of

LAJOS W. WINKLER

and in honouring the Hungarian School of Analytical Chemistry, of which he was the doyen, by presenting this special issue to which all the contributions have been made by members of that School.

It is appropriate to include also in our tribute the name of

ELEMER SCHULEK

whose seventieth anniversary this is.



LAJOS W. WINKLER



## L. W. WINKLER (1863–1939)

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(Received 14 August 1962)

L. W. WINKLER, a prominent Hungarian chemist with an international reputation in analytical chemistry, was born on 21 May 1863. The centenary of his birth, 1963, is a notable year for Hungarian analytical chemistry. A great number of Hungarian analytical chemists remember him with gratitude as their late tutor and teacher. Professor Winkler's scientific views are therefore now a part of the living heritage of Hungarian analytical chemistry.

The influence of a scientist on his contemporaries and on the sciences of his age is normally measured by the scientific results attained by him. In order to assess this influence adequately, some distance in time is needed. However, the two decades which have elapsed since the death of Winkler are certainly sufficient to permit an evaluation of his influence, particularly when also the dates at which he achieved his results, *i.e.*, of the publication and presentation to the scientific world of his works, are taken into account. The present paper aims to assess the activity of Winkler from this aspect.

L. W. Winkler, like many other excellent chemists of the last century, started his scientific career as a pharmacist, although he was shortly to attain a reputation in analytical chemistry throughout Europe. Professor K. Than, the first exponent of chemical science in Hungary, on detecting the prominent talent of Winkler, offered him an assistant professorship shortly after he obtained his diploma in 1885. At this date, problems concerning the analysis of Hungarian mineral waters were being studied very thoroughly in Professor Than's Institute. The interest was focussed mainly on the gases dissolved by the mineral waters. This was mainly because carbon oxysulphide had been discovered in 1867 by Than in the gases of the mineral water source at Harkány in Hungary. Apart from this, the gasometric investigations of R. Bunsen had, around this time, directed general attention to the physical chemistry and analysis of gases. Winkler, as a young man of only 23 years of age, found great interest in the determination of oxygen dissolved in water, because he understood immediately the biological importance of dissolved oxygen. His German and Hungarian papers on this subject, published in 1888, laid the foundations of his scientific reputation, and started the intensive scientific activity which was to gain an international appreciation for Hungarian analytical chemists. This work is mainly responsible for the fact that Winkler was known, and is known even today, by foreign scientists, as "Sauerstoff-Winkler," in order to distinguish him from Clemens Winkler, the discoverer of germanium, who was also a prominent gas analyst.

The iodometric method for determining oxygen dissolved in water, suggested by Winkler, became a classic method introduced into practice 70 years ago, and still

stands up to all the quite numerous scientific criticisms. It is true to say that the number of communications on oxygen dissolved in water, and on its determination by Winkler's method, are in the region of several hundred.

This outstanding success induced Winkler to deal comprehensively with the solubility of gases in water and in various liquids. He shortly detected that the absorption coefficients of gases as determined by Bunsen and his pupils were inaccurate. This arose, apart from experimental errors, from the fact that the concept of absorption coefficient had not been unequivocally defined by Bunsen. In fact, the original definition by Bunsen did not define whether the partial pressure of the absorbed gas or the combined pressures of the gas and of the saturated vapour of the solvent were equal to 760 mm of mercury. Therefore, two terms were introduced by Winkler: *absorption coefficient*, i.e., the amount of gas, expressed in normal ml, dissolved by 1 ml of the liquid at the given temperature when the partial pressure of the gas is equal to 760 mm (i.e., the tension of solvent must be deducted from the total pressure). In contrast, in the definition of the other term, *solubility coefficient*, the pressure of 760 mm denotes the combined pressure of the gas and of the vapour of the solvent.

For his absorptiometric measurements, Winkler evolved ingenious pieces of apparatus, which excelled in their simplicity, and particularly in their ease of operation and aesthetic proportions. Throughout, this holds for any apparatus devised by Winkler.

The perceptive mentality and depth of thought of this great analyst is characterised by his opinion, delivered while experimenting, to the effect that in carrying out absorptiometric and solubility measurements, chemical procedures must always be preferred. This opinion was apparently based on his observation of the fact that the tension of water in a given gaseous surrounding is apparently not identical with the tension measured in vacuum at the same temperature. In general, both tensions are still treated as being identical even up to the present.

Winkler extended his investigations also to the solubility in water of bromine, of organic ethers and esters, and of their vapours. The study of the solubility of bromine and bromine vapour in water gave the interesting results (*i*) that the Henry-Dalton law is also valid, at a fair approximation to the solubility in water of bromine vapour, and (*ii*) that it is possible to calculate, also at a fair approximation, the absorption coefficient of bromine vapour from the values for the solubility of bromine in water. This axiom could be generalised, and this was also proved by Winkler in his investigations of the absorption in water of the vapours of organic compounds immiscible with water.

The results of the gas investigations carried out by Winkler over nearly two decades were published in a number of communications. His values became internationally known when they were included in the *Tabellen* of Landolt-Börnstein, replacing the values of Bunsen. Although half a century has elapsed since that time, the Winkler values have not been replaced by more reliable or more accurate values than his.

Obviously, during these investigations, Winkler was obliged to deal also with the determination of the density of gases and vapours. He found the Dumas method of determination rather cumbersome. He therefore designed a method which simplifies the problem, and which renders superfluous the careful reading of the barometer during the procedure. In this method, the mass of an identical volume of a gas of

known density ( $\text{CO}_2$ ) measured at identical pressure is compared with the mass of air and of the unknown gas or vapour, measured under identical conditions.

The elimination of the errors of physical operations by compensation, and thus the simplification of the necessary calculations, are fundamental aspects of his activities which often recur. This trend is also prominent in his evolution and use of the various types of apparatus suggested for the analysis of gases. His researches into the composition of the air removed by boiling from water saturated with air at different temperatures are classical. In these investigations, he proved that, contradicting the original values of Bunsen, the oxygen content of air dissolved in water decreases with rise of temperature.

Two branches of his scientific activity are particularly concerned with practical or applied problems. One of these is the chemistry of drinking waters and mineral waters, and the other is the investigation of drugs. Both fields were early studied by his Institute.

After the thorough investigation of gases dissolved in water ( $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{H}_2\text{S}$ , *etc.*) his attention was attracted by the determination of other constituents dissolved in water, probably in part because these might have certain hygienic correlations. By the methods evolved in the course of these researches, Winkler became such a renowned water analyst that he was asked to prepare the Chapter on drinking water analysis in the comprehensive multi-volume Lunge-Berl book, widely used as the standard work of chemical analysis.

The Winkler methods for the so-called colorimetric titration of heavy metal contamination of waters, by iron, lead and copper, and the contamination by ammonia hydrogen sulphide, silica, *etc.*, are extremely ingenious. In essence, they are based on the principle that the colour reaction with the component to be determined in a known quantity (or volume) of the tested substance is carried out together with a so-called "blank" test, made under identical conditions and with the same volume, in a titration-like way; a standard solution is used of identical tint and colour, containing the component to be determined in a known concentration, or containing another substance yielding a solution of identical tint and colour (*e.g.*, a solution of  $\text{K}_2\text{CrO}_4$  for determining silica).

In connection with the analysis of mineral waters, Winkler carried out various investigations on halogens. From these, it was possible to evolve some general methods of investigation. Of these methods, the most successful were the determination of iodide and bromide. Although the original Winkler method for the determination of iodide has been modified by a number of authors since then, the fundamental principle of the procedure has been retained. By this method, essentially, iodide is oxidised with chlorine to iodate, excess chlorine is removed by boiling, and the amount of iodate (the six-fold quantity of the original amount of iodine) is measured by iodometry. Thus, the proposed method is a multiplication procedure. This principle was utilised by organic analysts, in the micro-iodometric methods for the determination of functional methoxyl or ethoxyl groups, by measuring the quantity of  $\text{CH}_3\text{I}$  or  $\text{C}_2\text{H}_5\text{I}$ .

To a considerable extent the success of the methods for the determination of halogens suggested by Winkler can be regarded as responsible for the fact that halogen analysis became an almost exclusively Hungarian field of investigation, because many pupils of Winkler devoted themselves to this theme.

**แผนกห้องสมุด กรมวิทยาศาสตร์  
กระทรวงอุตสาหกรรม**

In the course of his researches into halogen determination, Winkler's attention was attracted by the possibility of determining the content of iodine and bromine in sea water. The investigation in respect of iodine started with the qualitative analysis of iodine itself. His analytical critical ability manifested itself also in this case. Although his multiplication method was already evolved at that time, he preferred the isolation method because he preferred first to extract the iodine from sea water with carbon bisulphide. It is not possible here to describe this part of his classical investigations in detail. It is sufficient to mention that during these investigations he controlled his results by examining a "synthetic sea water" composed on the basis of the analytical researches. Essentially his method consisted in transferring the iodine liberated from a large volume of sea water by a slightly oxidising medium into a carbon bisulphide phase by shaking. The same process was repeated after a previous reduction by sulphite. According to his investigations, the water of the Adriatic Sea contains about 0.05 mg of iodine per litre, a minute part of this being in the form of iodate ions. (Iodine prepared from the water of the Adriatic Sea was kept in his "treasury", and it was gladly shown to his visitors.)

The content of iodine and bromine in the Stassfurt potassium salts was equally and carefully repeatedly controlled by Winkler, because some doubts arose among experts (Kubierschky) in respect of their iodine content.

Bromine was determined by him using the distillation method, mainly because he preferred actually to see the bromine, *i.e.*, its colour, on extraction. The distillation method evolved by him was for a long time the sole reliable procedure for the determination of minute amounts of bromide in the presence of much chloride. Using it, he was actually the first chemist to succeed in determining the bromides always present in sodium chloride in traces.

However, the methods evolved by him were successful not only in the field of drinking water analysis. He was also very much interested in drug investigations. At that time, Than was the Editor-in-Chief of the *Hungarian Pharmacopeia, I and II*. It is fairly obvious that Winkler, with his pharmacist's diploma, was predestined to participate in the preparation of the methods of investigation used for *Pharm. Hung. II*, published in 1888, and in developing the chemical part of *Pharm. Hung. III and IV*.

These chemical chapters of *Pharm. Hung.* may well have been responsible for inducing him to evolve analytical methods which can be carried out even under quite simple laboratory conditions. The principle of the "simplest possible methods" has been retained up to the present, although the up-to-date pharmaceutical industry cannot dispense with up-to-date methods of investigation. Our recent *Pharmacopeia* is really a collection of standards of great interest not only from the aspect of pharmacists but also of the pharmaceutical industry as a whole. The remarkable practical sense and keen critical ability of Winkler was able to create a great number of lasting methods also in this field. His excellent sense as a practical pharmacist solved, for example, the problem of preparing one of the everyday reagents of analytical chemists, water saturated with hydrogen sulphide. This he did in a radical way, introducing the use of a glycerol solution of sodium sulphide. This suggestion was taken over by a number of other *Pharmacopeias*, and even still the glycerol solution is used by many laboratories instead of the unstable aqueous solution of hydrogen sulphide.

The Winkler method for the determination of the "iodine bromine number,"

introduced as a characteristic value of oils and fats, is generally applied not only in this country, but also in many foreign laboratories throughout the world. For the determination of the saponification number, Winkler introduced the use of a solution of potassium hydroxide in *n*-propanol.

Winkler's activity in the field of gravimetric chemical analysis deserves to be mentioned separately, because this work contributes to a great extent to the evolution of a new aspect of chemistry which appears now to be quite obvious. His first gravimetric communications were devoted to the determination of carbon dioxide in drinking waters, mineral waters and carbonates. The simplified technique applied, the removal of carbon dioxide by gaseous hydrogen developed in the reacting medium itself, is a rather elegant and ingenious one. In this process, carbon dioxide is absorbed in a potassium hydroxide trap (also designed by him) and the weight increase of the trap is measured.

For the determination of the content of potassium, sodium and lithium, in drinking waters and mineral waters, an extraction method was suggested because the determination could not be carried out without enrichment. This problem is now much simpler. At that time, quantitative flame photometric methods were unknown or at least were very inaccurate. One of the secondary results of Winkler's investigations in this field is the removal of traces of water from ethanol or methanol by boiling with metallic calcium, a procedure still often used in many laboratories.

The precipitation of components to be determined in the form of insoluble precipitates and their measurement by gravimetry is the oldest method of chemical analysis proper. The drying and the subsequent ignition of the filtered precipitates provides substances which can be measured reliably. These methods in fact originated with Klaproth (1743-1817). However, the systematic supervision of the ways of actual precipitation were begun by Winkler.

For this purpose, the techniques of measurement and the preparation of the tested substance for weighing, *i.e.*, the fundamental operations of gravimetric analysis, had to be investigated. The crucibles with precipitates were at that time conventionally placed in desiccators filled with calcium chloride. Winkler was the first to emphasise that the crucible and precipitate were taken out of the desiccator just when the precipitate most urgently needed a dry atmosphere, *i.e.*, during the actual weighing process. In his analytical processes the filters or crucibles are placed in weighing bottles which have airtight closures, and are weighed on cooling. Care was taken always to weigh the filter or crucible without the precipitate in exactly the same way, and after allowing it to stand for the same time as the filter or crucible containing the precipitate. By this method, the reproducibility of the weighings is in the range of  $\pm 0.1$  mg with the conventional analytical balances. Obviously, the drying flasks used previously had to be removed from the balance, and the balance space had to be allowed to reach equilibrium with the state of the weighing room.

Nowadays everyone considers that these principles are quite obvious, and they are followed throughout in all microanalytical methods. However, in fact, the principle just described is actually the principle of compensation emphasised earlier in the present paper! And how remarkable is the fact that the fundamentally correct principle of compensation manifested itself in chemical operations in a rather distorted fashion. For, in the belief that precipitation processes were always stoichiometric, attempts were made to eliminate the observed errors by using methods of

precipitation which were loaded with unknown error sources. Today the methods evolved by Winkler furnish decisive evidence pointing to the importance of maintaining the prescribed experimental conditions strictly in all reproducible methods. In other words, the most important fundamental axiom of researches in natural sciences, the principle of reproducibility, of "repeatability," must prevail in research in analytical chemistry as elsewhere.

The consequent application of this fundamental principle in research in analytical chemistry is one of the greatest achievements of Winkler. It became possible to correct the results of analyses carried out under prescribed experimental conditions, using the correction factors evolved by Winkler. It is to be regretted that he stopped at the *determination* of these "correction factors," and did not elucidate the errors corrected by them, although he himself realised fully the importance of the theoretical and practical clarification of these processes, but only dealt with them practically. The methods of analytical determination evolved by Winkler are simple, precise and accurate. It is quite remarkable how he dealt, purely on an empirical basis, with problems later elucidated on theoretical grounds. Of his methods, the determination of magnesium in the form of  $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , and the determination of zinc, cadmium, lead, copper, *etc.*, are now carried out by our university students as practical exercises.

Today, we believe that gravimetry, by Winkler's methods, provides one of the most reliable methods known. Because his correction values are not always linear ones, investigations since his time indicate that the control of chemical processes is still incomplete. In this direction many more theoretical and experimental investigations are needed.

It is impossible, within the framework of this short memoir, to present a detailed picture of the intensive activity of Professor L. W. Winkler, and to appreciate separately the depth of the ideas concealed in his methods, the originality of his approaches to the solution of problems, the ingenuity of his procedures, *etc.* A list of his publications and books, amounting to more than 200, was compiled and published by one of his pupils, L. Szebellédy, who has since then died (18 years ago). It is sufficient, therefore, merely to refer to this list of publications.

Winkler dedicated the two small volumes summarising his scientific activity (*Untersuchungsverfahren für das chemische Laboratorium*) to the memory of his late and well-remembered professor, K. Than. Winkler sponsored the erection on the staircase of the Chemical Institute of Professor Than (now the Institute of Inorganic and Analytical Chemistry of the L. Eötvös University, Budapest) of a marble plate "To the memory of K. Than (1834–1908), the founder of Chemical Sciences in Hungary". The friends and admirers of both famous pupils of Professor Than, L. W. Winkler (1863–1939) and G. Buchböck (1869–1935) erected bronze reliefs of both Professors of Chemistry on marble plaques, located to the right and to the left of the memorial plaque of Than. The relief of Winkler is always decorated by a laurel wreath, which is periodically renewed through the faithful memory and good offices of pupils returning to the place of activity of their late Professor.

## Professor E. SCHULEK

PROFESSOR Elemér Schulek, Member of the Hungarian Academy of Sciences, Honorary Member of the Chemical Society of Poland, Head of the Institute of Inorganic and Analytical Chemistry of the L. Eötvös University of Budapest, celebrates his 70th birthday this year. This, then, provides a suitable occasion to review his career and his scientific work.

Elemér Schulek was born, the son of a pharmacist, in 1893. At the end of his secondary school education he matriculated with a first class award, and, following his father's advice and example, himself took up pharmacy in his university studies. Here he was fortunate to come under the notice of Professor L. W. Winkler, in consequence of his outstanding work in his first year at the university.

His studies were interrupted by the first World War, and for four years he was in the army. When he was able to return to his studies, Winkler offered him a post in the Chemical Institute of the University of Sciences in Budapest, where he was required to help the Professor in teaching and research.

His direct personal contact with Winkler, working on gas analysis, gravimetric analysis, and the determination of halogens, stimulated ideas which Schulek began to develop. The theme of his doctoral thesis was suggested by Winkler, and this, as well as original papers arising from his own work in the field of inorganic analysis were published in rapid succession.

Schulek worked with Winkler for six years, and was then appointed as Head of the Chemical Department of the Public Health Institute, just then established. This Department was required to analyse drinking waters, foods, and special drugs produced by the pharmaceutical companies. At the same time he was asked to organise methods of control for the Hungarian drug supply.

Before taking up this work, he held a Rockefeller Foundation Fellowship abroad, and travelled extensively in the United States of America, England, Switzerland, Germany, France and the Netherlands, studying the control of food and of potable water in the larger cities. His tour, which lasted for eighteen months, enabled him to undertake research, for varying periods, in the Universities of London, Berne, Zurich, Berlin and Leyden.

When he returned to Hungary he took up the work of drug control, and in this he had to solve numerous problems of method. During his 18 years at the Public Health Institute he published his well-known papers on the analysis of pyrazolone-type drugs, natural alkaloids, *p*-sulphamides by bromatometry, and the like, which were received with approval abroad. During this period he was twice offered posts abroad, and was invited to a Professorship in Hungary, but declined these offers.

In 1944 the University of Budapest invited him to become a Professor, and this he accepted. He developed the Institute of Inorganic and Analytical Chemistry gradually to include in its research projects not only classical analysis, but also work in various types of instrumental analysis, emission and absorption spectrophotometric methods, organic group analysis, ultramicro analysis and radiochemical methods.

Professor Schulek and his coworkers have published about 450 papers, of which a part has been published from the Public Health Institute. Since he became Professor he compiled and produced the Vth *Pharmacopia-Hungarica*, and was Chairman of the Advisory Board. At present he is directing the preparation of the VIth edition.

Included in his extensive analytical investigations has been much work on the analytical and inorganic aspects of interhalogen compounds. Utilising the different chemical behaviour of bromine cyanide and chlorine cyanide, he has worked out ingenious methods for halogen determination in water analysis and microanalysis, and has, at the same time, provided much new and valuable information on the chemical properties of interhalogen compounds.

His work on bromine chloride and iodine chloride enabled him to develop many new analytical methods, particularly in the field of bromatometric titrations, first proposed by Györy. Schulek's work on new indicators such as  $\alpha$ -naphthol flavone and, in particular, on *p*-ethoxychrysoïdine, emphasised the problems of indication in bromatometry, and elucidated many of the principles of this operation. The adsorption-indicator properties of *p*-ethoxychrysoïdine led to a new interpretation of the mechanism underlying the action of adsorption indicators, and of certain surface phenomena.

His work on sulphur and selenium compounds belongs mainly to the inorganic field. However, while clarifying the processes occurring in the hydrolysis of sulphur, he developed a number of new methods for the simultaneous determination of sulphur compounds containing sulphur in various oxidation states. In addition to bromine cyanide methods for polysulphide determinations in the presence of sulphide and thiosulphate, he published new procedures for the determination of selenium. Work on dithionites and rongalite led to new methods for their analysis.

This was followed by renewed work on formaldehyde. As side issues in this latter theme, new methods were developed for the analysis of aldehydes, ketones, polyalcohols and carbohydrates. In the field of organic group analysis, new quantitative methods were devised for decarboxylation and de-amination.

To replace the usual manometric and volumetric methods of gas analysis, Schulek introduced methods for the vapour-phase analysis of gaseous mixtures and liquids. He was able to simplify the determination of oxygen in the air and of various nitrogen oxides to accurate iodometric titrations.

Professor Schulek's analytical research has been characterised by his insistence on a thorough study of reaction products for the purpose of a quantitative clarification of chemical processes. As a result of this approach he was able to develop a new technique for the isolation of carbon dioxide which can be used in micro determinations. In addition, the Kjeldahl determination of nitrogen has been refined to an accurate ultramicro method.

Both analytical and inorganic research has been done on the systems sulphuric acid-Caro's acid-hydrogen peroxide-peroxydisulphate, and acetic acid-peracetic acid. This research has led to methods for the simultaneous determination of the components of these systems. Digestion with concentrated sulphuric acid and hydrogen peroxide has been studied, particularly in the case of metals with variable oxidation states, and the oxidation states of such metals in concentrated sulphuric acid and in Caro's acid have been elucidated.

It is of interest to note that antipyrine, which he studied intensively in his earlier



work on the analysis of drugs, proved to be an excellent medium for his later work on isotope-exchange reactions. Other later work has been in the micro-analysis of metals, and in the isolation of metals from extremely dilute solutions.

The topics mentioned in this memoir are only the more important from among Professor Schulek's extensive interests, for which he has already twice been awarded the Kossuth Prize, presented by the Hungarian Government for outstanding scientific or cultural contributions.

In this Jubilee year we are happy to wish Professor Schulek the opportunity for further work, good health and continuing success.

J. LASZLOVSZKY

## GESCHICHTE DER ANALYTISCHEN CHEMIE IN UNGARN

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(Received 14 August 1962)

ANALYTISCHE Chemie gab es in Ungarn schon im frühen Mittelalter. Ungarn war damals der bedeutendste Gold- und Silbererzeuger Europas; in den Bergstädten wurden die Erze und die Metalle auf ihren Edelmetallgehalt geprüft. Das erste Dokument darüber ist ein Erlass von König Karl I aus dem Jahr 1342, der über die Neugestaltung des Finanzwesens des Landes verfügte. Darin wurde es verordnet, dass in jeder Bergstadt ein "königliches Haus" aufgestellt werden soll, wohin die zu schmelzenden oder einzulösenden Erze und Metalle einzuliefern sind um durch den Königlichen "camerarius" auf ihren Goldgehalt untersucht zu werden. Nur er habe das Recht das Gold mit dem Karatgehalt und dem Königlichen Stempel zu bezeichnen. Da dasselbe Dekret auch über das Beschaffen von Blei verfügte, ist es offensichtlich, dass die Untersuchung durch Kupellation erfolgte,<sup>1</sup> welche Methode schon im Altertum bekannt war. In späteren Verordnungen findet man auch öfters das Probierwesen erwähnt. König Sigismund verordnete 1405, dass ausser dem dazu ermächtigten niemand das Recht habe Gold von Silber mit Wasser zu trennen (insuper nec separandi cum aqua aurem ab argento artem exercere, nisi ille, vel illi, quibus hujusmodi officia duximus specialiter committenda).<sup>2</sup> Zu dieser Zeit war folglich das Trennen von Gold und Silber auf nassem Weg mit Salpetersäure schon bekannt. Im 15. Jahrhundert erwarben sich die Bürger der Bergstädte das Recht sich selbst einen "Probierer" zu halten, offensichtlich um den königlichen Beamten zu kontrollieren. Dies gefiel aber dem königlichen Kammergrafen (Finanzbehörde bei den Bergstädten) nicht sehr. Man findet in den Archiven viele diesbezügliche gegenseitige Beschwerden. König Mathias wies z.B. 1459 den Kammergrafen an den Rat von Körmöcbánya (Kremnitz) im Ausüben seines Rechtes des Probierens nicht zu behindern. In einem anderen Dokument aus 1498 hingegen teilte der Kammergraf dem Rat von Selmec (Schemnitz) mit, sein Probierer erhalte stets andere Ergebnisse beim Probieren als der städtische Probierer. Nach einem Jahr beklagte sich dagegen der Rat beim König, dass der Kammergraf sein Amt missbraucht, dass bei der Probe des Goldes auf nassem Weg allerlei Rechtswidrigkeiten zum Schaden der Bürger begangen und die Analysen der städtischen Probierer ganz ausser Acht gelassen werden.

1569 regelte König Maximilian erneut das Bergwesen. Die Stellungen der Probierer wurden beibehalten, obwohl ihnen eine sehr niedrige Position in der Hierarchie der Kammer angewiesen wurde, sie waren dem Rang nach die vorletzten, mussten hingegen einen Eid ablegen. Hier folgt der Text des Eides: "Schwöret dem erlauchtesten und mächtigsten Herrscher, Maximilian, römischen Kaiser, ungarischen und tschechischen König, österreichischen Erzherzog, unserem gnädigsten Herrn, dass Ihr ihm und seinem Kammergrafen folgsam und treu sein werdet, in Eurer Stellung Euch ehrsam verhaltet und das Gold und Silber eines jeden ehrlich prüfet damit die

rechtmässige Abgabe seiner Majestät ordnungsgemäss bezahlet wird, weiterhin wenn jemand Euch Erze bringt, Ihr diese auch ehrsam prüfet und vor dem Kammergrafen und seinen Richtern Ihr nichts zurückhaltet und sowohl reichen als armen Ihr ohne Falschheit prüfet und darin Ihr weder Freundschaft noch Feindschaft kennet, keinen Lohn und kein Geschenk annehmet, Euch nicht täuschet und nicht täuschen lasset.”<sup>3</sup>

Zum Fördern des Bergwesens gründete König Karl III im Jahr 1735 zu Selmecbánya (Schemnitz) eine Bergschule, die durch Königin Maria Theresia 1763 zum Range einer Bergakademie erhoben wurde. In dieser Schule unternahmen die Studenten zuerst an der Welt obligatorisch Laboratoriumsübungen. Schon das Gründungsdekret aus 1735 schrieb es vor, dass die “scholares practice et manipulando” zu unterrichten sind und es wurde auch aufgezählt was für Übungen auszurichten sind. Diese waren:

1. Erlernen der Probieregewichte, der chemischen Zeichen, der Prüfstoffe und deren Bestandteile;
2. Errichten von Kupellen;
3. Probenahme der Erze und Gesteine, des Rohschwefelsteins, des Zinnsteins, des Schwarzkupfers und des Bleis auf Silber;
4. Probenahme der Erze, des Bleisteins, Eisensteins und Schwefelsteins auf Kupfer;
- 5–8. Probenahme verschiedener Gesteine, Erze und Metalle auf Blei, Zinn, Quecksilber und Wismut;
9. Trennen und Lösen von Gold, Silber und Kupfer;
10. Wie die Öfen beim Schmelzen einzurichten sind;
11. Wie die Erze im rohen Zustand zu schmelzen, wie Lech und Speise zu brennen ist;
12. Verbleien der Erze;
13. Wie zu behandeln und aufzuarbeiten arsenik- und antimon- und kobalthaltige und kieselige und andere schlechte Erze sind;
14. Erkennen des vollständigen Prozesses des Schmelzens und Brennens der Erze.<sup>4</sup>

Wie zu sehen, müssten die Schüler einen wahrlich ausführlichen analytischen und metallurgischen Kurs absolvieren. Nähere Einzelheiten über den Inhalt der Übungen kennen wir nicht, dagegen wissen wir dass anfänglich dieser Unterricht durch die Probirmeister der Kammer geleitet wurde und sie dafür je Student 50 Gulden erhielten.

1763 wurde ein Lehrstuhl für Chemie gegründet, dessen erster Leiter der Belgier Nicolas Jacquin (1727–1817) wurde, der sich einen europäischen Ruf erwarb. Jacquin übergang später an die Universität Wien. Unter Jacquin fing die wissenschaftliche Forschung an der Bergakademie an. In der zweiten Hälfte des Jahrhunderts erwarb sich die Bergakademie einen grossen europäischen Ruhm auf dem Gebiet der Chemie und Metallurgie. Ihre Glanzzeit war während der Professur Anton Ruprechts (1750–1802) der selbst schon Zögling der Akademie war. Von allen Teilen Europas kamen Studenten um hier analytische Chemie zu lernen, darunter F. Müller, Entdecker des Tellurs, M. del Rio, Entdecker des Vanadins, und J. d’Elhuyar, Entdecker des Wolframs. Die Bergakademie von Selmecbánya diente als Muster 1794 zur Begründung der École Polytechnique in Paris, wie dies aus deren Gründungsschrift und aus Fourcroys Rede im Konvent hervorgeht.” In Frankreich wurden Physik und Chemie bisher nur theoretisch unterrichtet. Die Bergakademie von Schemnitz in Ungarn zeigt uns ein gutes Beispiel, wie nützlich es ist, wenn die Studenten auch in der Praxis die Übungen ausführen die die Grundlage ihrer Wissenschaft bilden. . . . Der Wohlfahrtsausschuss ist der Meinung diese Methode sollte auch in der zu errichtenden

Schule eingeführt werden.”<sup>5</sup> Im folgenden Jahrhundert war dann an der Bergakademie Selmec ein langsamer chemischer Rückgang zu beobachten, dem nur Ende des Jahrhunderts ein neuer Aufschwung, doch nicht mehr analytischer Natur folgte.

Ungarn ist sehr reich an Heilquellen, deren viele schon unter der Römerzeit bekannt waren. Die chemische Analyse dieser begann erst im 18. Jahrhundert, als in jedem Komitat die Stellungen der Amtsärzte geschaffen wurden und diesen die Analyse der Heilquellen ihrer Amtsgebiete zu Pflicht gemacht wurde. Nacheinander erschienen derartige Bücher, alle in lateinischer Sprache verfasst. Das erste war L. Stoker's *Thermographia Budensis* (1721) die noch die ziemlich primitiven analytischen Methoden (Eindampfen und fraktionierte Kristallisation der Komponenten) des Zeitalters enthält. Besonders merkwürdig ist aber ein anderes Werk, das 1781 erschienene *Analyses aquarum Budensium* von J. Oesterreicher (1756–1831).

Das Buch enthält die wasseranalytischen Methoden von Professor Josef Winterl (1732–1809) der der erste Professor für Chemie und Botanik der Universität Budapest war. Winterl war der einzige in der Welt, der zur Bestimmung des Phlogistons eine Methode ausarbeitete, wodurch Oesterreicher den Phlogistongehalt der budapester Mineralwässer “tatsächlich” bestimmte. Die Bestimmung beruhte auf der Annahme Phlogiston verflüchtige mit Salpetersäure. Er setzte bekannte Menge Salpetersäure zum Wasser, dampfte auf ein Drittel des Volumens ein und bestimmte wieviel Salpetersäure zurückblieb. Die Salpetersäure wurde durch die Menge Fluorspat gemessen die die Säure zu lösen vermochte. Den Umrechnungsfaktor Fluorspat Phlogiston ermittelte er mit bekannter Menge Russ, das für reinen Phlogiston gehalten wurde.\* Diese Methode, eine einzigartige Kuriosität der Geschichte der analytischen Chemie, wurde abgesehen von der Grundreaktion, mit grosser analytischer Sorgfalt ausgearbeitet. Winterl trug sogar dafür Sorge, den “Phlogistongehalt” des destillierten Wassers zu bestimmen und in Korrektion zu nehmen. Dies ist die erste Blindwertbestimmung, die ich in der Literatur der analytischen Chemie finden konnte. Winterl hatte aber auch analytische Erkennungen von bleibendem Wert. Er beobachtete zuerst die rote Färbung, die Eisen mit Thiocyanat gibt und benützte Weinsäure zum Fällern des Kaliums. Man findet bei ihm auch eine Notiz über die Fällung des Bleis mit Schwefelwasserstoff, das war die erste Anwendung dieses Reagens seit Boyles vergessene Versuche.<sup>7</sup>

Ferenc Nyulas (1758–1808), ein Schüler Winterls, ämtlicher Oberarzt von Transsylvanien verfasste 1800 das erste Buch chemischen Inhalts in ungarischer Sprache. Es besprach die Analysen der transsylvanischen Heilquellen. Darin befindet sich der erste Nachweis des Mangengehalts von Wässern.<sup>8</sup>

Ein anderer Schüler Winterls, Pál Kitaibel (1757–1817), später Professor der Chemie und Botanik an der Universität Budapest, unternahm die erste systematische Analyse der Mineralwässer Ungarns, sein erst nach seinem Tod publiziertes Werk, *Hydrographia Hungarica* enthält die Analyseergebnisse von etwa 150 Mineralwässern.

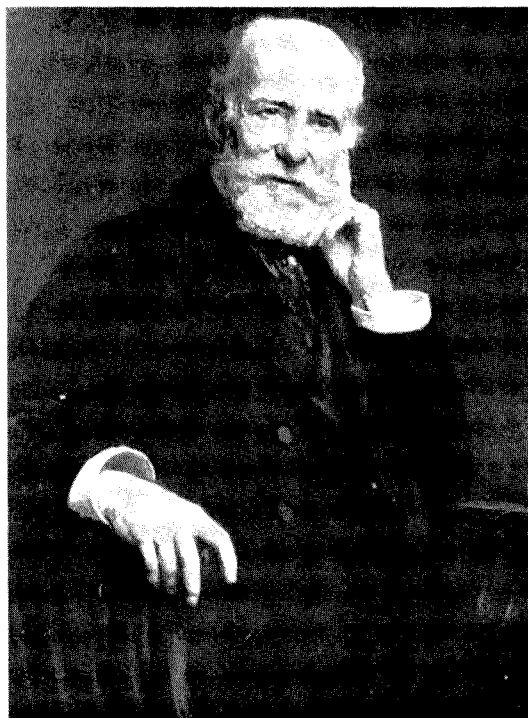
Die analytische Aufarbeitung der Bodenschätze des Landes wurde gegen die Mitte des vorigen Jahrhunderts mit grosser Intensität aufgenommen. Viele Chemiker betätigten sich auf diesem Gebiet, aus deren Reihe besonders Károly Nendtvich (1811–1892) zu nennen ist, der der erste Professor für Chemie des 1845 gegründeten Polytechnikums (heute Technische Universität) Budapest und der erste Chemikermittglied der 1825 gegründeten Ungarischen Akademie der Wissenschaften war.

\* Ausführlicher berichtete ich darüber schon am anderen Ort.<sup>6</sup>

Die moderne Epoche der Chemie in Ungarn trat ein als 1860 Károly Than (1834–1908), Schüler Bunsen's zum Leiter des ehemaligen Instituts Winterls der Universität Budapest ernannt wurde. Das nach seinen Plänen 1870–1880 gebaute neue chemische Institut war zu jener Zeit das modernste Europas. Than befasste sich mit anorganischer, analytischer und physikalischer Chemie. Auf dem Gebiet der Massanalyse ist bleibender Verdienst Thans das Empfehlen des Kaliumbijdats (1908) und des Kaliumbicarbonats (1889) als Urtitersubstanzen in der Jodometrie bzw. Acidimetrie.<sup>9</sup> Er schlug als erster vor—bevor noch Arrhenius seine Ionentheorie entfaltet hätte,— die Ergebnisse von Wasseranalysen nicht in Salzen darzustellen, sondern die Menge der Elemente und Radikale bzw. ihre Äquivalentprocente anzugeben. Die diesbezügliche Priorität Thans wurde später auch durch Ostwald anerkannt.

Than war ein hervorragender Lehrer, er erzog eine ganze Generation später leitender Chemiker. Hinsichtlich analytische Chemie ist von ihnen an erster Stelle sein Nachfolger an der Universität Lajos Winkler (1863–1939) zu nennen, dessen grosse analytische Verdienste in einem besonderen Artikel dieses Bandes gewürdigt sind. István Györy (1860–1954) führte die Kaliumbromatmasslösung 1893 in die Massanalyse ein.<sup>10</sup> Ein anderer Schüler Thans, Lajos Ilosvay (1851–1936) Nachfolger Nendtvich's im Institut für allgemeine Chemie an der Technischen Universität Budapest, untersuchte ausführlich die Anwendungsmöglichkeiten des ersten synthetischen Reagens der qualitativen Analyse, des von Griess empfohlenen Gemisches von  $\alpha$ -Naphthylamin und Sulfanilsäure zum Nitritnachweis. Er benützte dieses ausserdem zuerst zum Nachweis von Nitraten nach vorhergehender Reduktion (1889).<sup>11</sup> Der Professor für chemische Technologie der Technischen Universität Vince Wartha (1844–1914) entwarf 1882 seine wohlbekanntete Methode zur Wasserhärtebestimmung mit Hilfe einer NaOH—Na<sub>2</sub>CO<sub>3</sub> Masslösung die, bis zum Verbreiten der Komplexometrie in unserer Zeit, allgemein angewandt wurde. Die Methode erhielt ihre endgültige Form 1902 durch Warthas Assistent und späteren Nachfolger Ignác Pfeiffer (1868–1941).<sup>12</sup>

Der Rolle der Wasserstoffionenkonzentration bei chemischen Reaktionen wurde man erst am Anfang dieses Jahrhunderts bewusst. Die ersten Versuche zum kolorimetrischen Messen der Wasserstoffionenkonzentration unternahm 1903 der Arzt Pál Szily. Da seine Tätigkeit ziemlich unbekannt ist, soll sie hier ausführlicher erörtert werden. Er bestimmte die Farbe verschiedener Indikatoren in Lösungen von verschiedener Wasserstoffionenkonzentration, bestimmte den Umschlagspunkt und stellte fest, dass der Umschlag ausschliesslich von der Wasserstoff—bzw. Hydroxylionenkonzentration abhängig, aber völlig unabhängig von der stofflichen Art der Lösung ist. Er gab endlich eine Tabelle der Wasserstoffionenkonzentrationen und der zu ihnen gehörenden Färbungen der verschiedenen Indikatoren. Seine Beobachtungen benutzte Szily zur Bestimmung der Reaktion des Blutserums. Er stellte fest, dass dessen Reaktion sich zwischen  $5 \cdot 10^{-5}$  [OH] und  $6 \cdot 10^{-4}$  [H] befinden muss. Bemerkenswert ist die Feststellung Szily's, dass das Blutserum seine Reaktion gegen Einwirkung von Säuren und Basen beständig behält. Er fand dieselbe Wirkung bei einer mit Kohlensäure gesättigter Bikarbonatlösung auch. Dies war die Erkennung der Pufferwirkung.<sup>13</sup> Szily ging dann nach Berlin und arbeitete neben Professor Friedenthal. 1904 erschien ein Artikel über eine Methode zur genauen Bestimmung der Wasserstoffionenkonzentration mittels Indikatoren von Friedenthal.<sup>14</sup> Darin erwähnt der Verfasser, dass da es ihm in schwach saurem Gebiet nicht gelang mit



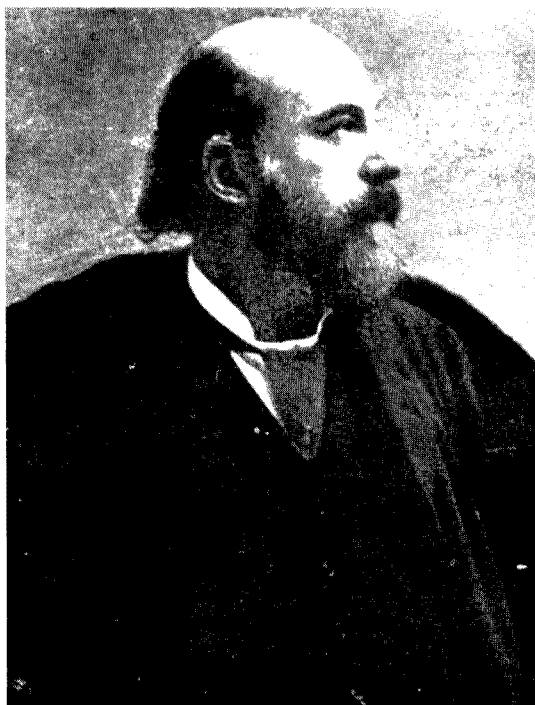
KÁROLY THAN  
1834-1908

FIG. 1.—Professor der Chemie an der Universität Budapest



LAJOS ILOSVAY  
1851-1936

FIG. 2.—Professor der Chemie an der Technischen Universität Budapest



VINCE WARTHA

1844-1914

FIG. 3.—Professor der chemischen Technologie an der  
Technischen Universität Budapest





LÁSZLO SZABELLÉDY

1901–1944

FIG. 4.—Professor der analytischen und anorganische Chemie an der  
Universität Budapest



ELEMER SCHULEK

FIG. 5.—Professor der anorganischen und analytischen  
Chemie an der Universität Budapest



LASZLO ERDEY

FIG. 6.—Professor der allgemeinen und analytischen  
Chemie an der Technischen Universität Budapest

Säuren Lösungen von beständiger Wasserstoffionenkonzentration zu bereiten, er diese auf dem Rat seines Mitarbeiters P. Szily durch verschiedene Mischungen von primären und sekundären Kaliumphosphat erzeugte. Dennach ist Szily als Erfinder der Pufferlösungen zu betrachten und in Kenntnis seiner besprochenen Vorarbeiten darf wohl angenommen werden, dass er die Anregung zu Friedenthals kolorimetrischer pH-Bestimmungsmethode gab, die die Grundlage zu jedem späteren derartigen Verfahren bot.

Obwohl die Erfindung<sup>15</sup> der Isotopen-Verdünnungsanalyse im Jahr 1913 ausserhalb Ungarns erfolgte, ist der eine der Erfinder, Georg Hevesy ebenfalls Ungar. Ihm ist übrigens auch die Aktivierungsanalyse (1936) zu verdanken,<sup>16</sup> der heute eine immer bedeutendere Rolle in der Spuren- und Ultrapurenanalyse zukommt.

Zwischen die zwei Weltkriege fällt die Tätigkeit von László Szebellédy (1901–1944), der Nachfolger von Winkler im Institut für anorganische und analytische Chemie der Universität Budapest war. Er erfand mit Zoltán Somogyi die coulometrische Analyse<sup>17</sup> und eröffnete mit seinen Mitarbeitern neue Gebiete der katalytischen Mikroanalyse.

Nach dem zweiten Weltkrieg nahm die analytische Forschung in Ungarn einen raschen Aufschwung, da die Forschertätigkeit vom Staat weitgehend gefördert wird. Die analytische Forschung erfolgt in erster Linie in den durch Mittel der Ungarischen Akademie der Wissenschaften unterstützten Universitätsinstituten für analytische Chemie. Die entsprechenden Lehrstühle sind: Das Institut für anorganische und analytische Chemie der Roland Eötvös Universität, Budapest, (gegründet 1769) unter der Leitung von Elemér Schulek, Mitglied der Ungarischen Akademie der Wissenschaften.

Das Institut für allgemeine Chemie der Technischen Universität Budapest (gegründet 1845) unter der Leitung von László Erdey, Mitglied der Ungarischen Akademie der Wissenschaften.

Das Institut für anorganische und analytische Chemie der Universität Szeged unter der Leitung von Zoltán G. Szabó, Mitglied der Ungarischen Akademie der Wissenschaften.

Das Institut für anorganische und analytische Chemie der Lajos Kossuth Universität Debrecen unter der Leitung von Pál Szarvas.

Das Institut für Chemie der Technischen Universität für Schwerindustrie Miskolc (das für Rechtsnachfolger des 1763 gegründeten chemischen Instituts der Bergakademie Selmečbánya gehalten werden kann) unter der Leitung von János Bognár.

Das Institut für analytische Chemie der Technischen Universität für Chemische Industrie Veszprém unter Leitung von Ernő Púngor.

Ausser den erwähnten Instituten befasst man sich natürlich auch in anderen Universitätsinstituten und in gewissen industriellen Forschungsinstituten erfolgreich mit analytischen Untersuchungen.

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## INDIRECT DETERMINATION OF HYPOCHLORITE AND HYPOBROMITE BY ASCORBINOMETRIC TITRATION OF THALLIUM<sup>III</sup> IONS

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(Received 14 August 1962)

**Summary**—An indirect determination of hypochlorite and hypobromite has been developed. To the hypochlorite or hypobromite solution an excess of thallium<sup>I</sup> sulphate solution is added, and thallium<sup>III</sup> ions, formed in equivalent amount, can be titrated with ascorbic acid in the presence of Variamine Blue as indicator.

HYPOCHLORITE and hypobromite are mostly titrated by iodometric methods<sup>1</sup> or with arsenious acid.<sup>2</sup> The problems arising in the latter method were recently solved by developments in indicator research.<sup>3,4</sup> Some years ago we were successful in developing ascorbinometric methods for hypochlorite and hypobromite determinations using the iron<sup>III</sup>-iron<sup>II</sup>,<sup>5</sup> the iodine-iodide<sup>6</sup> and the hexacyanoferrate<sup>III</sup>-hexacyanoferrate<sup>II</sup>,<sup>7</sup> intermediate redox systems.

In connection with the ascorbinometric determination of thallium<sup>8</sup> we tried to determine hypochlorite and hypobromite ions using thallium<sup>III</sup>-thallium<sup>I</sup> as an intermediate redox system. This method is more advantageous than those already mentioned, because it is not necessary to work in a carbon dioxide atmosphere, and furthermore, the method is selective for hypochlorite.

The formal redox potentials of the hypochlorite-chlorine-chloride and hypobromite-bromine-bromide systems vary with pH. The formal redox potential of the thallium<sup>III</sup>-thallium<sup>I</sup> system is influenced partly by pH, and partly by the anions present in the solution. In the presence of chloride or bromide ions the formal redox potentials are determined by the stability of the thallium<sup>III</sup>-bromide or chloride complexes. These formal redox potentials can be calculated from the following equation:<sup>9</sup>

$$E = 1.25 + 0.03 \log \frac{[\text{Tl}^{\text{III}}]}{[\text{Tl}^{\text{I}}]}$$

(see Table I). The standard redox potential of the thallium<sup>III</sup>-thallium<sup>I</sup> system, measured in perchloric acid solution and extrapolated for an ionic strength  $i = 0$ ,<sup>10</sup> is 1.25v. In these calculations we took  $10^{-2}$  mole as the total thallium concentration. The complex ion concentration in the instability constant we regarded as equal to the thallium<sup>I</sup> concentration, because the complexes are fairly stable ones.

The formal redox potentials of the hypochlorite-chlorine-chloride and thallium<sup>III</sup>-thallium<sup>I</sup> systems, and of the hypobromite-bromine-bromide and thallium<sup>III</sup>-thallium<sup>I</sup> systems are shown in Fig. 1(a) and 1(b) as a function of pH.<sup>11</sup> The formal redox potential of the thallium<sup>III</sup>-thallium<sup>I</sup> system is determined up to a certain pH value by the stability of the chloride or bromide complex. This particular value of pH is

TABLE I.—FORMAL REDOX POTENTIAL VALUES FOR THE THALLIUM<sup>III</sup>-THALLIUM<sup>I</sup> SYSTEM IN SOLUTIONS CONTAINING CHLORIDE OR BROMIDE (total thallium concentration  $10^{-2}$  mole)

Complex-forming ion		Stability constant		Formal redox potential, $V$	
Nature	Concn., mole	More stable ion	Less stable ion	More stable ion	Less stable ion
Chloride	1 $10^{-1}$	$K_{[TlCl_4]^-} = 4 \times 10^{-19}$	$K_{[TlCl]^{2+}} = 8 \times 10^{-9}$	+0.70	+1.01
				+0.82	+1.04
Bromide	$10^{-1}$ $10^{-2}$	$K_{[TlBr_4]^-} = 1.3 \times 10^{-24}$	$K_{[TlBr]^{2+}} = 2 \times 10^{-10}$	+0.62	+0.99
				+0.74	+1.02

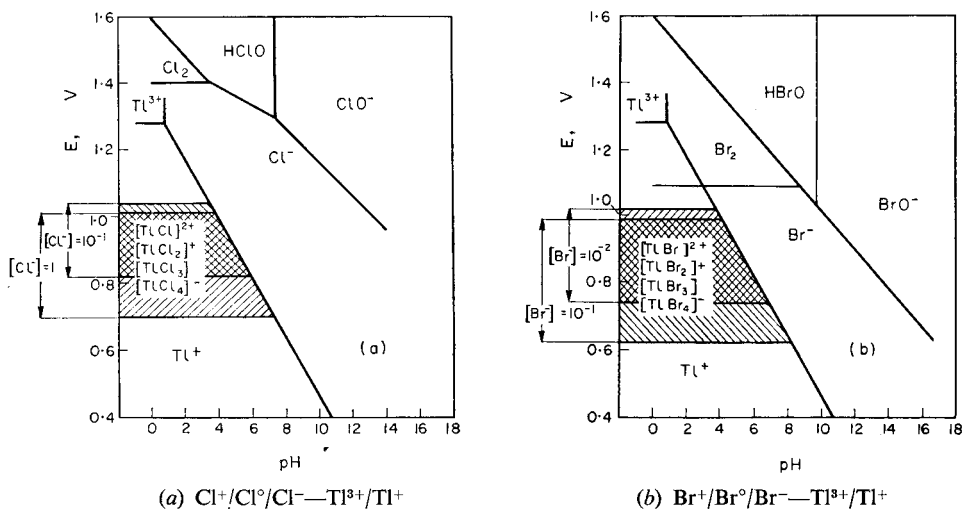


FIG. 1.—Formal redox potentials of the systems

that, at which the thallium<sup>III</sup> ion concentration, derived from the solubility of the thallium<sup>III</sup> hydroxide precipitate, becomes equal to the thallium<sup>III</sup> concentration arising from the dissociation of the complex. At a certain chloride or bromide concentration the various complexes cover the potential range.

## EXPERIMENTAL

### Reagents

**Ascorbic acid standard solution: 0.1N:** Nine g. of analytically pure ascorbic acid were dissolved in 1 litre of water, distilled from a glass apparatus. The solution was standardised against potassium iodate. If stored in air, ascorbic acid standard solution decomposes with a 1% daily loss in normality. This deterioration can be decreased by storing the ascorbic acid solution in a Winkler burette equipped with a carbon dioxide source.<sup>12</sup> 0.01N solution is prepared by weighing 0.9 g of ascorbic acid and dissolving in 1 litre of water. If stored under carbon dioxide, 0.01N ascorbic acid loses about 1% of its normality daily, and it is satisfactory to standardise it daily.

**Sodium hypochlorite solution: 0.1N:** This was prepared by saturation of water distilled from a glass apparatus with chlorine while cooling with ice water. Then sufficient 5N sodium hydroxide solution was added to turn the solution colourless, and finally sufficient was added in excess to render the solution 0.5N in sodium hydroxide. The hypochlorite content of the solution was determined with sodium arsenite in the presence of luminol,<sup>4</sup> or by iodometric titration. To conserve the solution, 20 ml of approximately 1M magnesium chloride solution and 4 ml of 6% sodium silicate solution were added to each litre with vigorous stirring. Finally sufficient 0.5N sodium hydroxide was added

to render the solution just 0.1*N* in sodium hypochlorite. The solution was shaken thoroughly. On the following day the clear portion of the solution was drawn off. (The solution, prepared in this way, is highly stable, because the precipitated magnesium hydroxide binds all traces of metal ions which might catalyse the decomposition of the solution.) The solution was then standardised with sodium arsenite.

0.01*N* solution is prepared by dilution of the 0.1*N* solution with 0.5*N* sodium hydroxide.

*Sodium hypobromite solution:* 0.1*N*: 500 ml of water, distilled from glass apparatus, were saturated with bromine and 500 ml of 1*N* sodium hydroxide were added. The solution was standardised with arsenious acid in the presence of luminol indicator,<sup>4</sup> or by iodometric titration. The normality of the solution was adjusted to exactly 0.1*N*, and the solution was newly standardised.

0.01*N* solution is prepared from the 0.1*N* solution by dilution with 0.5*N* sodium hydroxide.

*Thallium<sup>I</sup> sulphate standard solution:* 0.1*N*: 12.622 g of analytically pure thallium<sup>I</sup> sulphate were dissolved in water and made up to 1 litre.

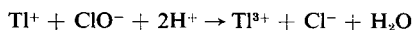
0.01*N* solution is prepared by dilution from the 0.1*N* solution.

*Acetic acid-acetate buffer:* This was a 1:2 (v:v) mixture of 2*N* sodium acetate and 2*N* acetic acid (pH about 4.1).

*Variamine Blue indicator:* 1 part of Variamine Blue (4-amino-4'-methoxydiphenylamine hydrochloride) was mixed with 400 parts of sodium chloride. Of this solid mixture about 0.2 g was used for each titration. The acetic acid salt can be also used.<sup>13</sup>

#### Procedures

In order to determine the best experimental circumstances, a series of titrations at various acid concentrations was performed. To 25 ml of thallium<sup>I</sup> sulphate solution 20 ml of 0.1*N* sodium hypochlorite and various amounts of sulphuric or hydrochloric acid were added. The solutions were mixed well and 2*N* sodium hydroxide was added until a brownish-yellow colour appeared. Then 10 ml of buffer solution and 0.2 g of indicator were added, and the solution was titrated with 0.1*N* ascorbic acid up to the decolorisation of the indicator. If acidification was carried out with 2*N* sulphuric acid, the oxidation to thallium<sup>III</sup> was incomplete. If, however, hydrochloric acid was used, even if 1 ml of 2*N* acid was present in excess, the reaction

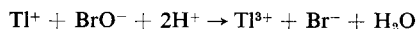


took place quantitatively. If a greater excess (30 ml) of the acid was added, the reaction continued to accord with this equation.

An excess of thallium<sup>I</sup> sulphate (1–40 ml) has no influence on the results.

The reaction begins even in alkaline medium, this being indicated by the formation of a brownish-black thallium<sup>III</sup> hydroxide precipitate when sodium hypochlorite is added to the thallium<sup>I</sup> sulphate solution. If hydrochloric acid is added, the precipitate either turns white, through formation of thallium<sup>I</sup> chloride precipitate, or, if the relative concentrations of thallium<sup>I</sup> and chloride ions are correct, the precipitate dissolves completely. The precipitate which is occasionally formed does not interfere in the ascorbinometric titration of thallium<sup>III</sup>.

It was found that for the reaction



to proceed quantitatively, at least 15 ml of 2*N* hydrochloric acid in excess are needed. If the amount of hydrochloric acid is less, a negative error of 1.0–1.6% occurs. It is advisable to add hydrochloric acid in this case in the form of a 4*N* solution to avoid large volumes in the titrations. The excess of thallium<sup>I</sup> ions does not influence the results in this case either.

If titrations were carried out on the 0.01*N* range, negative errors of about 1% were found. On the 0.01*N* scale the concentration ratio of chloride and thallium<sup>III</sup> ions is about 10-fold that on the 0.1*N* scale, and therefore it can be assumed that complex formation takes place to a greater extent. Therefore the redox potential of the thallium<sup>III</sup>-thallium<sup>I</sup> system becomes more negative, and at the end of the titration small amounts of thallium<sup>III</sup> ions remain untitrated when the colour of the Variamine Blue disappears. If part of the acid was added as sulphuric acid, the results became quantitative.

#### Procedure for hypochlorite determination

To a solution of 25–250 mg of hypochlorite add an excess (10–55 ml) of 0.1*N* thallium<sup>I</sup> sulphate solution. Mix the solution well, and add 15 ml of 2*N* hydrochloric acid. Mix once more. Then add 2*N* sodium hydroxide until precipitation begins, followed by 10 ml of buffer solution. After addition of 0.2 g of Variamine Blue solid indicator mixture, titrate the solution with 0.1*N* ascorbic acid solution until the indicator decolorises. In the 0.01*N* range the titration can be carried out similarly.

*Procedure for hypobromite determination*

To a solution of 47–470 mg of hypobromite add an excess of thallium<sup>I</sup> sulphate solution, mix well, add 20 ml of 4*N* hydrochloric acid and mix once more. Then add 2*N* sodium hydroxide until thallium<sup>III</sup> hydroxide precipitate is formed, and follow with 10 ml of buffer solution. Add 0.2 g of Variamine Blue solid indicator mixture, and titrate with 0.1*N* ascorbic acid solution to decolorisation.

If the titration is carried out in the 0.01*N* range, acidification must be made with a mixture of 12 ml of 4*N* sulphuric acid and 8 ml of 4*N* hydrochloric acid.

The results of hypochlorite and hypobromite determinations are summarised in Table II. The accuracies of the methods are given in Table III.

Determinations of hypochlorite were also made in the presence of chlorite ions. It was found that if the chlorite:hypochlorite ratio is not greater than 1, hypochlorite can be determined accurately.

The method can readily be applied in practice to such determinations as that of the active chlorine content of chlorinated lime. The method proved to be highly advantageous, because only the hypochlorite content was measured and chlorite was not titrated.

TABLE II—TITRATION RESULTS

0.1 <i>N</i> NaOCl true value, ml	0.1 <i>N</i> NaOCl found, ml	Deviation from true value		0.01 <i>N</i> NaOCl true value, ml	0.01 <i>N</i> NaOCl found, <sup>a</sup> ml	Deviation from true value	
		ml	%			ml	%
4.90	4.88	-0.02	-0.40	5.07	5.04	-0.03	-0.59
9.80	9.80	±0.0	±0.0	10.03	9.98	-0.05	-0.49
19.59	19.54	-0.05	-0.26	20.05	19.99	-0.06	-0.29
29.34	29.17	-0.17	-0.58	30.08	30.00	-0.08	-0.26
48.94	48.75	-0.19	-0.39	50.02	49.87	-0.17	-0.34

0.1 <i>N</i> NaOBr true value, ml	0.1 <i>N</i> NaOBr found, ml	Deviation from true value		0.01 <i>N</i> NaOBr true value, ml	0.01 <i>N</i> NaOBr found, ml	Deviation from true value	
		ml	%			ml	%
5.03	5.03	±0.0	±0.0	5.03	4.97	-0.06	-1.2
10.05	10.03	-0.02	-0.10	10.05	9.98	-0.07	-0.70
20.10	20.10	±0.0	±0.0	20.10	19.98	-0.12	-0.60
30.16	30.15	-0.01	-0.03	30.16	29.96	-0.20	-0.63
50.21	50.07	-0.14	-0.27	50.21	49.72	-0.49	-0.98

<sup>a</sup> Means of three determinations.

TABLE III—TITRATION OF NaOCl AND NaOBr

	Concen- tration, <i>N</i>	Number of measure- ments	Deviation from true value, %	Standard deviation	
				ml	%
NaOCl	0.1	6	-0.26	±0.01	±0.07
	0.01	6	-0.29	±0.01	±0.06
NaOBr	0.1	6	±0.0	±0.01	±0.06
	0.01	6	-0.55	±0.02	±0.09

**Zusammenfassung**—Eine indirekte Methode zur Bestimmung von Hypochlorit und Hypobromit wurde ausgearbeitet. Zur Hypochlorit oder -bromid Lösung wird Thallium(I)sulfat im Überschuss zugesetzt und das in äquivalenter Menge gebildete Thallium(III) mit Ascorbinsäure unter Verwendung von Variaminblau als Indicator titriert.



**Résumé**—Les auteurs ont étudié le dosage indirect des hypochlorites et des hypobromites. On ajoute un excès d'une solution de sulfate de thallium(I) et les ions Tl(III) formés sont titrés par l'acide ascorbique en présence de bleu de variamine comme indicateur.

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## INVESTIGATION OF THE OXIDATION STATE OF CERIUM IN HOT SULPHURIC ACID SOLUTIONS

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(Received 14 August 1962)

**Summary**—The reduction of cerium<sup>IV</sup> in hot concentrated sulphuric acid and in sulphuric acid hydrates, respectively, is investigated. It is found that on raising the concentration of sulphuric acid, the degree of reduction also increases. The degree of reduction depends to a great extent on the relative quantities of solid substance weighed and of sulphuric acid used for the boiling treatment. In contrast to other suggested mechanisms, no correlation is found to exist between the gaseous oxygen developed during reduction and the oxygen bound by sulphuric acid.

### INTRODUCTION

IN earlier communications<sup>1,2,3,4</sup> investigations of the changes in the oxidation states of various elements were described in detail, and we concluded that in boiling concentrated sulphuric acid and in sulphuric acid hydrates, respectively, the various elements behave in a different manner. On the basis of this behaviour it is possible to classify the elements into five groups:

1. No changes occur (*e.g.* silver, arsenic).
2. A higher oxidation state results (*e.g.* iron).
3. The element is converted into a lower oxidation state (*e.g.* thallium, chromium).
4. Reduction progresses to the metallic state (*e.g.* gold).
5. An equilibrium is set up between the higher and lower oxidation states (*e.g.* vanadium).

Previously we have succeeded in utilising the results of these investigations for analytical purposes: arsenic and thallium can be determined in the presence of each other without any preliminary separation.<sup>5</sup>

Investigation of the oxidation states of cerium has now been carried out in essence by the technique applied in the above-mentioned researches. Reduction of cerium<sup>IV</sup> was followed by iodometry. Consequently, the content of cerium<sup>IV</sup> in the cerium<sup>IV</sup> sulphate preparation was also controlled by iodometry, and the mean values of 12 measurements showing results in fair accordance were accepted as fundamental values for comparison.

### EXPERIMENTAL

#### *Content of cerium<sup>IV</sup> in cerium<sup>IV</sup> sulphate*

Weigh 3–5 cg of  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  ("Merck puriss." grade) into a 100-ml titration flask with a ground-glass stopper. Dissolve in 10 ml of distilled concentrated sulphuric acid<sup>6</sup> diluted with water (1:1), then dilute the solution with distilled water two-fold. Add 1 g of crystalline potassium hydrogen carbonate and 0.5 g of potassium iodide. Allow to stand 15 min, then titrate the liberated iodine with 0.01 *M* standard sodium thiosulphate solution in the presence of 10 drops of a 1% starch solution.

*Investigation of oxidation state of cerium*

The boiling treatment was carried out in the long neck Kjeldahl flasks successfully applied in our earlier investigations. These flasks can be equipped with reflux ball-condenser attachments with ground-glass joints. Boiling was performed on using a micro-flame under continuous water cooling.

Weigh by difference 40–50 mg of cerium<sup>IV</sup> sulphate into a flask. Add 10 ml of distilled concentrated sulphuric acid<sup>6</sup> or sulphuric acid hydrate and two glass beads. Boil 5 to 30 min in the case of concentrated sulphuric acid and 1–30 hr in the case of sulphuric acid hydrates, respectively. On cooling, dilute with 20 ml of distilled water, then add 1 g of crystalline potassium hydrogen carbonate and 0.5 g of potassium iodide. The amount of iodine equivalent to the quantity of cerium<sup>IV</sup> remaining after boiling was measured in the conventional way: allow to stand 15 min, then titrate with 0.01*N* standard sodium thiosulphate solution.

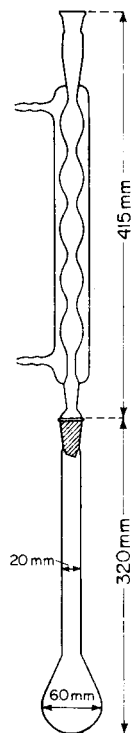


FIG. 1.

TABLE I—REDUCTION IN CONCENTRATED SULPHURIC ACID

Boiling period, <i>min</i>	Cerium <sup>IV</sup> sulphate		Degree of reduction, %
	Weighed, <i>mg</i>	Found, <i>mg</i>	
5	42.1	8.0	81.0
	40.4	8.1	79.9
10	42.2	2.5	94.1
	41.2	2.3	94.4
20	42.4	1.7	96.0
	42.2	1.9	95.5
30	Complete reduction attained		

It appears from Table I, that on boiling cerium<sup>IV</sup> in concentrated sulphuric acid, reduction takes place very quickly, and it becomes quantitative within a short period. Under the conditions described above, on boiling for 5 min, 80% of cerium<sup>IV</sup> is reduced to cerium<sup>III</sup>, while reduction is complete on boiling the solution for 30 min.

In Table II the mean values of the results of measurements carried out in many repetitions in various sulphuric acid hydrates are summarised. It appears that the degree of reduction decreases rapidly with rise of water content. In sulphuric acid octahydrate, even after boiling for 30 hr, no traces of any reduction could be observed.

In order to facilitate comparison, the data presented in Tables I and II are also shown graphically in Fig. 2.

TABLE II—REDUCTION IN VARIOUS SULPHURIC ACID HYDRATES

Boiling period, <i>hr</i>	Degree of reduction of cerium <sup>IV</sup> sulphate, %				
	Monohydrate	Dihydrate	Tetrahydrate	Hexahydrate	Octahydrate
1	30.8	16.1	12.6	2.3	
3	39.1	20.2	14.4	2.8	
5	42.0	20.8	14.4	3.3	
7	46.0	21.0	14.5	3.5	
15	54.8	21.1	15.0	4.0	
30	55.9	21.7	16.1	4.0	No reduction observed

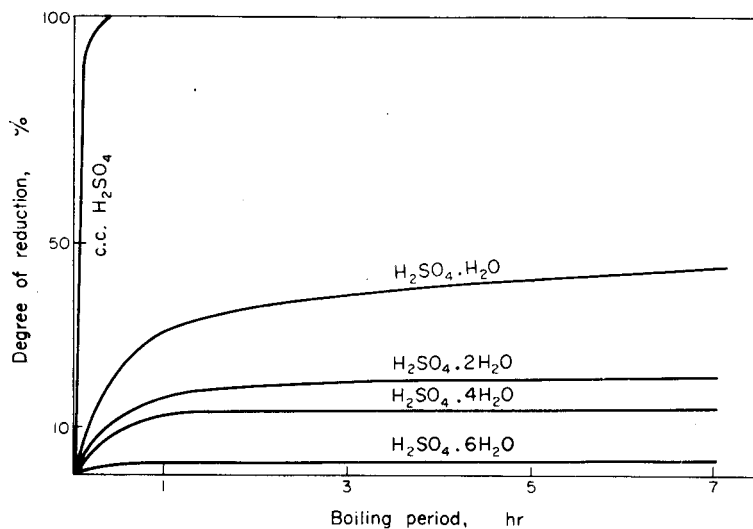


FIG. 2.

In further investigations, experiments were carried out to establish the dependence of the degree of reduction of cerium<sup>IV</sup> on the ratio of the quantity of sulphuric acid used in the boiling procedure to that of cerium sulphate weighed. As expected, on raising the ratio sulphuric acid:cerium sulphate, the degree of reduction also rapidly increases.

In one series of measurements, various amounts of cerium<sup>IV</sup> sulphate were boiled with 10 ml of concentrated sulphuric acid. In another series of experiments, the weighed quantity of cerium<sup>IV</sup> sulphate ranged from 80 to 85 mg while the volume of concentrated sulphuric acid was varied. The mean values of the results of the measurements are presented in Tables III and IV.

TABLE III—MEASUREMENTS IN THE PRESENCE OF 10 ml OF CONCENTRATED SULPHURIC ACID

Boiling period, <i>min</i>	Degree of reduction of cerium <sup>IV</sup> sulphate, %					1 g
	10–20 mg	40–50 mg	80–100 mg	160–200 mg	400–500 mg	
5	90.5	80.1	49.4	5.0	3.1	—
10	96.5	94.3	66.5	9.9	5.5	—
20	c.r.	c.r.	95.5	13.3	6.7	3.2
30	c.r.	c.r.	95.5	21.2	13.1	5.9
40	c.r.	c.r.	98.1	37.0	19.0	7.0
60	c.r.	c.r.	c.r.	55.8	34.5	8.1

c.r. = complete reduction

In future experiments we plan to continue our investigations with measurements in an ultrathermostat, in order to examine the dependence of the reduction process on temperature.

Results of great value from the aspect of analytical chemistry are expected from an examination of the decomposition of peroxydisulphuric acid in the presence of cerium<sup>IV</sup>.

TABLE IV—MEASUREMENTS IN THE PRESENCE OF 80–85 mg OF CERIU<sup>IV</sup> SULPHATE

Boiling period, <i>min</i>	Degree of reduction, %			
	3 ml	5 ml	10 ml	20 ml of conc. H <sub>2</sub> SO <sub>4</sub>
5	28.4	38.1	49.6	67.1
10	31.3	45.8	66.5	81.0
20	38.0	60.1	85.1	89.2
30	42.2	65.2	95.6	97.6
40	44.5	70.9	98.0	c.r.
60	52.7	78.4	c.r.	c.r.

c.r. = complete reduction

Lastly, we mention here that, just as in one of our earlier communications,<sup>7</sup> measurements were also carried out using sulphuric acid enriched in <sup>18</sup>O in order to establish the origin of the gaseous oxygen liberated during the reduction of cerium. According to our results, the mechanism observed in the case of chromium<sup>VI</sup> and manganese<sup>VII</sup> does not hold for the reaction of cerium<sup>IV</sup> with sulphuric acid, where not even a simple isotope exchange was proved to take place.

**Zusammenfassung**—Die Reduktion von Cer/IV/ in heisser konzentrierter Schwefelsäure bzw. in Schwefelsäurehydraten wurde untersucht. Es wurde festgestellt, dass durch Erhöhung der Schwefelsäurekonzentration auch das Mass der Reduktion zunimmt. Nach den Untersuchungsergebnissen ist das Mass der Reduktion von den relativen Mengen der eingewogenen festen Substanz und der zum Kochen angewandten Schwefelsäure stark abhängig. In Gegensatz zu anderen vorgeschlagenen Mechanismen wurde bestätigt, dass zwischen dem während der Reaktion entwickelten Sauerstoffgas und dem durch Schwefelsäure gebundenen Sauerstoff kein Zusammenhang besteht.

**Résumé**—La réduction du cérium(IV) dans l'acide sulfurique concentré et chaud et dans les hydrates de l'acide sulfurique respectivement a été étudiée. Il a été montré qu'en augmentant la concentration de l'acide sulfurique le degré de réduction augmente. D'après le résultat des mesures effectuées le degré de réduction dépend en grande partie des quantités relatives de substances solides utilisées et de l'acide sulfurique utilisé pour le traitement à l'ébullition. Contrairement à d'autres mécanismes proposés il a été montré qu'il n'existe pas de corrélation entre l'oxygène gazeux dégagé au cours de la réduction et l'oxygène lié à l'acide sulfurique.

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## INDUCED REACTIONS IN THE PEROXY COMPOUNDS—IV

### A STUDY OF THE $\text{H}_2\text{O}_2$ - $\text{OsO}_4$ - $\text{KMnO}_4$ [AND $-\text{Ce}(\text{SO}_4)_2$ ] SYSTEM

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**Summary**—It has been observed that the decomposition of hydrogen peroxide is induced if it is oxidised by 1-equivalent reagents (potassium permanganate or cerium<sup>IV</sup> sulphate). The main factors of this induced chain decomposition as well as the effects of foreign substances are described in detail.

It is known that during the oxidimetric determination of hydrogen peroxide in the presence of osmium tetroxide, a considerable negative error occurs. Because at the acid concentration employed osmium tetroxide sparingly catalyses the decomposition of hydrogen peroxide, it is reasonable to suppose that in the  $\text{H}_2\text{O}_2$ - $\text{OsO}_4$ - $\text{KMnO}_4$  [or  $-\text{Ce}(\text{SO}_4)_2$ ] system the induced decomposition of hydrogen peroxide takes place. A study of this induced reaction appears interesting not only because the results obtained may contribute to a more correct knowledge of induced reactions of peroxy compounds, but also because data may be obtained to elucidate the mechanism of osmium tetroxide catalysis.

#### EXPERIMENTAL

##### Reagents

0.1N  $\text{KMnO}_4$  and 0.1N  $\text{As}_2\text{O}_3$  reagents: Prepared from c.p. chemicals and standardised in the usual manner.

0.01M  $\text{OsO}_4$  solution in 0.1N sulphuric acid: Prepared and diluted with 0.1N sulphuric acid as required.

0.44N (about 2%) nitric acid solution: Prepared by diluting c.p. concentrated acid.

To study the effect of foreign substances c.p. chemicals were employed.

##### Procedure

For the study of the induced decomposition of hydrogen peroxide it was desirable to establish such experimental conditions under which, on the one hand, there appears a considerable error and, on the other, which assure the greatest reproducibility.

According to the preliminary investigations the acid concentration decreases the induction error. Samples of 150-ml initial volume contained 20 ml of 0.44N nitric acid.

Alteration of the stirring rate similarly exerts a marked influence on the measurements. To avoid a fluctuation in data from changes in the stirring rate, a synchronous motor of high output, fitted with a glass propeller, was employed.

It was necessary to keep the rate of the titration constant. A capillary of corresponding diameter was therefore fitted to the burette by means of a rubber tube. The average delivery rate of the reagent was  $2.52 \pm 0.18$  ml/min in the 1 to 10-ml range (Table I) and the reproducibility was sufficient.

Because hydrogen peroxide reacted too slowly, with permanganate at the applied low acid concentration and at great dilution at the beginning of the titration the permanganate colour temporarily remained. The slow initial rate of the reaction does not disturb the determination of the end-point; however, it is not without influence on the results.

According to Tables II and III permanganate, accumulated during slow periods of the reaction but disappearing instantaneously after some time, does not cause an induced error. Therefore the initial period of the reaction cannot be well reproduced in spite of the utmost care and before titration 2 ml of 1% manganese<sup>II</sup> nitrate solution were added to each sample. This amount of manganese<sup>II</sup> ensures the instantaneous reaction of potassium permanganate from the very beginning.

TABLE I—DELIVERY RATE OF THE  
PERMANGANATE SOLUTION

0.1N KMnO <sub>4</sub> , ml	Time, min	Delivery rate, ml/min
1.00	0.370	2.70
2.00	0.762	2.62
3.00	1.168	2.57
4.00	1.550	2.58
5.00	1.990	2.51
6.00	2.390	2.50
7.00	2.790	2.50
8.00	3.242	2.47
9.00	3.700	2.44
10.00	4.269	2.34
Average: 2.523		

TABLE II—EFFECT OF INITIAL RATE OF THE REACTION BETWEEN H<sub>2</sub>O<sub>2</sub>—KMnO<sub>4</sub>  
ON THE INDUCED ERROR

0.1N H <sub>2</sub> O <sub>2</sub> , ml		0.1N As <sub>2</sub> O <sub>3</sub> , ml	0.1N KMnO <sub>4</sub> , ml	OsO <sub>4</sub>	ΔH <sub>2</sub> O <sub>2</sub> ,* ml
Taken	Found				
8.92	7.02	—	1.90	+	1.82
—	7.10	9.90	2.80	—	—
8.92	6.82	—	2.10	+	2.02
—	6.90	9.90	3.00	—	—
8.92	6.92	—	2.00	+	2.02
—	6.90	9.90	3.00	—	—
8.92	6.90	—	2.02	+	2.07
—	6.85	9.90	3.05	—	—

\* 20 ml of 2% KNO<sub>3</sub> added to a known amount of hydrogen peroxide, diluted to 150 ml with water and stirring started (1260 rpm). Then 2 ml of  $6 \times 10^{-4}M$  OsO<sub>4</sub> added to the solution and the titration begun at a constant delivery rate. First the permanganate colour remained. The burette was closed when the solution suddenly lost its colour. This consumption was noted. Then arsenous acid was added and its excess determined permanganometrically. By this method the amount of untitrated hydrogen peroxide in the solution was determined.

TABLE III—EFFECT OF MANGANESE<sup>II</sup> IONS ON THE INDUCED  
ERROR

0.1N H <sub>2</sub> O <sub>2</sub> , ml		OsO <sub>4</sub>	2 ml of 1% Mn(NO <sub>3</sub> ) <sub>2</sub>	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
10.00	10.00	—	—	0.00
10.00	6.45	+	—	-3.55
10.00	6.55	+	—	-3.4
10.00	6.37	+	—	-3.63
10.00	5.67	+	+	-4.33
10.00	5.67	+	+	-4.33
10.00	5.67	+	+	-4.33

In view of the above mentioned facts, the following method was developed for the study of the induced reaction: Measure 20 ml of 0.44N nitric acid, 10 ml of 0.1N hydrogen peroxide and 2 ml of 1% manganese<sup>II</sup> nitrate solution into a 250-ml beaker and dilute to 150 ml. Then add 2 ml of  $6 \times 10^{-4}M$  osmium tetroxide solution and start the stirring at 1260 rpm. Begin the titration 1 min after the addition of osmic acid and continue till the permanganate colour remains.

Besides the direct method, there was frequently used an indirect one which made it possible to determine the hydrogen peroxide content without induced error. To this end arsenous acid in known quantity was added to the solution at the required phase of the permanganometric titration, and the excess of arsenous acid was back-titrated permanganometrically.

## RESULTS

## I. Induced decomposition of hydrogen peroxide in absence of foreign substances

(1) The rate of the titration markedly influences the induced decomposition (Table IV). On decreasing the delivery rate the error first strongly increases, then after about 5 min it reaches a limiting value.

TABLE IV—EFFECT OF TITRATION RATE ON THE INDUCED REACTION

0.1N H <sub>2</sub> O <sub>2</sub> , ml		OsO <sub>4</sub> *	Time, min	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
9.30	9.30	—	—	0.00
9.30	8.69	+	0.23	-0.61
9.30	8.57	+	0.26	-0.73
9.30	7.31	+	0.72	-1.99
9.30	7.03	+	0.84	-2.27
9.30	6.79	+	1.22	-2.61
9.30	5.99	+	1.99	-3.31
9.30	5.33	+	2.08	-3.97
9.30	4.32	+	3.26	-4.98
9.30	3.72	+	4.61	-5.58
9.30	3.66	+	4.83	-5.64
9.30	3.45	+	6.95	-5.85
9.30	3.18	+	9.82	-6.12

\*  $7.8 \times 10^{-6}M$  OsO<sub>4</sub>

(2) With increasing dilution of the titrated solution, keeping the acid concentration constant, the induced error considerably increases (Fig. 1).

(3) Increasing the stirring rate markedly increases the induced reaction (Fig. 2).

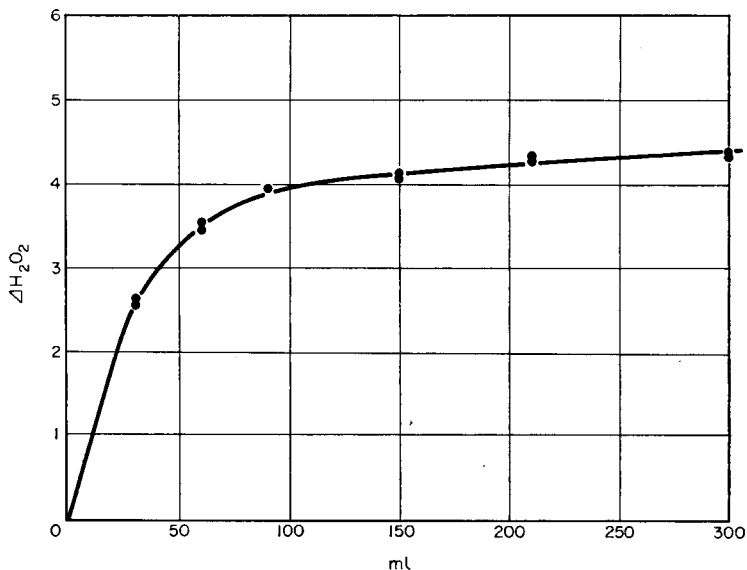


FIG. 1.



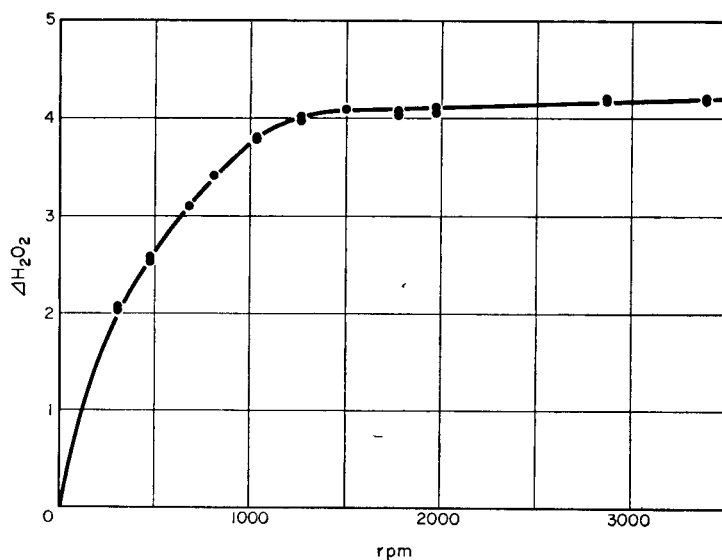


FIG. 2.

(4) Increase of the acid concentration lowers the induced error (Table V). From Tables V and VI the error-decreasing effect depends on the strength of the acids:  $HClO_4 > HNO_3 > H_2SO_4 > H_3PO_4$ .

TABLE V—EFFECT OF ACID CONCENTRATION OF THE SOLUTION ON THE INDUCED ERROR

0.1N $H_2O_2$ , ml		$OsO_4$	$HNO_3$ , N	$\Delta H_2O_2$ , ml
Taken	Found			
9.30	9.30	—	—	0.00
9.30	4.77	+	0.0147	-4.53
9.30	4.75	+	0.0147	-4.55
9.30	5.38	+	0.0588	-3.92
9.30	5.38	+	0.0588	-3.92
9.30	5.42	+	0.07	-3.88
9.30	5.96	+	0.1176	-3.34
9.30	5.95	+	0.1176	-3.35
9.30	6.65	+	0.236	-2.65
9.30	6.75	+	0.236	-2.55
9.30	7.39	+	0.354	-1.91
9.30	7.41	+	0.354	-1.89
9.30	7.53	+	0.7000	-1.77
9.30	7.81	+	1.000	-1.49
9.30	7.80	+	1.000	-1.50
9.30	8.50	+	2.65	-0.80
9.30	8.67	+	3.000	-0.63
9.30	8.63	+	3.000	-0.67
9.30	8.96	+	5.000	-0.34
9.30	9.00	+	5.000	-0.30

(5) The induced decomposition is proportional to the hydrogen peroxide concentration (Table VII).

(6) With an increase in the osmium tetroxide concentration the induced error strongly increases (Table VIII). At a fairly high osmic acid concentration ( $10^{-4}M$ ) the hydrogen peroxide-permanganate reaction becomes perceptibly slow.

TABLE VI—EFFECT OF THE QUALITY OF ACID ON THE INDUCED REACTION

0.1N H <sub>2</sub> O <sub>2</sub> , ml		OsO <sub>4</sub>	Acid concn., N	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
<b>HCl</b>				
9.32	9.32	—	—	0.00
9.32	6.85	+	0.07	-2.47
9.32	6.86	+	0.07	-2.46
9.32	8.66	+	0.70	-0.66
9.32	8.61	+	0.70	-0.71
9.32	8.83	+	7.75	-0.49
9.32	8.87	+	7.75	-0.45
<b>HClO<sub>4</sub></b>				
9.32	9.32	—	—	0.00
9.32	5.53	+	0.069	-3.79
9.32	5.58	+	0.069	-3.74
9.32	7.61	+	0.690	-1.71
9.32	7.63	+	0.690	-1.69
9.32	8.26	+	3.780	-1.06
9.32	8.21	+	3.780	-1.11
<b>H<sub>2</sub>SO<sub>4</sub></b>				
9.32	9.32	—	—	0.00
9.32	4.75	+	0.03	-4.57
9.32	4.76	+	0.09	-4.56
9.32	5.68	+	0.30	-3.64
9.32	5.70	+	0.30	-3.62
9.32	6.44	+	1.10	-2.88
9.32	6.41	+	1.10	-2.91
9.32	8.34	+	3.32	0.98
<b>H<sub>3</sub>PO<sub>4</sub></b>				
9.32	9.32	—	—	0.00
9.32	4.36	+	0.07	-4.96
9.32	4.72	+	0.70	-4.60
9.32	4.71	+	0.70	-4.61
9.32	5.85	+	3.00	-3.47
9.32	6.75	+	7.25	-2.57
9.32	6.72	+	7.23	-2.60

TABLE VII—EFFECT OF CHANGES IN HYDROGEN PEROXIDE CONCENTRATION ON THE INDUCED REACTION

0.1N H <sub>2</sub> O <sub>2</sub> , ml		OsO <sub>4</sub>	H <sub>2</sub> O <sub>2</sub> , N × 10 <sup>3</sup>	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
3.76	2.71	+	3.3	-1.05
7.53	4.50	+	6.6	-3.03
11.30	6.36	+	9.9	-4.94
11.30	6.38	+	9.9	-4.92
15.04	7.90	+	13.2	-7.14
15.04	7.93	+	13.2	-7.11
22.56	11.31	+	19.8	-11.25
22.56	11.38	+	19.8	-11.18
30.08	14.92	+	26.4	-15.16
37.60	18.61	+	33.0	-18.99

(7) With the aid of the indirect method the distribution of the induced error during titration was examined. At a constant delivery rate permanganate was added to the solution in varying quantity, then the hydrogen peroxide remaining was determined. The specific error,  $H_2O_2^*$  (the error caused by the reaction of 1 ml of permanganate) proved to be practically constant in the different phases of titration (Table IX).

(8) Measurements were made at the given delivery rate with 0.5-ml portions of permanganate added to the solution and waiting for 15, 30 and 50 sec after the addition of each portion. On comparing the obtained results with the data of continuous titration it appears that the waiting causes a slight increase in the error. The longer the waiting period, the greater is the deviation (Table X).

TABLE VIII—EFFECT OF CHANGES IN THE CONCENTRATION OF OSMIC ACID ON THE INDUCED REACTION

0.1N $H_2O_2$ , ml		$OsO_4$ ,	$\Delta H_2O_2$ ,
Taken	Found	$M \times 10^6$	ml
9.30	9.30	—	0.00
9.30	9.15	0.01	-0.15
9.30	8.96	0.10	-0.34
9.30	8.15	1.0	-1.15
9.30	8.15	1.0	-1.15
9.30	6.20	5.0	-3.10
9.30	6.22	5.0	-3.08
9.30	5.06	10.0	-4.24
9.30	5.12	10.0	-4.18
9.30	3.45	50.0	-5.85
9.30	3.47	50.0	-5.83
9.30	2.99	100.0	-6.31
9.30	2.91	100.0	-6.39
9.30	1.83	500.0	-7.47
9.30	1.86	500.0	-7.44

TABLE IX—DISTRIBUTION OF INDUCED ERROR DURING TITRATION

0.1N $H_2O_2$ , ml		$H_2O_2$ ,	0.1N $KMnO_4$ , ml		0.1N $As_2O_3$ ,	$\Delta H_2O_2^*$
Taken	Found	ml	Formerly added	Consumed	ml	ml
14.37	12.31	1.06	1.00	12.54	24.85	1.06
14.37	10.35	2.02	2.00	14.50	24.85	1.01
14.37	8.29	3.08	3.00	16.56	24.85	1.02
14.37	4.70	4.67	5.00	20.15	24.85	0.93
14.37	0.74	6.63	7.00	24.11	24.85	0.95
14.37	0.00	6.83	7.55	—	—	0.90

TABLE X—EFFECT OF FRACTIONAL TITRATION ON THE INDUCED REACTION

0.1N $H_2O_2$ , ml		$OsO_4$	Waiting time,	$\Delta H_2O_2$ ,
Taken	Found		sec	ml
9.58	9.58	—	—	0.00
5.64	9.58	+	—	-3.94
5.58	9.58	+	15	-4.00
5.35	9.58	+	30	-4.25
5.27	9.58	+	50	-4.31

(9) According to the data of Table XI, under optimal experimental conditions the limiting value of the induction factor is about 7.5.

TABLE XI

0.1N H <sub>2</sub> O <sub>2</sub> , ml		$\Delta$ H <sub>2</sub> O <sub>2</sub> , ml	OsO <sub>4</sub> , M × 10	H <sub>2</sub> O <sub>2</sub> *	F <sub>I</sub>	F <sub>e</sub>
Taken	Found					
1.92	0.68	1.24	6.67	0.65	1.82	1.93
3.84	1.16	2.68	6.67	0.70	2.31	3.78
5.76	1.37	4.39	6.67	0.76	3.20	6.34
7.68	1.49	6.19	6.67	0.81	4.15	10.55
9.60	1.62	7.98	6.67	0.83	4.93	16.30
14.40	2.18	12.22	6.67	0.85	5.60	25.00
18.14	2.54	15.60	6.67	0.86	6.15	38.70
27.21	3.25	23.96	6.67	0.88	7.37	482.0
48.00	5.78	42.22	6.67	0.88	7.30	310.0

(10) Experiments described under 1–9 were repeated with cerium<sup>IV</sup> sulphate instead of permanganate. The results agreed qualitatively with those obtained with permanganate but striking quantitative differences appeared. With cerium<sup>IV</sup> sulphate the induced error was always smaller than in the case of permanganate. It was observed that the induced error is partly reduced because cerium<sup>IV</sup> sulphate reacts more rapidly with hydrogen peroxide and moreover, the ferroin used as indicator exerts an inhibiting effect. The error-decreasing effect of ferroin can be well studied by permanganometric titrations. Ferroin indicator is irreversibly oxidised during titration: the colour of the indicator completely disappears before the end-point.

## II. Effect of foreign substances on the induced decomposition of hydrogen peroxide

A study of the effect of foreign substances was carried out as follows:

Acidify 10 ml of 0.1N hydrogen peroxide with 20 ml of 0.44N nitric acid and add 2 ml of 1% manganese<sup>II</sup> nitrate solution. Before the titration add osmium tetroxide solution ( $7.8 \times 10^{-8}M$ ) and dilute to 150 ml. Adjust the stirring rate to 1260 rpm (the delivery rate was  $2.52 \pm 0.18$  ml/ml).

Results are summarised below.

(1) Alkali metal and ammonium ions do not influence the induced reaction even in great quantity (Table XII).

(2) Alkaline earth metal ions proved to be ineffective (Table XIII).

(3) Beryllium, magnesium, zinc and cadmium ions were found to be ineffective (Table XIV). It must be noted, however, that the ions mentioned did not increase the induction error only if the salts employed were entirely pure. To remove the impurities D'Ans and Matter's method was applied.<sup>1</sup> We believe, that in the case of beryllium and cadmium ions the moderate increase in the error can be ascribed to impurities remaining in spite of purification, the solubility product of the hydroxide of these ions being smaller than that of magnesium hydroxide.

In contrast to the previous ions mercury<sup>II</sup> causes a marked increase in the induced error.

(4) In the presence of boric acid the induction error increases. A similar effect was experienced in the case of aluminium ions (Table XV). In the latter case the activity can be ascribed to the iron impurities.

Metasilicate ions increase the error (iron and copper impurities were found to be present). Tin<sup>IV</sup> ions practically do not influence the induced error.

TABLE XII—EFFECT OF ALKALI-METAL AND AMMONIUM IONS ON THE INDUCED REACTIONS

0.1 <i>N</i> H <sub>2</sub> O <sub>2</sub> , ml		Salt concn., <i>M</i> × 10 <sup>3</sup>	OsO <sub>4</sub>	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
<b>LiNO<sub>3</sub></b>				
8.98	8.98	—	—	0.00
8.98	5.50	—	+	-3.48
8.98	5.41	1.0	+	-3.57
8.98	5.38	1.0	+	-3.60
8.98	5.35	5.0	+	-3.63
8.98	5.50	5.0	+	-3.48
8.98	5.32	10.0	+	-3.66
8.98	5.38	10.0	+	-3.60
8.98	5.50	50.0	+	-3.48
8.98	5.50	50.0	+	-3.48
<b>NaNO<sub>3</sub></b>				
9.00	9.00	—	—	0.00
9.00	4.93	—	+	-4.07
9.00	4.93	1.0	+	-4.07
9.00	4.93	1.0	+	-4.07
9.00	4.83	5.0	+	-4.18
9.00	4.85	5.0	+	-4.15
9.00	4.93	10.0	+	-4.07
9.00	4.93	50.0	+	-4.05
9.00	4.93	50.0	+	-4.07
<b>KNO<sub>3</sub></b>				
9.58	9.58	—	—	0.00
9.58	5.64	—	+	-3.94
9.58	5.64	1.0	+	-3.94
9.58	5.64	1.0	+	-3.94
9.58	5.62	5.0	+	-3.96
9.58	5.64	5.0	+	-3.94
9.58	5.66	10.0	+	-3.92
9.58	5.64	10.0	+	-3.94
9.58	5.66	50.0	+	-3.92
<b>NH<sub>4</sub>NO<sub>3</sub></b>				
9.39	9.39	—	—	0.00
9.39	4.74	—	+	-4.65
9.39	4.82	1.0	+	-4.57
9.39	4.89	1.0	+	-4.50
9.39	4.74	5.0	+	-4.65
9.39	4.87	5.0	+	-4.52
9.39	4.80	10.0	+	-4.59
9.39	4.82	10.0	+	-4.57
9.39	4.80	50.0	+	-4.59
9.39	4.82	50.0	+	-4.57

(5) Halide ions strongly influence the induced decomposition. On adding fluoride ions the error increases, while in the case of chloride, bromide and iodide ions a strong decrease was found in the order given. Further, iodine also decreases the induced decomposition (Table XVI).

(6) As can be seen from data of Table XVII, lanthanum<sup>III</sup>, cerium<sup>III</sup> and uranium<sup>VI</sup> ions markedly decrease the induced decomposition, the effect of uranium<sup>VI</sup> being extremely strong.

(7) Manganese<sup>II</sup> ions, as has already been seen from Tables II and III, cause an increase in the induced error. On the other hand, chromium<sup>III</sup> ions exert a strong error-decreasing effect (Table XVIII).

TABLE XIII—EFFECT OF ALKALINE EARTH METAL IONS ON THE INDUCED REACTION

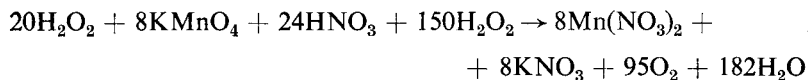
	0.1 <i>N</i> H <sub>2</sub> O <sub>2</sub> , ml Taken	Found	Salt concn., <i>M</i> × 10 <sup>3</sup>	OsO <sub>4</sub>	ΔH <sub>2</sub> O <sub>2</sub> ml
Ca(NO <sub>3</sub> ) <sub>2</sub>					
	9.32	9.32	—	—	0.00
	9.32	5.01	—	+	-4.31
	9.32	5.12	1.0	+	-4.20
	9.32	5.10	1.0	+	-4.22
	9.32	5.22	5.0	+	-4.10
	9.32	5.11	5.0	+	-4.21
	9.32	5.11	10.0	+	-4.21
	9.32	5.10	10.0	+	-4.22
	9.32	5.36	50.0	+	-3.96
	9.32	5.40	50.0	+	-3.92
Sr(NO <sub>3</sub> ) <sub>2</sub>					
	9.32	9.32	—	—	0.00
	9.32	4.83	—	+	-4.57
	9.32	4.95	1.0	+	-4.60
	9.32	4.82	1.0	+	-4.68
	9.32	5.01	5.0	+	-4.64
	9.32	4.98	5.0	+	-4.55
	9.32	5.00	10.0	—	
	9.32	4.96	10.0	+	-4.39
	9.32	5.00	50.0	+	-4.64
	9.32	4.86	50.0	+	-4.69
Ba(NO <sub>3</sub> ) <sub>2</sub>					
	9.39	9.39	—	—	0.00
	9.39	4.82	—	+	-4.57
	9.39	4.79	1.0	+	-4.60
	9.39	4.71	1.0	+	-4.68
	9.39	4.75	5.0	+	-4.64
	9.39	4.84	5.0	+	-4.55
	9.39	4.92	10.0	+	-4.47
	9.39	5.00	10.0	+	-4.39
	9.39	4.75	50.0	+	-4.64
	9.39	4.70	50.0	+	-4.69

(8) Iron<sup>III</sup> ions in small quantity strongly increase the error, while in greater quantity they decrease it. Cobalt<sup>II</sup> ions scarcely influence the induced error. Nickel<sup>II</sup> ions, however, result in an increase of error (Table XIX).

(9) Copper<sup>II</sup> and silver<sup>I</sup> ions are strong catalysts of the induced decomposition (Table XX).

#### DISCUSSION

From the data of Table XI it appears that under the most favourable experimental conditions the limiting value of function  $F_1 = f(Ac/I)_0$  is 7.3-7.5, which means that reacting 1 equivalent of permanganate induces the decomposition of about 7.5 equivalents of hydrogen peroxide. On the basis of this result the induced decomposition can be written formally by the following overall equation:



which points to this induced reaction belonging to the group of induced chain reactions.

TABLE XIV—EFFECT OF IONS OF THE ZINC GROUP ON THE INDUCED REACTION

0.1N H <sub>2</sub> O <sub>2</sub> , ml		Salt concn., M × 10 <sup>3</sup>	OsO <sub>4</sub>	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
<b>Be(NO<sub>3</sub>)<sub>2</sub></b>				
9.58	9.58	—	—	0.00
9.58	5.52	—	+	-4.06
9.58	5.48	1.0	+	-4.10
9.58	5.34	5.0	+	-4.24
9.58	5.08	10.0	+	-4.50
9.58	4.65	50.0	+	-4.93
<b>Mg(NO<sub>3</sub>)<sub>2</sub></b>				
9.32	9.32	—	—	0.00
9.32	5.58	—	+	-3.74
9.32	5.58	1.0	+	-3.74
9.32	5.62	1.0	+	-3.70
9.32	5.63	5.0	+	-3.69
9.32	5.62	5.0	+	-3.70
9.32	5.58	10.0	+	-3.74
9.32	5.64	10.0	+	-3.68
9.32	5.56	50.0	+	-3.76
9.32	5.58	50.0	+	-3.74
<b>Zn(NO<sub>3</sub>)<sub>2</sub></b>				
9.57	9.57	—	—	0.00
9.57	5.71	—	+	-3.86
9.57	5.66	1.0	+	-3.91
9.57	5.64	1.0	+	-3.93
9.57	5.69	5.0	+	-3.88
9.57	5.67	5.0	+	-3.90
9.57	5.69	10.0	+	-3.88
9.57	5.71	10.0	+	-3.86
9.57	5.69	50.0	+	-3.88
9.57	5.69	50.0	+	-3.88
<b>Cd(NO<sub>3</sub>)<sub>2</sub></b>				
9.70	9.70	—	—	0.00
9.70	5.65	—	+	-4.05
9.30	5.76	1.0	+	-3.94
9.70	5.70	5.0	+	-4.0
9.70	5.75	10.0	+	-3.95
9.70	5.80	50.0	+	-3.90
<b>Hg(NO<sub>3</sub>)<sub>2</sub></b>				
9.57	9.57	—	—	0.00
9.57	5.37	—	+	-4.20
9.57	5.33	1.0	+	-4.24
9.57	5.11	1.0	+	-4.46
9.57	4.77	5.0	+	-4.80
9.57	4.82	5.0	+	-4.75
9.57	4.23	10.0	+	-5.34
9.57	3.76	50.0	+	-5.81

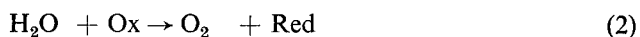
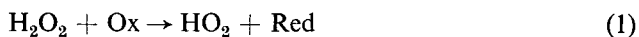
To understand the reaction in detail it is necessary to take into consideration the following potential equilibria:<sup>3</sup>



TABLE XV

0.1N H <sub>2</sub> O <sub>2</sub> , ml		Salt concn., M × 10 <sup>3</sup>	OsO <sub>4</sub>	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
<b>H<sub>3</sub>BO<sub>3</sub></b>				
9.57	9.57	—	—	0.00
9.57	5.64	—	+	-3.93
9.57	5.64	1.0	+	-3.93
9.57	5.58	1.0	+	-3.99
9.57	5.30	5.0	+	-4.27
9.57	5.34	5.0	+	-4.23
9.57	5.07	10.0	+	-4.50
9.57	5.14	10.0	+	-4.43
9.57	4.34	50.0	+	-5.23
9.57	4.32	50.0	+	-5.25
<b>Al(NO<sub>3</sub>)<sub>3</sub></b>				
9.57	9.57	—	—	0.00
9.57	5.60	—	+	-3.88
9.57	5.63	1.0	+	-3.94
9.57	5.64	1.0	+	-3.93
9.57	5.20	5.0	+	-4.37
9.57	5.18	5.0	+	-4.39
9.57	4.84	10.0	+	-4.73
9.57	4.87	10.0	+	-4.70
9.57	4.22	50.0	+	-5.35
<b>Na<sub>2</sub>SiO<sub>3</sub></b>				
9.58	9.58	—	—	0.00
9.58	5.64	—	+	-3.94
9.58	5.68	1.0	+	-3.90
9.58	5.53	5.0	+	-4.05
9.58	5.48	10.0	+	-4.10
9.58	5.38	50.0	+	-4.20
<b>Pb(NO<sub>3</sub>)<sub>2</sub></b>				
9.45	9.45	—	—	0.00
9.45	5.68	—	+	-3.77
9.45	5.68	1.0	+	-3.77
9.45	5.72	1.0	+	-3.73
9.45	5.78	5.0	+	-3.67
9.45	5.79	5.0	+	-3.66
9.45	5.88	10.0	+	-3.57
9.45	5.92	10.0	+	-3.53
9.54	5.72	50.0	+	-3.73

From this data it would be expected that the reaction of hydrogen peroxide with 1-equivalent oxidants would take place in two steps:



From the estimations of Baxendale<sup>5</sup> and Sigler and Masters<sup>6</sup> reaction (1) is about eight times slower than reaction (2). Therefore it would be expected that the HO<sub>2</sub> radical formed in reaction (1), having strong reducing properties, attacks the oxidant present in the solution. Such an oxidising agent in the H<sub>2</sub>O<sub>2</sub>-OsO<sub>4</sub> system may be the osmium tetroxide itself<sup>7</sup> and peroxyosmic acid formed by the interaction of the two partners. From the results of a polarographic study of the H<sub>2</sub>O<sub>2</sub>-OsO<sub>4</sub> system it can be concluded that in neutral and weakly acidic solutions (pH 7.5-6.0) peroxyosmic



TABLE XVI—EFFECT OF HALIDE IONS ON THE INDUCED REACTION

0.1N H <sub>2</sub> O <sub>2</sub> , ml		Salt concn., M × 10 <sup>3</sup>	OsO <sub>4</sub>	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
NaF				
9.45	9.45	—	—	0.00
9.45	5.59	—	+	-3.86
9.45	5.56	1.0	+	-3.89
9.45	5.53	1.0	+	-3.92
9.45	5.39	5.0	+	-4.06
9.45	5.45	5.0	+	-4.00
9.45	5.27	10.0	+	-4.18
9.45	5.29	10.0	+	-4.16
9.45	4.62	50.0	+	-4.83
9.45	4.57	50.0	+	-4.88
KCl				
9.43	9.43	—	—	0.00
9.43	5.52	—	+	-3.91
9.43	5.58	1.0	+	-3.85
9.43	5.55	1.0	+	-3.88
9.43	6.09	5.0	+	-3.34
9.43	6.12	5.0	+	-3.31
9.43	6.55	10.0	+	-2.88
9.43	6.47	10.0	+	-2.96
9.43	7.03	50.0	+	-2.40
9.43	6.99	50.0	+	-2.44
KBr				
9.44	9.44	—	—	0.00
9.44	5.63	—	+	-3.81
9.44	6.44	1.0	+	-3.00
9.44	6.43	1.0	+	-3.01
9.44	6.93	5.0	+	-2.51
9.44	6.92	5.0	+	-2.52
9.44	7.21	10.0	+	-2.23
9.44	7.18	10.0	+	-2.26
9.44	7.72	50.0	+	-1.72
9.44	7.78	50.0	+	-1.66
KI				
9.46	9.46	—	—	0.00
9.46	5.63	—	+	-3.83
9.46	5.87	0.2 × 10 <sup>3</sup>	+	-3.57
9.46	5.77	0.2 × 10 <sup>3</sup>	+	-3.69
9.46	6.72	0.66 × 10 <sup>3</sup>	+	-2.74
9.46	6.72	0.66 × 10 <sup>3</sup>	+	-2.74
9.46	7.72	2.0 × 10 <sup>3</sup>	+	-1.74
9.46	7.69	2.0 × 10 <sup>3</sup>	+	-1.77
9.46	7.85	3.3 × 10 <sup>3</sup>	+	-1.61
9.46	7.87	3.3 × 10 <sup>3</sup>	+	-1.59
9.46	8.53	6.6 × 10 <sup>3</sup>	+	-0.93
9.46	8.53	6.6 × 10 <sup>3</sup>	+	-0.93
9.46	8.92	33.3 × 10 <sup>3</sup>	+	-0.54
9.46	8.82	33.3 × 10 <sup>3</sup>	+	-0.64
9.46	9.05	100.0 × 10 <sup>3</sup>	+	-0.41
9.46	9.03	100.0 × 10 <sup>3</sup>	+	-0.43
9.46	9.18	160.0 × 10 <sup>3</sup>	+	-0.26
I <sub>2</sub>				
9.44	9.44	—	—	0.00
9.44	9.02	Saturated solution	+	-0.42
9.44	8.97	Saturated solution	+	-0.47

TABLE XVII

0.1N H <sub>2</sub> O <sub>2</sub> , ml		Salt concn., M × 10 <sup>3</sup>	OsO <sub>4</sub>	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
La(NO <sub>3</sub> ) <sub>3</sub>				
9.40	9.40	—	--	0.00
9.40	5.12	—	+	-4.28
9.40	5.15	1.0	+	-4.25
9.40	5.16	1.0	+	-4.24
9.40	5.20	5.0	+	-4.20
9.40	5.22	5.0	+	-4.18
9.40	5.34	10.0	+	-4.06
9.40	5.34	10.0	+	-4.06
9.40	5.55	50.0	+	-3.85
9.40	5.54	50.0	+	-3.86
Ce(NO <sub>3</sub> ) <sub>3</sub>				
9.45	9.45	—	—	0.00
9.45	5.38	—	+	-4.10
9.45	5.48	1.0	+	-3.97
9.45	5.74	5.0	+	-3.71
9.45	6.45	10.0	+	-3.00
9.45	6.86	50.0	+	-2.59
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>				
9.58	9.58	—	—	0.00
9.58	5.64	—	+	-3.94
9.58	5.84	1.0 × 10	+	-3.74
9.58	6.40	5.0 × 10	+	-3.18
9.58	6.73	10.0 × 10	+	-2.85
9.58	7.81	50.0 × 10	+	-1.77

TABLE XVIII

0.1N H <sub>2</sub> O <sub>2</sub> , ml		Salt concn., M × 10 <sup>3</sup>	OsO <sub>4</sub>	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
Mn(NO <sub>3</sub> ) <sub>2</sub>				
9.40	9.40	—	—	0.00
9.40	5.13	—	+	-4.27
9.40	5.98	0.02	+	-3.42
9.40	5.84	0.066	+	-3.56
9.40	5.66	0.33	+	-3.74
9.40	5.35	1.0	+	-4.05
9.40	5.36	1.0	+	-4.04
9.40	4.48	5.0	+	-4.92
9.40	4.46	5.0	+	-4.94
9.40	4.34	10.0	+	-5.06
9.40	4.31	10.0	+	-5.09
9.40	5.12	50.0	+	-4.28
Cr(NO <sub>3</sub> ) <sub>3</sub>				
8.85	8.85	—	—	0.00
8.85	4.85	—	+	-4.00
8.85	4.93	1.0	+	-3.92
8.85	4.85	1.0	+	-4.00
8.85	5.08	5.0	+	-3.77
8.85	5.12	5.0	+	-3.73
8.85	5.38	10.0	+	-3.47
8.85	5.38	10.0	+	-3.47
8.85	6.62	50.0	+	-2.23
8.85	6.52	50.0	+	-2.33

TABLE XIX

0.1N H <sub>2</sub> O <sub>2</sub> , ml		Salt concn., M × 10 <sup>3</sup>	OsO <sub>4</sub>	ΔH <sub>2</sub> O <sub>2</sub> , ml
Taken	Found			
Fe(NO <sub>3</sub> ) <sub>3</sub>				
9.46	9.46	—	—	0.00
9.46	5.65	—	+	-3.81
9.46	5.23	0.066	+	-4.23
9.46	4.72	0.33	+	-4.74
9.46	4.50	1.00	+	-4.96
9.46	4.52	1.00	+	-4.94
9.46	4.66	2.00	+	-4.80
9.46	5.08	3.30	+	-4.38
9.46	5.47	5.00	+	-3.99
9.46	5.42	5.00	+	-4.04
9.46	6.03	10.00	+	-3.43
9.46	6.07	10.00	+	-3.39
9.46	5.97	50.00	+	-3.49
Co(NO <sub>3</sub> ) <sub>2</sub>				
9.45	9.45	—	—	0.00
9.45	5.99	—	+	-3.46
9.45	5.97	1.0	+	-3.48
9.45	5.94	1.0	+	-3.51
9.45	5.96	5.0	+	-3.49
9.45	5.94	5.0	+	-3.51
9.45	5.91	10.0	+	-3.54
9.45	5.89	10.0	+	-3.56
9.45	5.74	50.0	+	-3.71
9.45	5.72	50.0	+	-3.73
Ni(NO <sub>3</sub> ) <sub>2</sub>				
9.57	9.57	—	—	0.00
9.57	5.68	—	+	-3.89
9.57	5.03	0.066	+	-4.54
9.57	2.14	0.33	+	-7.43
9.57	1.97	1.00	+	-7.60
9.57	1.93	1.0	+	-7.64
9.57	1.81	5.0	+	-7.76
9.57	1.82	5.0	+	-7.75
9.57	1.96	10.0	+	-7.61
9.57	1.93	10.0	+	-7.64
9.57	3.30	50.0	+	-6.27

acid forms. In more acid solutions (pH 6.0–3.5) the kinetic current is furnished very probably by the Os<sup>VIII</sup>/Os<sup>VI</sup> electron transfer. Considering all of these results it can be said that in neutral and very weakly acid solution the peroxyosmic acid and in more acid media the Os<sup>VIII</sup>/Os<sup>VI</sup> couple play an important role in the induced decomposition of hydrogen peroxide. We believe that the HO<sub>2</sub> radical attacks osmium<sup>VIII</sup> (and/or peroxyosmic acid). The reduction product of osmium compounds reacts with hydrogen peroxide and an OH radical is formed. In this way, without adding any extra oxidising agent, a considerable amount of hydrogen peroxide is decomposed. In more acid media the decomposition may be represented schematically:

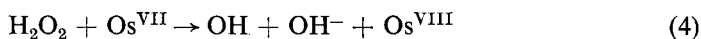
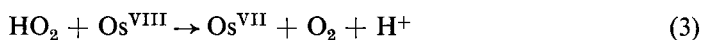
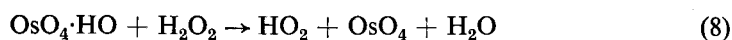
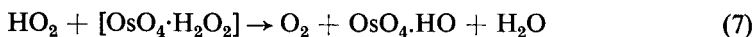
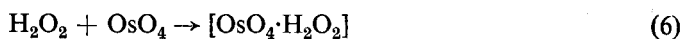


TABLE XX

	0.1N H <sub>2</sub> O <sub>2</sub> , ml Taken	Found	Salt concn., M × 10 <sup>3</sup>	OsO <sub>4</sub>	ΔH <sub>2</sub> O <sub>2</sub> , ml
Cu(NO <sub>3</sub> ) <sub>2</sub>	9.20	9.20	—	—	0.00
	9.20	5.22	—	+	-3.98
	9.20	1.96	0.02	+	-7.24
	9.20	1.65	0.066	+	-7.55
	9.20	1.62	0.33	+	-7.58
	9.20	1.75	1.0	+	-7.45
	9.20	1.72	1.0	+	-7.48
	9.20	2.30	5.0	+	-6.90
	9.20	2.27	5.0	+	-6.93
	9.20	2.64	10.0	+	-6.56
	9.20	2.69	10.0	+	-6.51
	9.20	4.14	50.0	+	-5.06
	9.20	4.12	50.0	+	-5.08
AgNO <sub>3</sub>	9.30	9.30	—	—	0.00
	9.30	5.08	—	+	-4.22
	9.30	4.88	0.33	+	-4.42
	9.30	4.75	1.0	+	-4.55
	9.30	4.77	1.0	+	-4.53
	9.30	4.46	5.0	+	-4.84
	9.30	4.52	5.0	+	-4.78
	9.30	4.12	10.0	+	-5.18
	9.30	4.08	10.0	+	-5.22
	9.30	3.16	50.0	+	-6.14
	9.30	3.10	50.0	+	-6.20

and in neutral or very weakly acid media:



The experimental results agree completely with the above reaction schemes.

(1) It was found that increasing the delivery rate of permanganate considerably decreased the induced decomposition. With rapid titration, because of the relatively high local permanganate concentration, the competing reaction (2) considerably lowers the concentration of the HO<sub>2</sub> radical together with the extent of the induced decomposition.

(2) Increasing the dilution of the titrated solution, other factors remaining constant, results in the increasing of the induced decomposition because of the decrease of the local permanganate concentration, and the concentration of HO<sub>2</sub> radical increases. The opposite effect can be clearly seen from Table II, according to which the induced error practically ceases when permanganate is present transiently in excess.

(3) The increase of the stirring rate promotes the even distribution of permanganate, thus the local permanganate concentration decreases, and together with it the extent of the induced decomposition increases. With the increasing of the stirring rate, the rate of the diffusion cannot increase without limit, so that the induced error alters according to a curve having a limiting value.

(4) The induced error is decreased by increasing the hydrogen ion concentration. This can be interpreted in that the potential of the  $\text{Os}^{\text{VIII}}/\text{Os}^{\text{VI}}$  couple becomes strongly positive and inhibits the regeneration of osmium tetroxide [reaction (4)].

(5) The kinetic nature of the induced error is supported by the fact that the increase of both hydrogen peroxide and osmium tetroxide concentrations brings about an increase of the induced decomposition.

(6) The chain character of the induced decomposition seems to be supported by the observation that on titrating with small portions and waiting a given time after the addition of each portion, the induced error is greater than with continuous titration. In the case of titrations performed fractionally, the chain-carriers can react for a longer time than in continuous titrations because the concentration of permanganate will be lower in the pause of the addition.

The chain character of the reaction is further supported by the halide and halogen inhibition. These substances annihilate chain carriers. Halide ions react mainly with  $\text{OH}$  or  $\text{OsO}_4\cdot\text{HO}$  radicals and the halogen molecules with the  $\text{HO}_2$  radical. Because the mentioned intermediates are not capable of oxidising fluoride ions, the error-decreasing effect is not experienced in the presence of fluoride. The error increasing in the presence of fluoride ions comes back to the increase of the pH of the titrated solution, when adding alkali fluoride, hydrogen fluoride being a weak acid.

(7) Cerimetric titration results in a moderate induced error. This can be partly ascribed to the rate of reactions (1) and (2) in the case of cerium<sup>IV</sup> sulphate being higher than in the case of permanganate. The other reason is that the ferroïn used as indicator reacts with the radicals, thus consuming the chain-carriers and exerting an inhibiting effect. In the 1,10-phenanthroline molecule the bond between carbon atoms 5 and 6 can be mostly easily attacked. Therefore it can be assumed that this bond is split by  $\text{OH}$  radicals (and  $\text{OsO}_4\cdot\text{HO}$ ) and oxidised to carboxyl groups. In this way 2'-bipyridyl-3,3'-dicarboxylic acid forms and this is not capable of forming complexes in acid solutions.

To prove this assumption the end-product of the oxidation of ferroïn was collected and compared chromatographically with 2,2'-bipyridyl-3,3'-dicarboxylic acid. The  $R_{\text{T}}$ -value of the oxidation product agreed satisfactorily with that of the mentioned dicarboxylic acid, thus the above supposition seems qualitatively to be correct.

(8) It was found that alkali and alkaline earth metal, zinc group, tin<sup>IV</sup>, aluminium and silicate ions do not influence the induced decomposition. The error-increase found in the case of beryllium, aluminium and silicate ions can, according to qualitative tests, be ascribed to impurities.

A marked increase in the induced error is generally caused by ions which are good catalysts of the self-decomposition of hydrogen peroxide, e.g., iron<sup>III</sup>, copper<sup>II</sup>, silver<sup>I</sup>, nickel<sup>II</sup>, manganese<sup>(II)</sup>, etc.

Besides halide ions, ferricyanide, uranium<sup>VI</sup>, cerium<sup>III</sup>, chromium<sup>III</sup> and lanthanum<sup>III</sup> ions considerably decrease the induced error. The interaction between ferricyanide and osmium tetroxide can be observed optically and supposedly this is the reason of the decrease of the catalytic activity, for example, in the reaction between cerium<sup>IV</sup> and arsenous acid. Chromium<sup>III</sup>, lanthanum<sup>III</sup> and cerium<sup>III</sup> and probably uranium<sup>VI</sup> ions interact with osmic acid and decrease the catalytic activity. There is no direct experimental proof of this supposition, but we believe that osmium forming polyacid reacts with chromium<sup>III</sup> and the ions mentioned, and results in stable

complexes as can be found in the case of polymolybdates.<sup>9</sup> In this direction spectrophotometric measurements are now in progress.

**Zusammenfassung**—Weim Wasserstoffperoxyd in Anwesenheit von Osmiumtetroxyd mit 1-äquivalenten Oxydationsmitteln (zB. Kaliumpermanganat, Cer(IV) sulfate) titriert wird eine induzierte Zersetzung des Wasserstoffperoxyd ist zu beobachten. Die Einzelheiten dieser induzierten Reaktion werden ausführlich erörtert.

**Résumé**—La décomposition de l'eau oxygénée est induite si elle est oxydée par des réactifs tels que le permanganate de potassium ou le sulfate de cérium(IV). Les principaux facteurs de cette décomposition induite en chaîne de même que l'influence de substances étrangères sont décrites en détail.

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## TITRATION OF THALLIUM<sup>I</sup> IONS WITH A CHEMILUMINESCENT END-POINT

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(Received 14 August 1962)

**Summary**—Thallium<sup>I</sup> ions can be titrated accurately in a strong hydrochloric acid medium with potassium dichromate standard solution. The reaction was first examined by potentiometric titration. Siloxene proved to be suitable as a chemiluminescent indicator for detection of the end-point, emitting an orange-red chemiluminescence as soon as the titrant is present in excess.

In investigation of the ascorbinometric determination of thallium<sup>III</sup> ions, measurements on the formal redox potential values of thallium-halide complexes<sup>1</sup> showed that the redox potential of the thallium<sup>III</sup>-thallium<sup>I</sup> system depends largely on the nature and concentration of the halide present. Thus, in the presence of bromide, certain substances could oxidise thallium<sup>I</sup> ions which according to their redox potential values, should otherwise be unable to do this.

Although potassium dichromate as an oxidising titrant has favourable characteristics because of its stability, it has been used for thallium<sup>I</sup> titration only by Rao.<sup>2</sup> He carried out titrations in a strong hydrochloric acid medium in the presence of iodine monochloride as catalyst. The end-point was detected by carbon tetrachloride. This procedure yields accurate results. Its disadvantage is, however, that the end-point is detected in a separate phase, and therefore the solutions must be thoroughly shaken near the end-point to avoid over-titration.

The present investigation was carried out to discover the most favourable circumstances for a rapid and stoichiometric reaction between dichromate and thallium<sup>I</sup> ions, and to find a suitable indicator.

The formal redox potential of the dichromate-chromium<sup>III</sup> system is +1.36 v in a strongly acidic medium. This value decreases markedly, however, with the hydrogen ion concentration. At higher pH values the equilibrium between chromium<sup>VI</sup> and chromium<sup>III</sup> ions can only be reached slowly, and therefore titrations with dichromate are carried out always in strongly acidic, sulphuric or hydrochloric acid-containing media.<sup>3-6</sup>

The formal redox potential of the thallium<sup>III</sup>-thallium<sup>I</sup> system also varies inversely with pH.<sup>7</sup> In a 1*N* sulphuric acid medium the potential is +1.21 v. It would therefore appear that thallium ions cannot be titrated with dichromate because of the small difference between the redox potentials. The circumstances are, however, different in hydrochloric acid medium. Thallium<sup>III</sup> ions form stable complexes with chloride ions, and therefore in a 1*N* hydrochloric acid medium the redox potential of the thallium<sup>III</sup>-thallium<sup>I</sup> system is only +0.8 v. If, therefore, thallium<sup>I</sup> ions are titrated with potassium dichromate in hydrochloric acid medium, the reaction takes place rapidly and stoichiometrically.

## EXPERIMENTAL

*Reagents*

*Thallium<sup>I</sup> sulphate solution: 0.1N:* 12.622 g of analytically pure thallium<sup>I</sup> sulphate were dissolved in water and diluted to 1 litre. Standardisation was carried out with ascorbic acid.<sup>1</sup>

*Potassium dichromate solution: 0.1N:* 4.9035 g of analytically pure potassium dichromate, dried at 150°, were dissolved in water and diluted to 1 litre.

*Indicator:* Siloxene.<sup>10</sup> This was prepared from calcium silicide by boiling with concentrated hydrochloric acid. The precipitate was gathered on a filter paper, and dried at room temperature. For one titration 50–100 mg of the solid preparation are enough.

*Investigation of the reaction*

Potentiometric titrations were first carried out to confirm the theoretical basis. Thallium<sup>I</sup> sulphate (9.98 ml of 0.1N solution) was titrated with 0.1N potassium dichromate using potentiometric

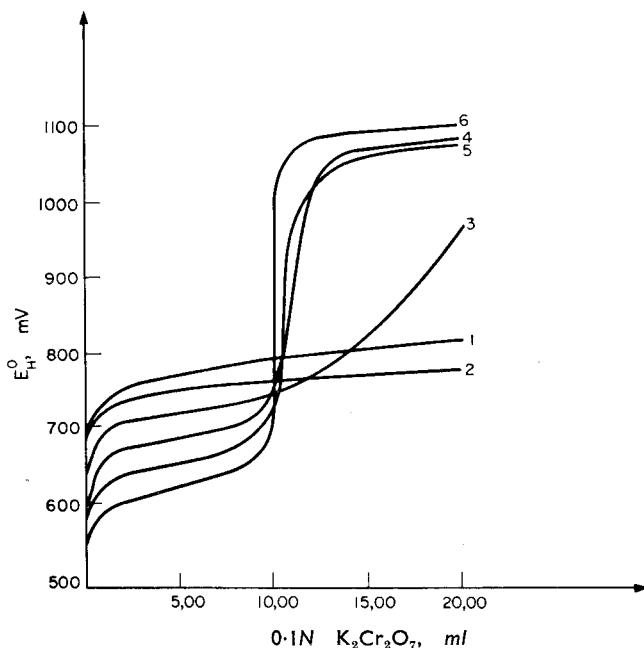


FIG. 1.—Titration of 0.1N  $Tl_2SO_4$  with 0.1N  $K_2Cr_2O_7$  (9.98 ml of  $Tl_2SO_4$  1, 2%; 2, 4%; 3, 10%; 4, 12%; 5, 16%; 6, 20% HCl.)

end-point detection. Platinum and saturated calomel electrodes were used. A Polymetrohm-type millivoltmeter was used. Results of titrations at various hydrochloric acid concentrations are shown in Fig. 1. This shows that in solutions with low hydrochloric acid concentrations the reaction does not take place (curves 1–3). In solutions containing about 20% of hydrochloric acid results are accurate (curves 4–6).

To investigate the reproducibility of the method various amounts of thallium<sup>I</sup> sulphate were titrated in a strong hydrochloric acid medium. As may be seen in Fig. 2, the potential changes are large and the end-points can be determined easily.

In an effort to avoid too high concentrations of hydrochloric acid, various amounts of potassium chloride in 2N sulphuric acid were added. Even if extremely high amounts (5 g) of the salt were added, however, the end-points were not good.

The redox indicators most generally used in chromatometric titrations, such as diphenylamine or diphenylamine sulphonic acid, cannot be used here, because they are destroyed during the titration, and the green colour of the chromium<sup>III</sup> ions masks the colour change of the indicator. Previous investigations<sup>8–9</sup> showed that chemiluminescent indicators can be used satisfactorily for the titration of coloured solutions. Siloxene, which emits an orange-red light in the presence of strong oxidising agents, has already been used as indicator in cerimetric and chromatometric titrations.<sup>10–12</sup>



In the titration of thallium, if titration is carried out in a dark room, light emission can be perceived at the point where the dichromate solution drops into the mixture. At the end-point of the titration a steady chemiluminescence appears in the entire solution. The light emission lasts for about 1–2 min. In the presence of the indicator the acid concentration requires to be similar to that in potentiometric titrations. If the hydrochloric acid concentration is less, a constant chemiluminescence appears, even at the beginning of the titration, indicating, that the reaction does not take place. A high hydrochloric acid concentration is also needed for the chemiluminescent end-point detection.

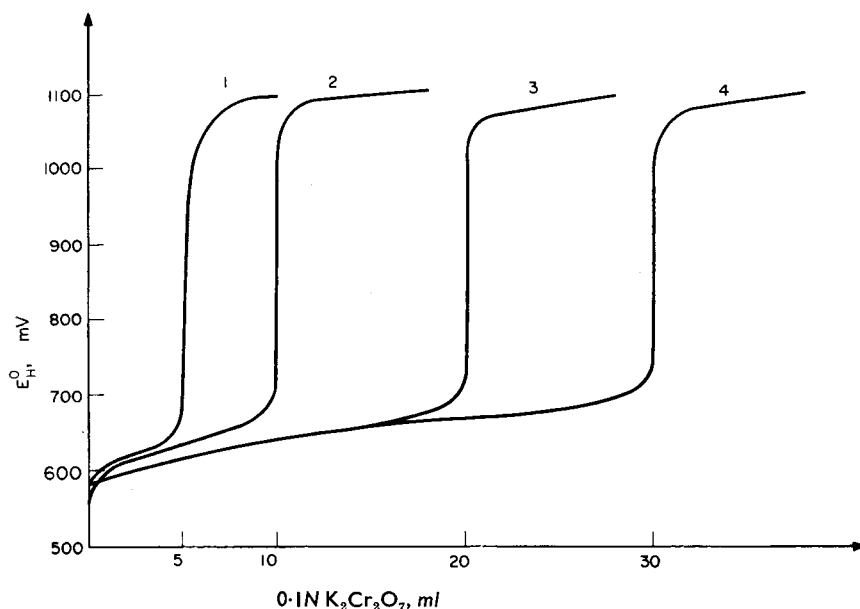


FIG. 2.—Titration of 0.1N  $Tl_2SO_4$  with 0.1N  $K_2Cr_2O_7$ .  
(1, 5.01; 2, 9.98; 3, 20.04; 4, 30.06 ml of 0.1N  $Tl_2SO_4$  in 20% HCl.)

#### Procedure

To a solution of 50–300 mg of thallium<sup>I</sup>, in a 200-ml flask, add 50 ml of concentrated hydrochloric acid, and dilute with water, so that at the end of the titration the volume will be about 100 ml. Add 50–100 mg of siloxene to the solution and titrate in the dark, at room temperature, with 0.1N potassium dichromate solution until a steady chemiluminescence appears. (1 ml of 0.1N potassium dichromate solution is equivalent to 12.62 mg of Tl.)

The reproducibility of the method may be judged from the results in Table I. All results are the mean of three titrations.

TABLE I

0.1N $Tl_2SO_4$ true value, ml	0.1N $K_2Cr_2O_7$ consumed, ml	Difference from true value, %	Maximum deviation, %
5.01	5.04	+0.6	+2.0
9.98	9.99	+0.1	+0.7
20.04	20.00	-0.2	-0.4
30.06	30.01	-0.2	-0.4

The error of the method was established by the titration of 20.00 ml of 0.1N thallium<sup>I</sup> sulphate solution in six parallel determinations. The deviation from the true value in this case is +0.24%, and the standard deviation of the method is  $\pm 0.02$  ml, or  $\pm 0.09\%$ .

**Zusammenfassung**—Thallium(I) ionen können in stark salzsaurer Lösung mit Kaliumdichromat genau titriert werden. Die Reaktion wurde mittels potentiometrischer Titration untersucht. Siloxen war ein geeigneter Chemiluminescensindicator der orangefarbenes Licht aussendet, wenn das Titrationsmittel im Überschuss anwesend ist.

**Résumé**—Les ions thallium(I) peuvent être dosés avec précision en milieu acide chlorhydrique fort par une solution étalon de bichromate de potassium. La réaction a d'abord été étudiée par potentiométrie. Le siloxène convient comme indicateur chimiluminescent pour la détermination du point équivalent. Il émet en effet une lumière rouge orangée lorsque le réactif titrant est en excès.

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## 2-HYDROXY-4-AMINO-4'-METHOXYDIPHENYLAMINE

### A NEW REDOX INDICATOR

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**Summary**—2-Hydroxy-4-amino-4'-methoxydiphenylamine has been prepared and has been found useful for the detection of the end-point in the ascorbinometric titration of hexacyanoferrate(III) ions.

In an earlier paper<sup>1</sup> we reported on the preparation of 2-hydroxy-4-amino-4'-methoxydiphenylamine (2-hydroxy-Variamine Blue.) Investigation of this Variamine Blue derivative and of the structural isomer 3-hydroxy-Variamine Blue showed that not only is there a shift in standard redox potential because of the substitution of hydroxyl, as would be expected, but also that the stability of the oxidised forms of these substances was extended towards more alkaline regions; this is important from the view of the practical application of these derivatives. The bluish-violet colour of the oxidised forms of Variamine Blue and a number of its other derivatives is stable up to about pH 5-7, and over this range becomes yellow; the colour changes of 2-hydroxy- and 3-hydroxy-Variamine Blue occur only above pH 12.

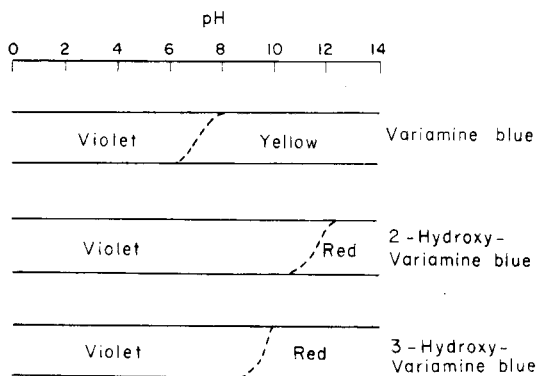
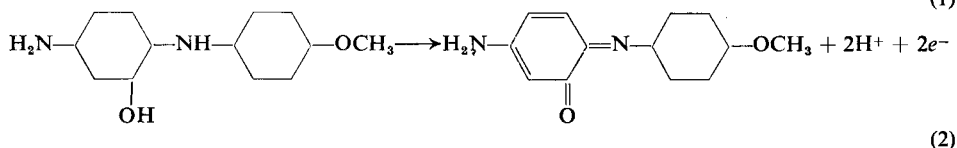
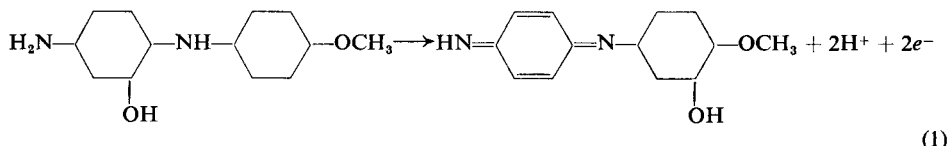


FIG. 1.—Colour changes of Variamine Blue and derivatives.

Variamine Blue and those of its derivatives so far tested are suitable only for indication in redox reactions carried out in acidic medium. 2-Hydroxy-Variamine Blue can, however, be used both in acidic and alkaline media as a redox indicator.

This special property of 2-hydroxy-Variamine Blue probably arises because its molecular structure is similar to that of indophenol-type redox indicators, which are suitable also for indication in alkaline medium. On the other hand this derivative also shows the properties of Variamine Blue.

When oxidised, two types of quinoidal structure may be formed:



Because in acidic medium the first, and in alkaline medium the second reaction is more probable, it can be assumed that both oxidation reactions take place simultaneously, but in acidic medium mainly according to the first, while in alkaline medium mainly according to the second equation. It is interesting that the absorption spectra of the oxidised form of the indicator are similar in shape in all the pH regions investigated (pH 2,3,4,8,10); that is, the absorption peaks occur at the same wavelengths, but the corresponding molar extinction values are higher in alkaline than in acidic medium. The identity of the wavelengths of the maxima shows that the excitation energies of the two oxidised forms are almost the same.

The indicator combines the properties of the Variamine Blue and the indophenol types of redox indicators.

In neutral and slightly alkaline solutions hexacyanoferrate(III) ions can easily be titrated with ascorbic acid in a stoichiometric and rapid reaction.<sup>2</sup> The hexacyanoferrate(III)-hexacyanoferrate(II) system, used as an intermediate redox couple, permits the determination of a number of ions. Oxidising agents oxidise hexacyanoferrate(II) ions, and the hexacyanoferrate(III) ions, formed during this reaction can be titrated with ascorbic acid. Reducing agents can be determined by adding an excess of hexacyanoferrate(III), and titrating the excess with ascorbic acid.

2-Hydroxy-Variamine Blue has been used as an indicator for end-point detection in ascorbinometric hexacyanoferrate(III) titrations.

As shown in Figs. 2 and 3, the formal redox potential of the indicator ( $E_0'$ ) at pH

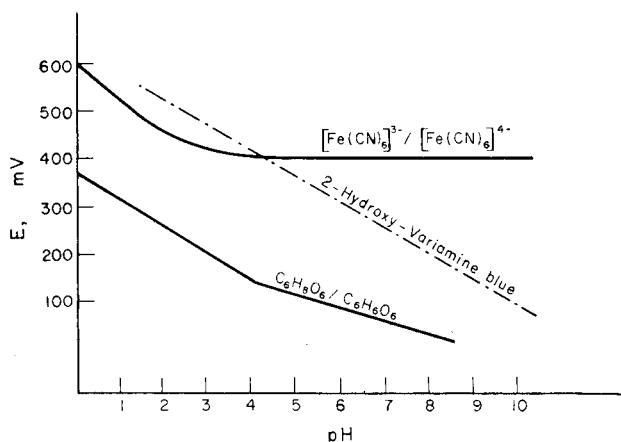


FIG. 2.—Redox potentials for indicator and redox systems.

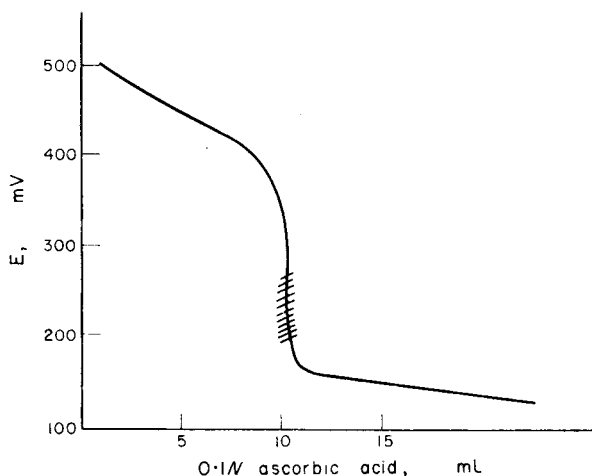


FIG. 3.—Behaviour of the indicator in hexacyanoferrate(III)-ascorbic acid titration. (10 ml of 0.1N  $K_3[Fe(CN)_6]$ , 10 ml of 10%  $KHCO_3$ , 30 ml of water, 0.3 g of hydroxy-2-Variamine Blue indicator: shaded portion indicates decolorisation of the indicator.)

6-8 makes the indication of the hexacyanoferrate(III)-ascorbic acid reaction possible. It has been shown experimentally that the oxidation of the indicator by hexacyanoferrate(III) ions and the reduction of its oxidised form by ascorbic acid are reversible, because, as illustrated in Fig. 4, the redox potential values shown are identical whether the titration is begun from the oxidising or the reducing side. If known amounts of the indicator were oxidised by hexacyanoferrate(III), iodine or bromine standard solutions, at various pH values, potential jumps are observed after addition of amounts of oxidising agents corresponding to a two-electron oxidation.

The stability of the oxidised form of the indicator is poor in strongly acidic media (pH 2), but in the range pH 2-12 it is fairly stable.

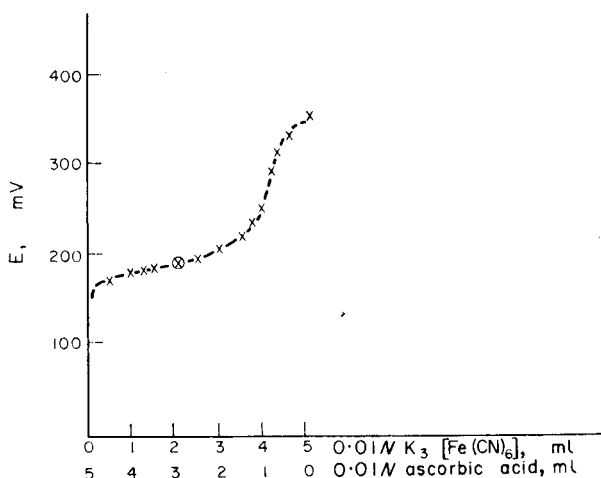


FIG. 4.—Change of redox potential with composition of solution (pH 8.6)

## EXPERIMENTAL

The investigation of the redox properties of 2-hydroxy-variamine Blue was carried out using the methods and apparatus already described.<sup>1</sup>

*Reagents*

*Ascorbic acid solution: 0.1N:* This was prepared<sup>3,4</sup> as follows: 8.9 g of ascorbic acid were dissolved in 1 litre of water, distilled from a glass apparatus. The solution was standardised against 20.00 ml of 0.1N potassium iodate solution. Ascorbic acid solutions must be standardised daily.

*Indicator:* A 1:500 solid mixture of 2-hydroxy-Variamine Blue and sodium chloride. For one titration 0.3–0.5 g must be used in a 100-ml final volume.

*Potassium hexacyanoferrate(III) solution: 0.1M:* This was prepared from analytically pure  $K_3[Fe(CN)_6]$  after drying at 120°. Its concentration was also checked by iodometric titration.

*Potassium hydrogen carbonate and potassium hexacyanoferrate(II)* were used as analytically pure

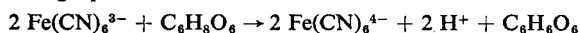
TABLE I.—DETERMINATION OF HEXACYANOFERRATE(III)

Fe(CN) <sub>6</sub> <sup>3-</sup>		Deviation	
Taken, mg	Found, mg	mg	%
423.9	424.1	+0.2	+0.05
	423.9	±0.0	±0.00
	424.5	+0.6	+0.14
	423.9	±0.0	±0.00
	424.3	+0.4	+0.10
	423.9	±0.0	+0.00
	424.5	+0.6	+0.14
	423.9	±0.0	±0.00
	424.5	+0.6	+0.14
	423.9	±0.0	±0.00
	424.1	+0.2	+0.05
	424.8	+0.9	+0.27
	Mean	424.2	+0.3
317.9	318.3	+0.4	+0.1
	318.6	+0.7	+0.2
	318.3	+0.4	+0.1
	317.9	±0.0	±0.0
	318.3	+0.4	+0.1
	317.9	±0.0	±0.0
Mean	318.2	+0.3	+0.1
211.9	212.4	+0.5	+0.2
	212.6	+0.7	+0.3
	211.9	±0.0	±0.0
	212.6	+0.7	+0.3
	212.6	+0.7	+0.3
	212.6	+0.7	+0.3
Mean	212.4	+0.5	+0.2
106.0	105.7	-0.3	-0.3
	106.4	+0.4	+0.4
	106.2	+0.2	+0.2
	106.0	±0.0	±0.0
	105.5	-0.5	-0.5
	106.2	+0.2	+0.2
Mean	106.0	±0.0	±0.0

reagents. Potassium hexacyanoferrate(II) solutions were standardised by permanganometric titrations.

#### Determination of hexacyanoferrate(III)

The reaction between ascorbic acid and hexacyanoferrate(III) proceeds stoichiometrically according to the following equation:



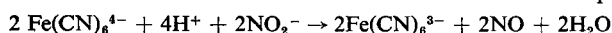
*Procedure:* To a neutral solution of 100–500 mg of  $\text{Fe(CN)}_6^{3-}$  add 1 g of potassium hydrogen carbonate, and, for 80–100 ml final volume add 0.3–0.5 g of 2-hydroxy-Variamine Blue-sodium chloride solid indicator mixture. Titrate with 0.1*N* ascorbic acid standard solution. The solution, originally brownish-red, becomes more and more blue as the end-point is approached; just before the equivalence point it becomes bluish-violet, and decolorises completely at the end-point over a few sec, when 1 drop of the standard solution is added. One ml of 0.1*M* ascorbic acid solution is equivalent to 21.196 mg of  $\text{Fe(CN)}_6^{3-}$  or 32.925 g of  $\text{K}_3[\text{Fe(CN)}_6]$ .

The results of some determinations are summarised in Table I.

The standard deviation of the method is  $\pm 0.3$  mg ( $\pm 0.07\%$ ), and the standard deviation of the mean of 12 determinations is  $\pm 0.09$  mg ( $\pm 0.02\%$ ).

#### Determination of hexacyanoferrate(II)

Hexacyanoferrate(II) can be oxidised to hexacyanoferrate(III), and the latter can be titrated with ascorbic acid. Oxidation can be carried out in acidic solution with sodium or potassium nitrite:<sup>5-7</sup>



The excess of nitrite can be decomposed by amidosulphonic acid.

TABLE II.—DETERMINATION OF HEXACYANOFERRATE(II)

$\text{Fe(CN)}_6^{4-}$		Deviation		
Taken, mg	Found, mg	mg	%	
420.9	418.6	-2.3	-0.5	
	421.6	+0.7	+0.2	
	418.4	-2.5	-0.5	
	421.6	+0.7	+0.2	
	421.4	+0.5	+0.1	
	421.6	+0.7	+0.2	
	Mean	420.5	-0.4	-0.4
211.7	211.1	-0.6	-0.3	
	211.5	-0.2	-0.1	
	211.9	+0.2	+0.1	
	210.9	-0.8	-0.4	
	211.1	-0.6	-0.3	
	210.9	-0.8	-0.4	
	211.9	+0.2	+0.1	
	211.7	$\pm 0.0$	$\pm 0.0$	
	212.2	+0.5	+0.2	
	211.3	-0.4	-0.2	
	211.3	-0.4	-0.2	
	210.7	-1.0	-0.4	
	Mean	211.4	-0.3	-0.15
	105.8	105.9	+0.1	+0.1
105.9		+0.1	+0.1	
105.7		-0.1	-0.1	
Mean	105.83	+0.03	+0.03	

**Procedure:** To a solution containing 100–500 mg of  $\text{Fe}(\text{CN})_6^{4-}$ , add 0.5 g of sodium or potassium nitrite and 10 ml of 2*N* hydrochloric acid. After shaking for 1–2 min, add 1 g of amidosulphonic acid to the solution. When gas evolution has ceased, add 4–5 g of potassium hydrogen carbonate and 0.3–0.5 g of solid indicator mixture. Titrate with 0.1*N* ascorbic acid solution as described above. One ml of 0.1*N* ascorbic acid solution is equivalent to 36.836 mg of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  or to 42.241 mg of  $\text{K}_2[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ .

The results of some determinations are summarised in Table II.

The standard deviation of the method is  $\pm 0.47$  mg ( $\pm 0.22\%$ ), and the standard deviation of the mean of 12 determinations is  $\pm 0.13$  mg ( $\pm 0.06\%$ ).

**Zusammenfassung**—2-Oxy-4-amino-4'-methoxy-diphenylamin, dessen Synthese kürzlich beschrieben wurde, ist als Indicator bei der ascorbinometrischen Bestimmung von Hexacyanoferrat(III)-ionen sehr gut geeignet.

**Résumé**—La 2-hydroxy-4-amino-4'-méthoxydiphénylamine préparée récemment par les auteurs, peut être utilisée pour la détermination du point équivalent lors du dosage des ions hexacyanoferrate(III) par l'acide ascorbique.

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## UNTERSUCHUNGEN ÜBER DAS KAKOTHELIN ALS REDOX-INDICATOR

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(Eingegangen am 14 August 1962)

**Zusammenfassung**—Das Kakothelin ist nach früheren Untersuchungen der Verfasser<sup>6</sup> bei den meisten stannometrischen Bestimmungen als ein vorzüglicher reversibler Redox-Indicator sehr gut brauchbar. Um eine exakte Unterlage zur weiteren Verwendung des Kakothelins zu bieten, wurden die Redoxpotential-Farbumschlagskurven des Indicators aufgenommen, die scheinbaren standard Redoxpotentiale und der  $p_H$ -Wert des Kakothelins in saueren Lösungen bestimmt und das Wesen des Reduktionsmechanismus ermittelt.

Das Kakothelin (4-Nitro-brucichinonsäure-nitrat) wurde wie bekannt von *Gutzeit*<sup>1</sup> als ein empfindlicher Reagens für Zinn (II)-Ionen empfohlen. Die gelbe Lösung des Kakothelins gibt nämlich in Gegenwart von Sn (II)-Ionen in sauren Lösungen eine tief violette Farbe. Diese Farbreaktion ist auf die Reduktion des Kakothelins zurückzuführen und wird ausser den Zinn (II)-Ionen auch von anderen Reduktionsmitteln hervorgerufen<sup>2</sup>.

Als Redox-Indicator wurde das Kakothelin zum erstenmal von *Kutschment* und *Gengrinovitch*<sup>3</sup> bei Bestimmung von Eisen (III)-Ionen, und neuerdings von *Hume* und *Kolthoff*<sup>4</sup> bei der Oxydation von Zinn (II)-Ionen durch Ce (IV) verwendet. Wertvolle Angaben über die Wirkung einiger Redox-Systeme auf Kakothelin, findet man in der Arbeit von *Lang*.<sup>5</sup> Die Verwendbarkeit des Kakothelins als Redox-Indicator in der Stannometrie wurde vor einigen Jahren von uns<sup>6</sup> näher untersucht. Als Ergebnis dieser Untersuchungen wurde festgestellt, dass das Kakothelin bei den meisten stannometrischen Bestimmungen als ein vorzüglicher, reversibler Redox-Indicator sehr gut brauchbar ist. Unter Verwendung von Kakothelin sind z.B.  $Fe^{3+}$ ,  $Ce^{4+}$ ,  $JO_3^-$ ,  $VO_3^-$ ,  $[Fe(CN)_6]^{3-}$  Ionen, sowie freies Jod stannometrisch sehr einfach und genau zu bestimmen. Ausserdem ist die Bestimmung von Eisen (III) und Dichromat-, sowie Eisen (III)- und Vanadat-Ionen in einer Lösung nebeneinander durch die Verwendung von Kakothelin, kombiniert mit einem anderen Indicator, z.B. mit Diphenylamin, einfach durchführbar.

Die bisherigen Angaben über die Redox-Indicator Eigenschaften des Kakothelins waren aber mehr von empirischem und qualitativem Charakter. Um eine exakte Unterlage zur weiteren Verwendung des Kakothelins zu bieten, stellten wir also vor uns die Aufgabe die Redoxpotential-Farbumschlagskurven des Kakothelins in saueren Lösungen aufzunehmen, die Bedingungen der Reversibilität zu bestimmen und womöglich auch den Mechanismus der Reduktion durch die Zinn (II)-Ionen aufzuklären.

### EXPERIMENTELLER TEIL

Die Redoxpotentiale und die pH-Werte der Lösungen wurden mit einem Titriskop von *Metrohm A. G.* (Herisau) Typ. E 116 unter Verwendung von Pt-bzw. Glas-Elektroden und als Bezugs-Elektrode,

einer gesättigten Kalomel-Elektrode gemessen. Die Lichtabsorption der Lösungen wurde mit einem VSU. 1. (Zeiss) Photometer, und mit dem Stufenphotometer (Zeiss) bestimmt.

Die verschiedene Lösungen wurden unter Verwendung von zweifach destilliertem Wasser folgendermaßen bereitet:

0.5 %-ige und 0.1 %-ige Lösungen von Kakothelin: aus Kakothelin p.a. (Riedel de Haën)

0.1 n und 0.01 n  $\text{SnCl}_2$ -Lösungen: durch Verdünnung einer Stammlösung in  $\text{CO}_2$ -Atmosphäre. Die Stammlösung wurde durch Auflösen von Zinn p.a. (Vegyi KTSz) in cc. Salzsäure p.a. (Reanal) hergestellt und ihre Konzentration gravimetrisch bestimmt.

0.1 n und 0.01 n  $\text{SnCl}_4$ -Lösungen: durch Verdünnung mit Salzsäure einer Stammlösung. Die Stammlösung wurde aus  $\text{SnCl}_4 \cdot 4\text{H}_2\text{O}$  p.a. (Riedel de Haën) bereitet und ihre Konzentration gravimetrisch bestimmt. 0,15 n  $\text{TiCl}_3$ -Lösung, aus  $\text{TiCl}_3$  durch elektrolytische Reduktion unter Verwendung von Platin-Kathode und einer Kohlenstoff-Anode.

Die  $\text{SnCl}_2$  und  $\text{TiCl}_3$ -Lösungen wurden unter Kohlensäure in Nachfüllbüretten nach *Winkler*<sup>7</sup> gehalten.

## VERSUCHSERGEBNISSE UND DISKUSSION

Zur Bestimmung der Redox-Umschlagspotentialwerte des Kakothelins benötigten wir die Kenntnis der photometrischen Eigenschaften sowohl des Kakothelins als auch des Reduktionsproduktes. Deshalb nahmen wir vor allem die optischen Absorptionsskurven in 2 n HCl gegen destilliertes Wasser auf. Um die eventuelle Oxydation des Reduktionsproduktes während der Aufnahmen zu vermeiden, wurden die Lösungen mit sauerstoff-freiem Wasser bereitet, die Küvetten über der Lösungen mit  $\text{CO}_2$ -Gas gefüllt und die Lösungen öfters gewechselt. Unter solchen Umständen blieben die Extinktionswerte während der Bestimmungen, nach den Kontrollmessungen, konstant.

Die Absorptionskurven sind auf der Abbildungen 1. und 2. dargestellt. Die E-Werte geben die Extinktion  $\left(\log \frac{I_0}{I}\right)$  an. Im pH-Intervall von  $-0,3$  bis  $+1$  zeigen die Absorptionskurven praktisch keine Unterschiede.

Wie man sieht, läuft die Kurve des Kakothelins—entsprechend der rötlich gelben Farbe der Lösung—ziemlich steil nach den kürzeren Wellenlängen ohne einen Maximum im sichtbaren Gebiet zu zeigen.

Die kurve des Reduktionsproduktes weist aber—entsprechend der schönen violetten Farbe der Lösung—einen gut ausgeprägtem Maximum bei  $\lambda = 530 \text{ m}\mu$  auf. Bei dieser Wellenlänge weisen also die Extinktionswerte der beiden Lösungen einen grossen Unterschied auf. Diese Tatsache gab uns die Möglichkeit die Farbumschlagkurven aufzunehmen. Dies geschah folgendermaßen.

Wir bestimmten die Extinktionswerte einfach mit dem Stufenphotometer, mit Filter S 53 in solcher Kakothelin-Lösungen, gegebener Konzentration, welche mit verschiedenen relativen Mengen von  $\text{SnCl}_2$  und  $\text{SnCl}_4$  auf verschiedene Redoxpotentialwerte, und mit Salzsäure auf verschiedene pH-Werte eingestellt wurden.

In jeder Probe wurden also die Redoxpotentialwerte, die pH-werte bei  $25^\circ$  und die Extinktionswerte bei  $\lambda = 530 \text{ m}\mu$  bestimmt.

Die gewonnenen Daten sind in den Abb. 3-7. zusammengestellt. Die einzelnen Lösungen enthielten in 100 ml Endvolumen 5 ml 0,5 %-iger Kakothelin-Lösung, 50 ml 0,01 n Redox-Puffer-Gemisch aus verschiedenen relativen Mengen von 0,01 n  $\text{SnCl}_2$  und  $\text{SnCl}_4$  Lösungen und cc. Salzsäure, mit sauerstoff-freiem destilliertem Wasser unter Stickstoff auf 100 ml aufgefüllt. Die Extinktionswerte (E) beziehen sich auf  $d = 1 \text{ cm}$  Schichtdicke.

Von den Abbildungen 3-7. ist zu entnehmen, dass die vollständige Reduktion des Indicators in einem wohldefinierten schmalen Potential-Intervall erfolgt. Die, von

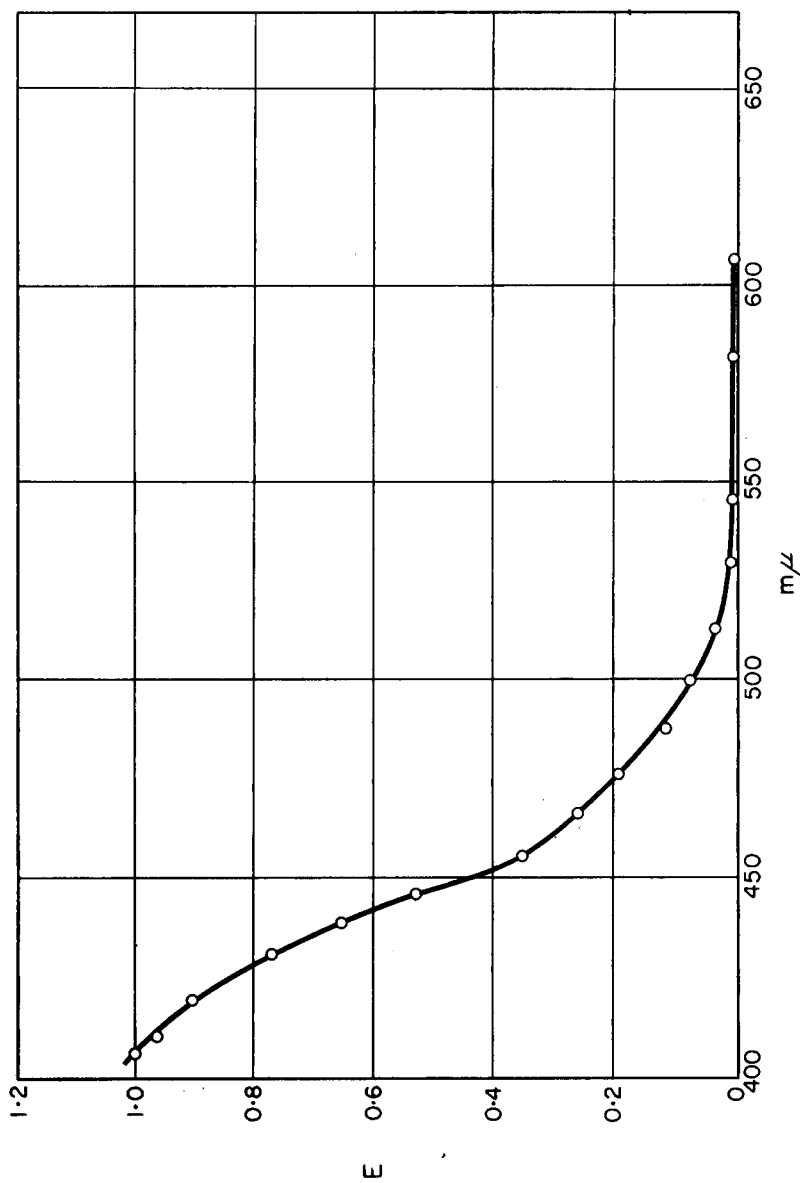


ABB. 1.—Absorptionskurve des Kakothelins  
( $c = 4,9 \cdot 10^{-4}$  M/Lit.  $d = 0,5$  cm)

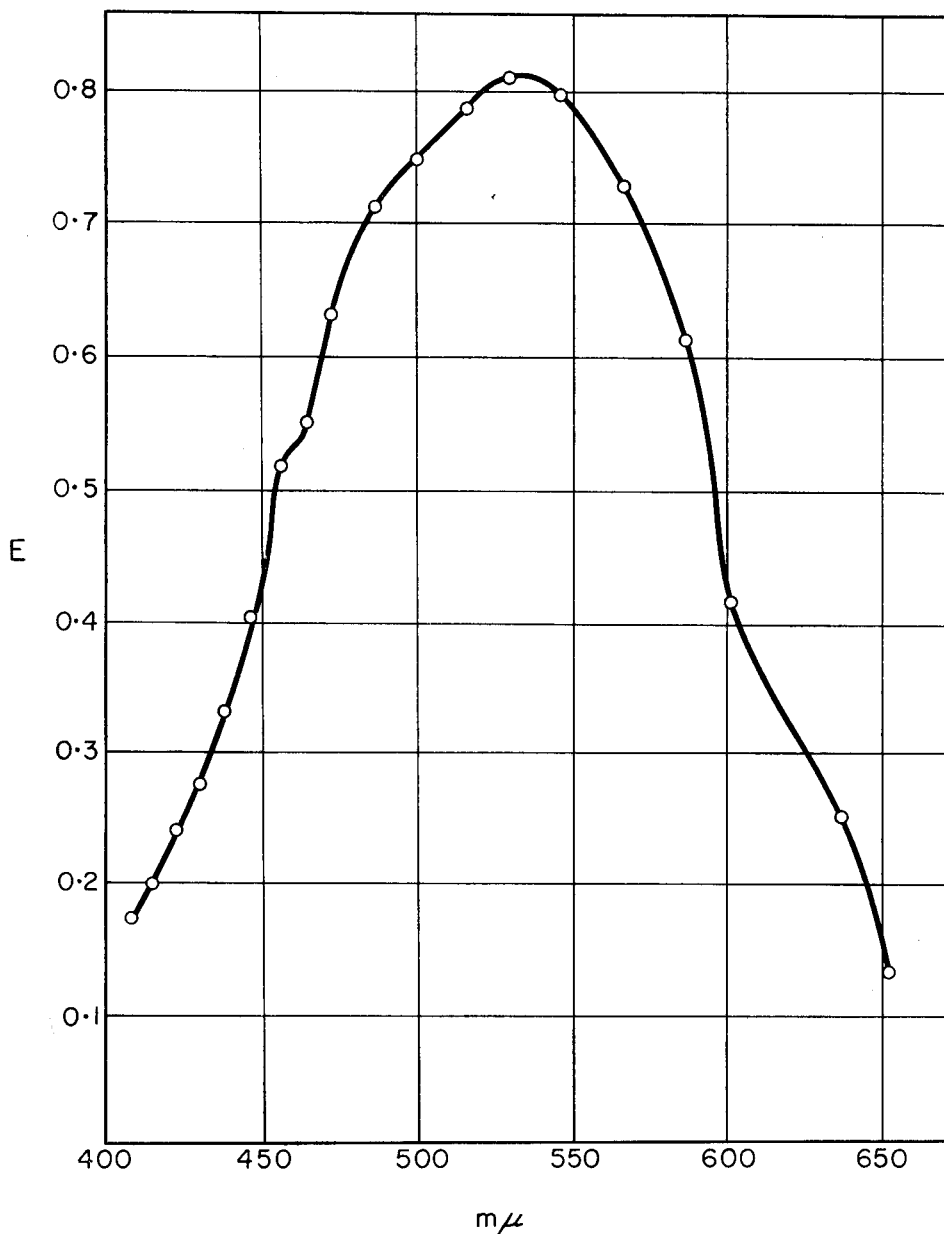
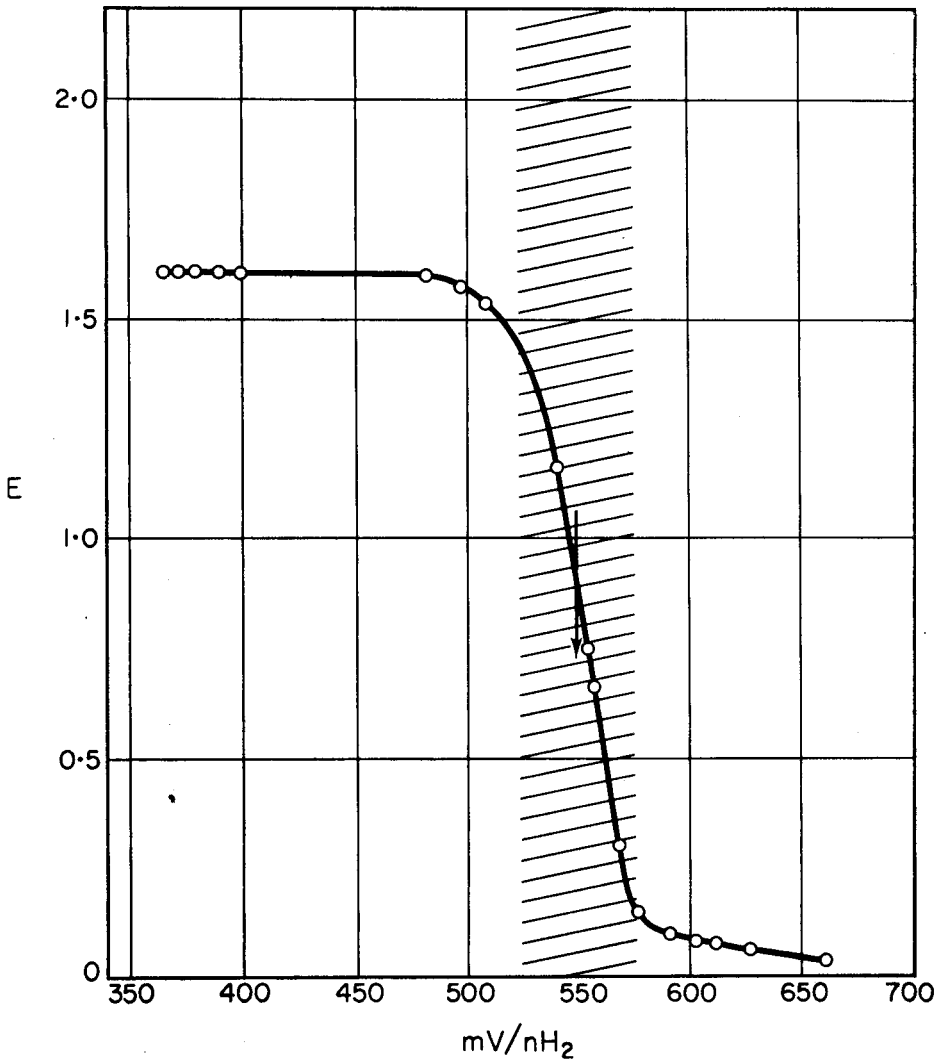


ABB. 2.—Absorptionskurve des Reduktionsproduktes in Gegenwart von Zinn (II)-Ionen.  
( $c = 4,9 \cdot 10^{-4}$  M/Lit.,  $d = 0,5$  cm)

ABB. 3.—Die Umschlagskurve des Kakothelins bei  $a_{H^+} = 2,0$  Mol/L.

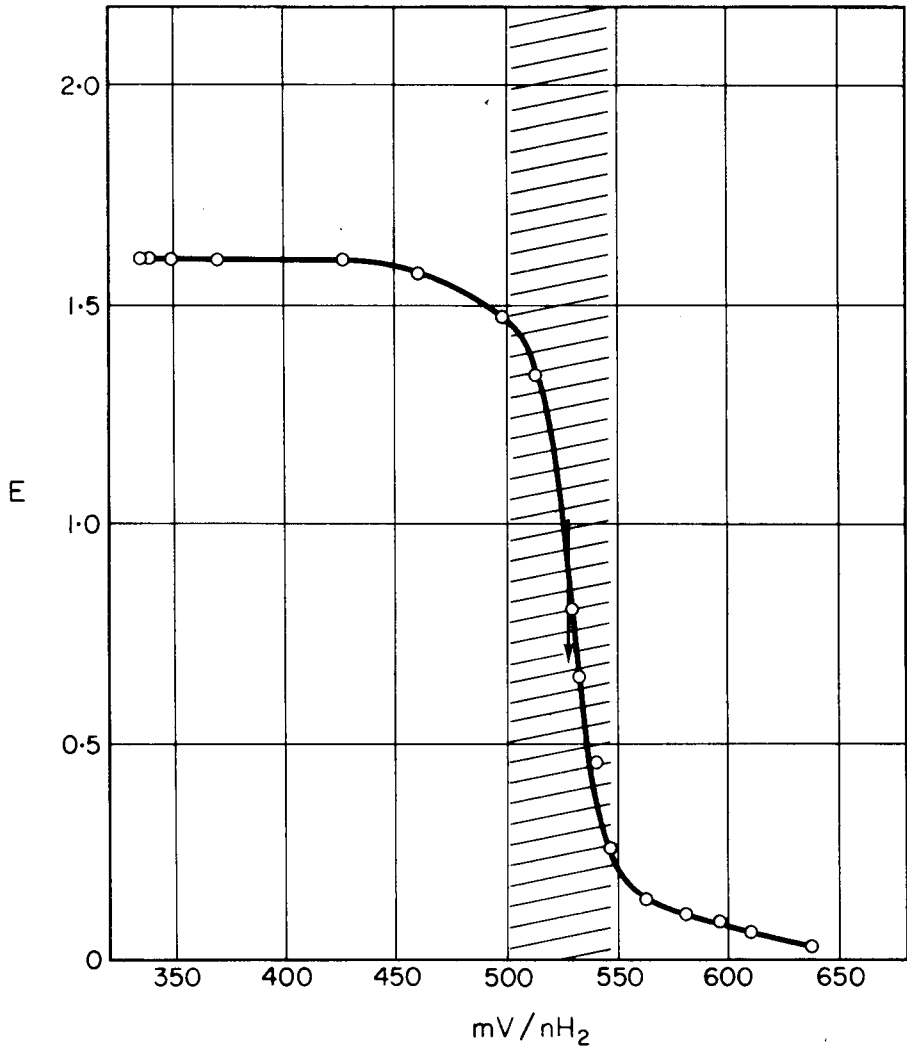


ABB. 4.—Die Umschlagskurve des Kakothelins bei  $a_{H^+} = 7,94 \cdot 10^{-1}$  Mol/L.

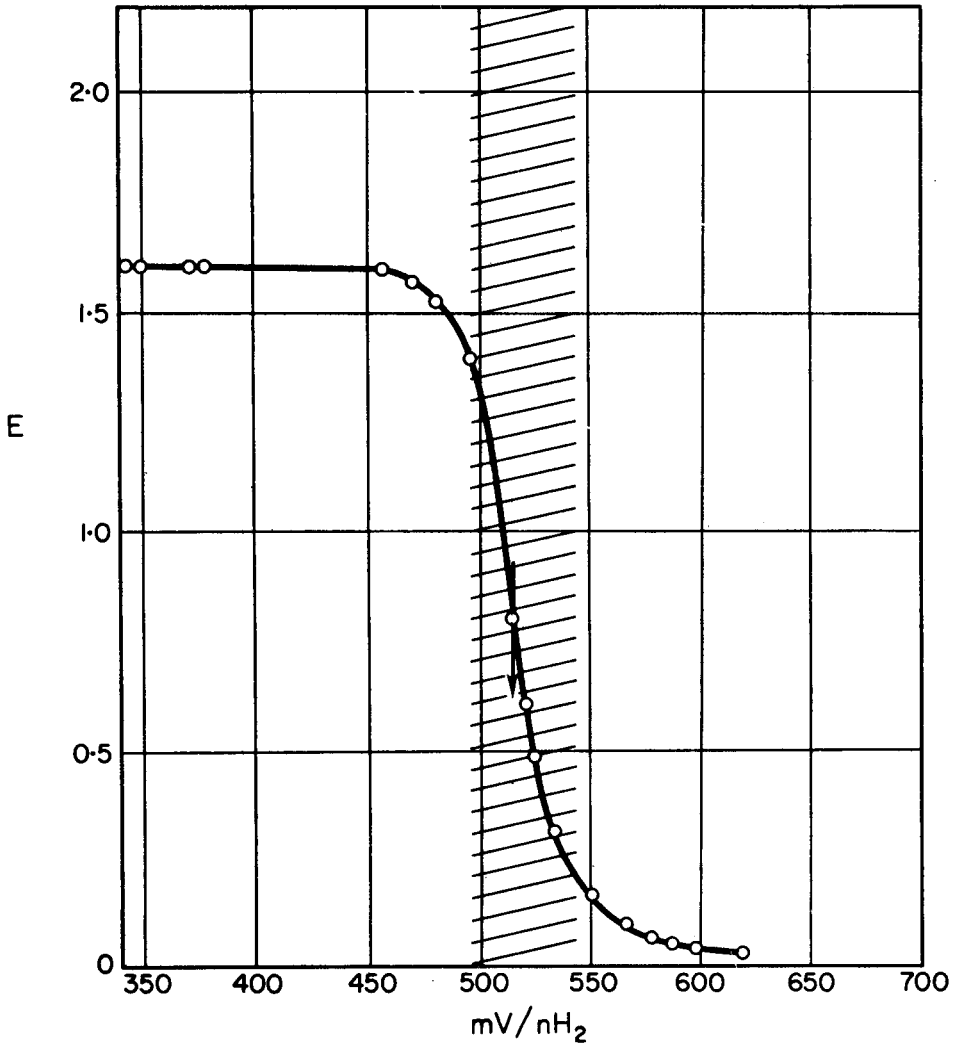


ABB. 5.—Die Umschlagskurve des Kakothelins bei  $a_{H^+} = 5,01 \cdot 10^{-1}$  Mol/L.

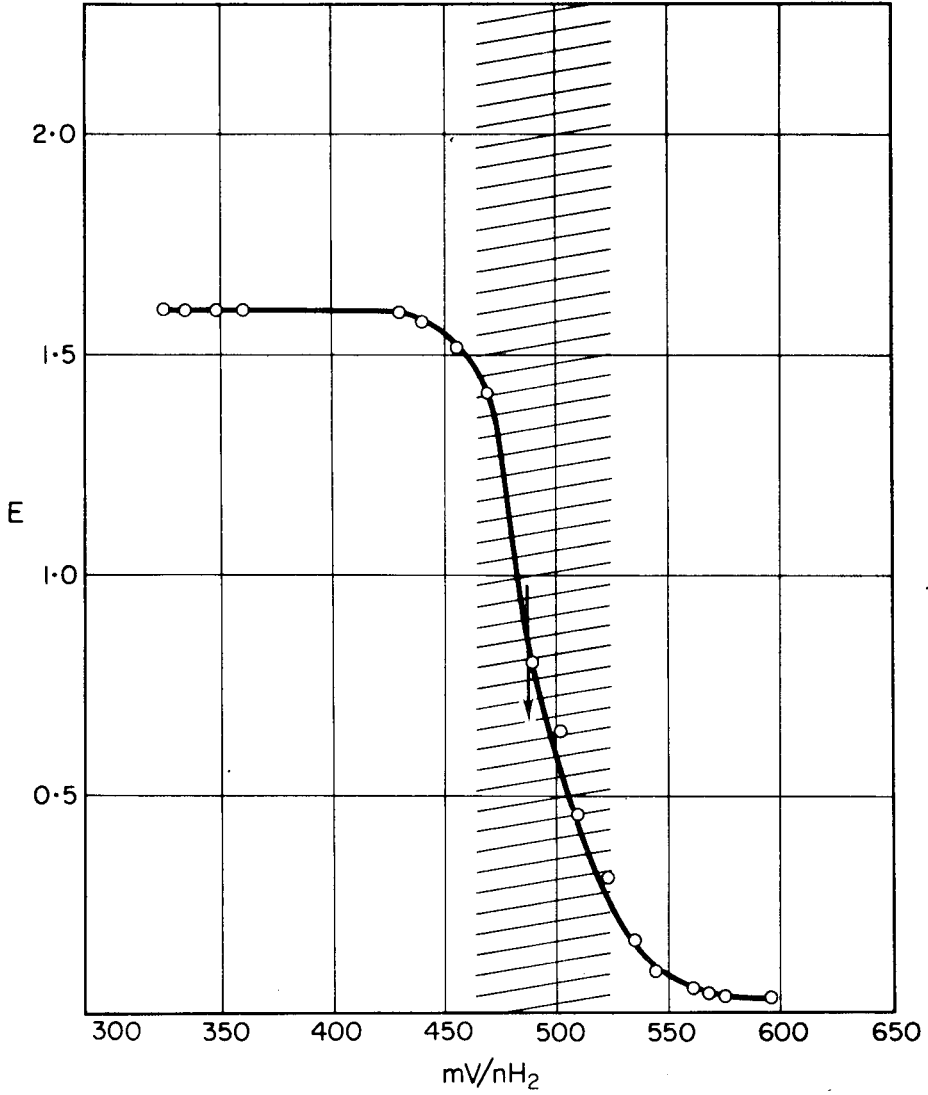


ABB. 6.—Die Umschlagskurve des Kakothelins bei  $a_{H^+} = 1,78 \cdot 10^{-1}$  Mol/L.



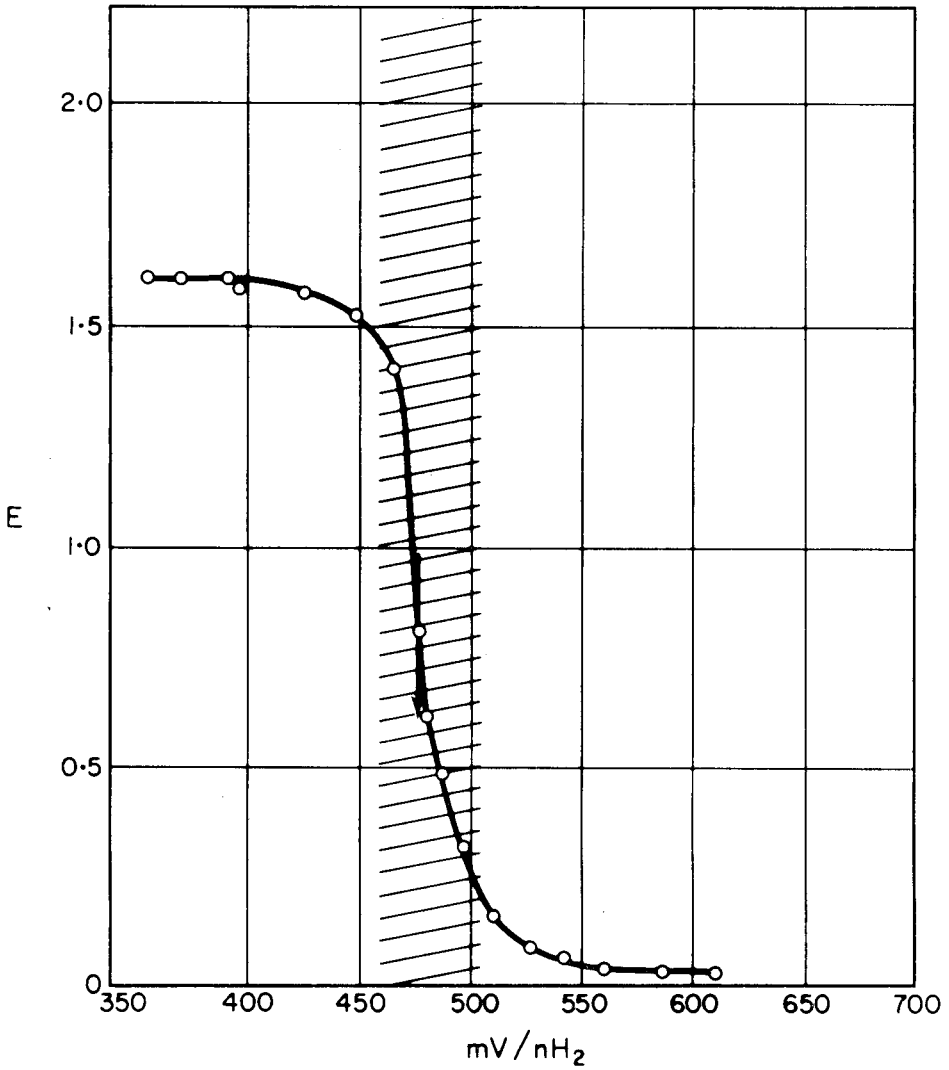


ABB. 7.—Die Umschlagskurve des Kakothelins bei  $a_{H^+} = 7,08 \cdot 10^{-2}$  Mol/L.

den einzelnen Kurven ablesbaren Umschlagspotentialwerte verschieben sich mit der Abnahme der Wasserstoffionenaktivität nach kleinere Potentialwerte.

Die Bestimmung der Umschlagspotentialwerte geschah auf Grund der Gleichung von Nernst:

$$\varepsilon = \varepsilon_0' + \frac{0,059}{n} \log \frac{c_{\text{ox}}}{c_{\text{red}}} \quad (1)$$

wo  $c_{\text{ox}}$  bzw.  $c_{\text{red}}$  die Konzentrationen der oxydierten bzw. reduzierten Form des Indicators bedeuten. Im Falle, wenn die Hälfte des Indicators in der reduzierten Form vorliegt, d.h.  $c_{\text{ox}} = c_{\text{red}}$ , wird aber die Extinktion der Lösung bei 530 m $\mu$  auch dem Mittelwerte der Extinktionen zwischen der vollständig reduzierten und oxydierten Form entsprechen. Das zweite Glied an der rechten Seite der Gleichung (I) verschwindet in diesem Falle, und die so gemessene Potentialwerte geben also die scheinbaren Standard-Redoxpotentialwerte ( $\varepsilon_0'$ ) an.

Diese scheinbaren Standard-Redoxpotentialwerte (bezogen auf n H<sub>2</sub>-Elektrode) sind in der Tabelle I. bei den verschiedenen Wasserstoffionenaktivitäten zusammengestellt.

TABELLE I.—DIE SCHEINBAREN STANDARD-REDOXPOTENTIALWERTE DES KAKOTHELINS BEI VERSCHIEDENEN WASSERSTOFFIONENAKTIVITÄTEN

$a_{\text{H}^+}$ , Mol/L	$\varepsilon_0$ , V
$7,08 \cdot 10^{-2}$	0,477
$1,78 \cdot 10^{-1}$	0,490
$5,01 \cdot 10^{-1}$	0,515
$7,94 \cdot 10^{-1}$	0,526
2,00	0,549

Wenn man die  $\varepsilon_0'$ -Werte als Funktion der pH-Werte aufzeichnet, ergibt sich in diesen saueren Lösungen eine Gerade, (siehe Abb. 8.) der  $r_{\text{H}}$ -Theorie von Clark entsprechend. Der  $r_{\text{H}}$ -exponent des Kakothelins ergibt sich also im Mittelwert:

$$r_{\text{H}} = \frac{\varepsilon_0' + 0,059 \text{ pH}}{0,0295} = 18,1$$

Aus den Grenzwerten des Redox-Umschlagintervalles ist annäherungsweise auch die Anzahl der in der in der Reduktionsvorgang teilnehmenden Elektronen bestimmbar. Wenn nämlich, das Konzentrationsverhältnis  $\frac{c_{\text{ox}}}{c_{\text{red}}} = \frac{10}{1}$  ist so wird die Extinktion der Lösung bei 530 m $\mu$  ungefähr gleich dem  $\frac{1}{10}$  Teil des maximalen Extinktionswertes und die gemessene Redoxpotentialwerte werden um  $\frac{0,059}{n}$  Volt höher liegen als  $\varepsilon_0'$ . Umgekehrt bei dem Konzentrationsverhältnis  $\frac{c_{\text{ox}}}{c_{\text{red}}} = \frac{1}{10}$ , bekommt man den  $\frac{9}{10}$  Teil des maximalen Extinktionswertes, und die Redoxpotentialwerte liegen in diesem Falle um  $\frac{0,059}{n}$  Volt niedriger als  $\varepsilon_0'$ .

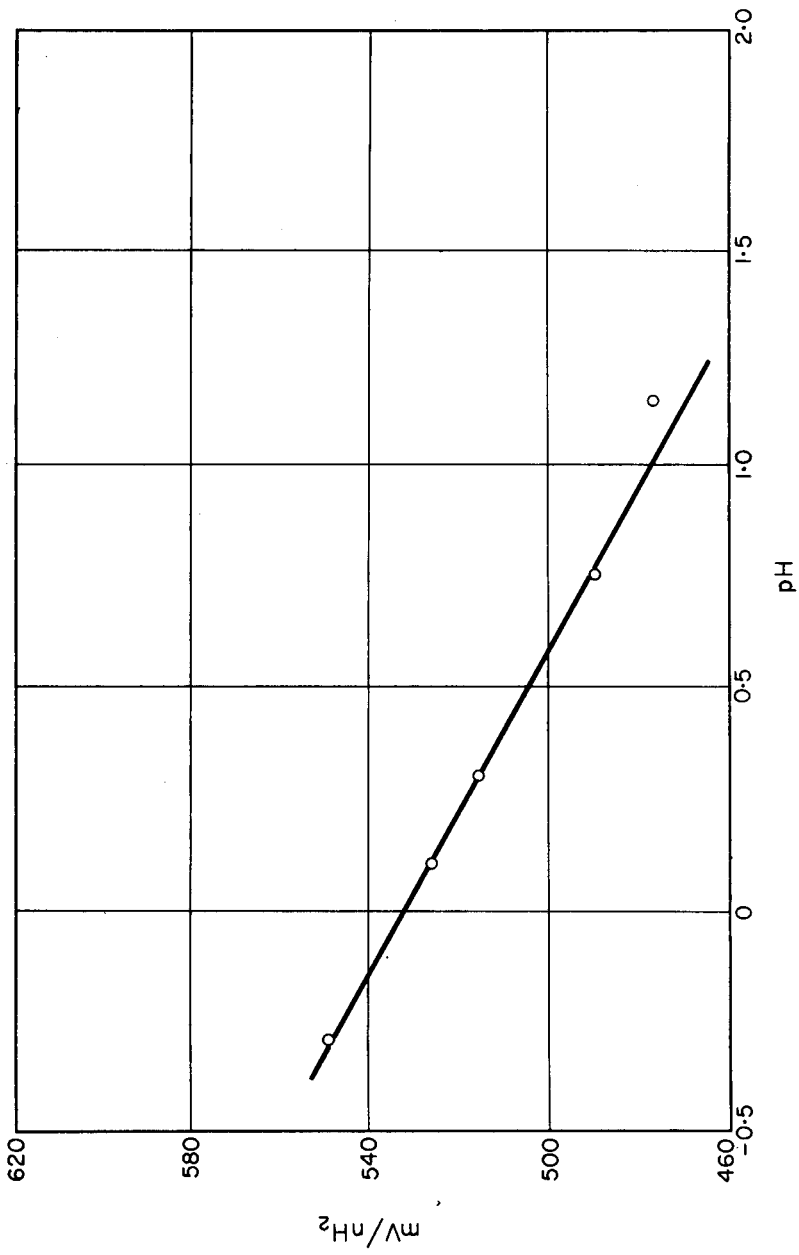


ABB. 8.—Die scheinbaren Standard-Redoxpotentialwerte des Kakothelins als Funktion der pH-Werte.

Aus den Nernst-schen Gleichungen:

$$\varepsilon_1 = \varepsilon_0' + \frac{0,059}{n} \log \frac{1}{10} \text{ und}$$

$$\varepsilon_2 = \varepsilon_0' + \frac{0,059}{n} \log \frac{10}{1}$$

bekommt man für  $n$  also

$$n = 2 \frac{0,059}{\varepsilon_2 - \varepsilon_1} \sim 2$$

d.h. im Reduktionsvorgange nehmen zwei Elektronen pro Mol Kakothelin Teil.

Wir nahmen außerdem auch die potentiometrischen Titrationskurven des Kakothelins mit  $\text{SnCl}_2$  und  $\text{TiCl}_3$  Lösungen auf. Die Ergebnisse sieht man auf den Abb. 9. und 10.

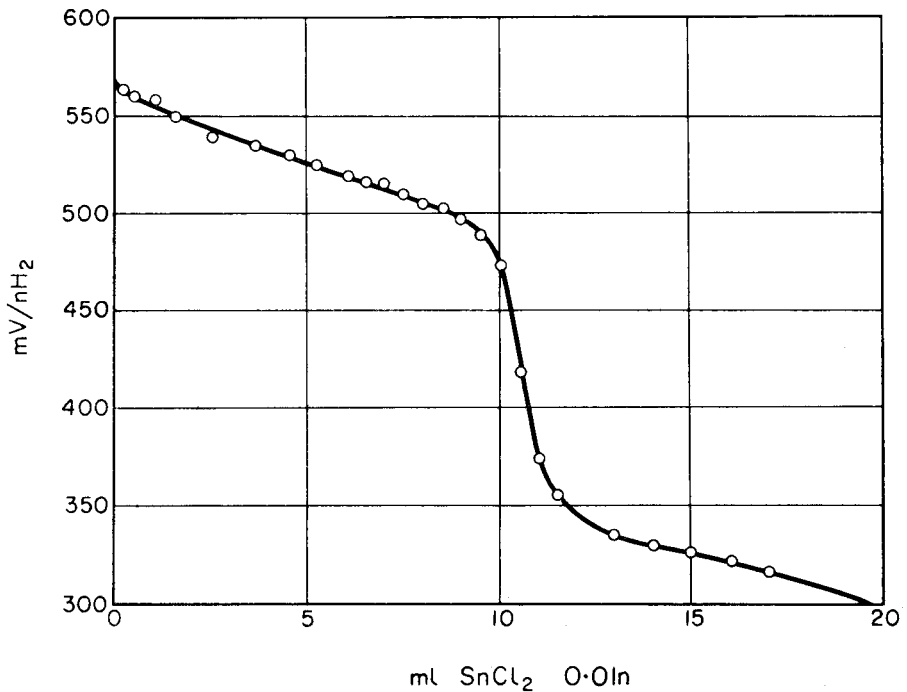


ABB. 9.—Potentiometrische Titrationskurve von 5 ml  $9,83 \cdot 10^{-3}$  M Kakothelin mit 0,01 n  $\text{SnCl}_2$ , in 100 ml Lösung, bei  $a_{\text{H}^+} \sim 1$ .

Bei dem Titrieren mit  $\text{SnCl}_2$  bildet sich wie man sieht eine wohldefinierte Stufe, entsprechender vollkommenen Reduktion des Kakothelins aus. Nach Zugabe von 10 ml 0,01 n  $\text{SnCl}_2$  Lösung schlägt die Farbe der Lösung vollständig in die charakteristische tief violette Reduktions-Farbe um. Der Potentialwert entsprechend der 50%-igen Reduktion (nach Zugabe von 4,9 ml  $\text{SnCl}_2$ -Lösung) liegt bei 525 mv in sehr guter Übereinstimmung mit dem 526 mv, gewonnen durch die Umschlagskurven (siehe Tab. I.)

Vom Erscheinen der obenerwähnten wohldefinierten Stufe lässt es sich darauf

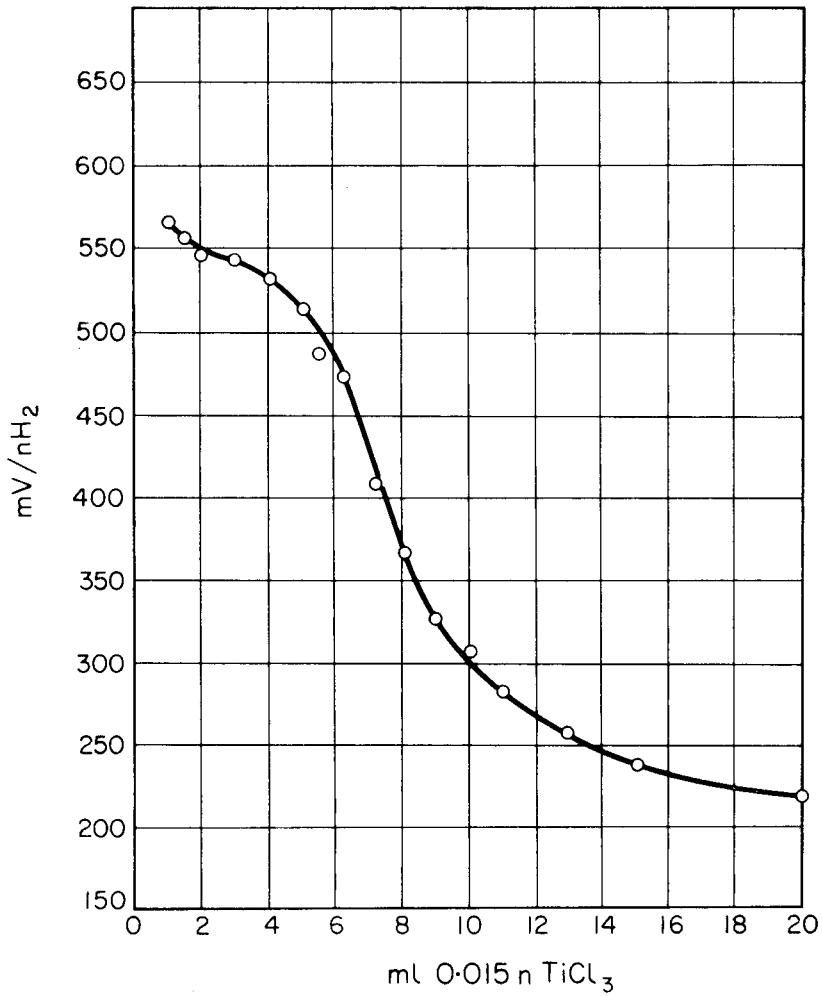


ABB. 10.—Potentiometrische Titrationskurve von 5 ml  $9,83 \cdot 10^{-3}$  M Kakothelin mit  $0,015$  n  $\text{TiCl}_3$ , in 100 ml Lösung, bei  $a_{\text{H}^+} \sim 1$ .

schliessen, dass die Reduktion des Kakothelins durch  $\text{SnCl}_2$  schnell und quantitativ nur bis zum violettfarbigen Reduktionsprodukt erfolgt. Dieser Reduktionsvorgang ist leicht reversibel, auch durch den Luftsauerstoff.

Bei dem Titrieren mit  $\text{TiCl}_3$  (siehe Abb. 10) geht aber die Reduktion parallel mit der ersten Stufe gleich weiter zu einem farblosen Reaktionsprodukt. Diese zweite

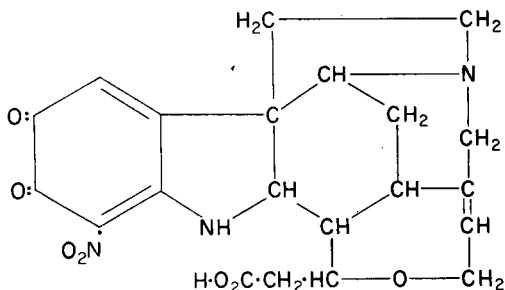


ABB. 11.—4-Nitro-brucichinonsäure (Bisdesmethylnitrobrucinhydrat) Base des Kakothelins.

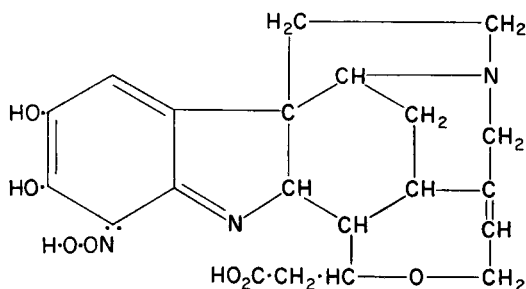


ABB. 12.—4-Iso-nitro-2,3-dioxy-strychninsäure (4-Isonitro-bisapomethylbrucinsäure).

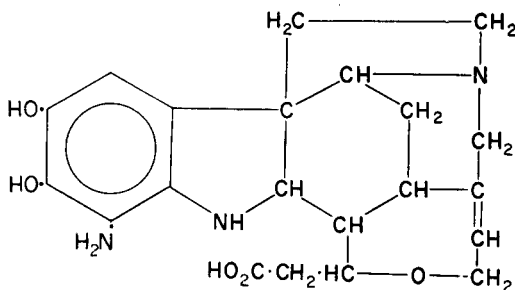


ABB. 13.—4-Amino-2,3-dioxystrychninsäure (4-Amino-bisapomethylbrucinsäure).

Stufe ist aber schon irreversibel, durch Oxydation bildet sich weder das violettfarbige Produkt, noch das gelbe Kakothelin mehr zurück.

Auf Grund unserer Untersuchungen erscheint uns folgendes Bild für den Reaktionsmechanismus der Reduktion des Kakothelins als sehr wahrscheinlich. Die Nitro-ortho-chinon Struktur des Kakothelins verwandelt sich bei der Reduktion mit  $\text{Sn}^{2+}$ -Ionen durch Aufnahme von zwei Elektronen und zwei Protonen und Umlagerung der benachbarten NH-Gruppe um eine Isonitro-hydrochinon Struktur (Siehe Abb. 11. und 12.)

Die schöne violette Farbe des Reduktionsproduktes wird durch diese desmotrope Form mit chinoid gebundener Isonitrogruppe vollkommen verständlich.

Bei weiterer Reduktion, z.B. mit  $\text{TiCl}_3$  wird ziemlich schnell schon auch die Isonitrogruppe zur Aminogruppe reduziert. Es bildet sich in diesem Falle die farblose 4-amino-2,3-dioxystrychninsäure (4-Amino-bisapomethyl-brucinsäure Abb. 13.)

Dieser Vorgang ist aber selbstverständlich schon irreversibel.

Diese Auffassung steht in vollem Einklang mit den neueren Vorstellungen der organischen Chemie über die Brucinderivate.<sup>8</sup>

**Summary**—The authors have already shown that cacotheline is an excellent reversible redox indicator for most stannometric titrations. The potential-colour curves of the indicator have now been measured, and the formal potential and  $r_H$  values in acid medium. The mechanism of the reduction reaction has been studied.

**Résumé**—D'après une étude précédente des auteurs, la cacotheline est un indicateur d'oxydo-réduction excellent et réversible pour la plupart des titrages par l'étain. Afin de rassembler le plus de données théoriques possible, les auteurs ont tracé les courbes de variation potential-couleur de l'indicateur et mesuré son potentiel normal apparent ainsi que les valeurs de  $r_H$  en milieu acide. Le mécanisme de la réaction de réduction a été étudié.

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## INDIKATORSYSTEME AUF VANADIUM-KOMPLEXONATBASIS

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(Eingegangen am 14 August 1962)

**Zusammenfassung**—Das fünfwertige Vanadium wird durch fast alle mit AeDTA reagierende Metalle aus dem AeDTA Komplex verdrängt. Das aus dem AeDTA Komplex verdrängte Vanadium gibt mit verschiedenen Farbstoffen lebhafte Farbreaktionen. Dieser Effekt kann bei komplexometrischen Titrationen zur Anzeige des Endpunktes benützt werden. Auf Grund dieser Beobachtung können viele Indikatorsysteme aufgebaut werden mit Vanadium(V)-Komplexonat als Grundlage; hier haben wir die Vanadium(V)-Komplexonat-Diphenylkarbazon-, -Brenzcatechinviolett -Karminsäure und -Morinsysteme beschrieben.

DAS fünfwertige Vanadium bildet in dem pH-Bereich 3–6,8 mit der Aethylendiamin-tetraessigsäure einen stabilen Komplex. In diesem pH-Bereich liegt der Logarithmus der Bildungskonstante des Komplexes in ammonazetathaltiger Lösung zwischen 7 und 8 und ist praktisch unabhängig vom pH-Wert der Lösung.<sup>1</sup> Um ein Kation mit AeDTA titrieren zu können, muss der Logarithmus der Bildungskonstante dieses Kations wenigstens 8 betragen; also wird das fünfwertige Vanadium durch alle diejenigen Kationen, welche in dem pH-Bereich 3–6,8 mit AeDTA titriert werden können, aus dem AeDTA-komplex verdrängt.

Das fünfwertige Vanadium gibt mit vielen organischen Farbstoffen lebhafte Farbreaktionen, also wird in Gegenwart dieser Farbstoffe das Verdrängen des Vanadium(V) aus dem AeDTA-Komplex durch einen lebhaften Farbumschlag angezeigt.

Zur Anzeige des Endpunktes der Titration können nur solche organische Indikatoren benützt werden, bei denen der Logarithmuswert der Bildungskonstante des Komplexes höchstens 4 beträgt. Wenn dies nicht zutrifft, so wird der Indikator durch das Vanadium blockiert. Von den untersuchten Farbstoffen haben wir bis jetzt das Diphenylkarbazon, das Brenzcatechinviolett, die Karminsäure, das Morin und das Diphenylkarbazid zur Anzeige des Endpunktes anwenden können.

Die Vanadationen sind in schwach saurer Lösung zur Bildung von Polysäuren geneigt. Das im Laufe der Polykondensation gebildete Penta- und Oktavanadat reagiert nur langsam mit dem AeDTA, also muss die Polykondensation möglichst verhindert werden. Je ärmer eine Lösung an Vanadationen ist, desto weniger kann die Polykondensation auftreten. In einer 0,001 molaren Lösung spielt sich die Polykondensation so langsam ab, dass sie praktisch überhaupt nicht mehr in Betracht kommt. Wenn man in der Lösung mit einer Vanadation-Konzentration über 0,001 m rechnen muss, so ist es vorteilhaft die Lösung mit einigen ml Glycerin zu versetzen, weil das Glycerin die Polykondensation der Vanadationen infolge einer andersartigen schwachen Komplexbildung verhindert.



Bei den meisten Kationen sinkt die Stabilität des AeDTA-Komplexes beim Absinken des pH-Wertes dem  $\alpha_H$ -Wert proportional ab. Die Stabilität des Vanadium-AeDTA-Komplexes ist dagegen in einem weiten pH-Bereich praktisch unverändert. Das Indikatorsystem bietet also die Möglichkeit, durch Aenderung des pH-Wertes in demselben Lösungsanteil nebeneinander mehrere Kationen zu bestimmen.

Die Stabilität des Vanadium(V)-Komplexonats wird in Gegenwart von organischen Lösungsmitteln nicht wesentlich erhöht. Dagegen steigt die Stabilität der AeDTA-Komplexe von vielen Kationen in einer solchen Lösung an und dadurch ergibt sich die Möglichkeit der Bestimmung einiger Kationen mit diesem Indikatorsystem, die mit anderen Indikatoren nur schwer zu bestimmen sind. [Z. B. Titrieren von Antimon(III), Molybden(VI), oder Ca bei einem pH-Wert unter 6,8.]

#### EXPERIMENTELLER TEIL

##### Reagenzien

0,1 m AeDTA Messlösung

0,05 m AeDTA Messlösung

0,1 m Ammoniummetavanadatlösung

0,05 m Vanadium(V)Komplexonat: die 0,1 m AeDTA-Lösung und die 0,1 m Ammoniummetavanadatlösung werden im Verhältnis 1:1 vermischt.

*Herstellung von festem Vanadium(V)-Komplexonat:* In ein 400 ml Becherglas wird 18,72 g Äthylendiamintetraessigsäures Dinatrium und 5,85 g Ammoniummetavanadat eingewogen und in 30 ml 10%-iger Natronlauge unter langsamem Erhitzen bis zur völligen Klärung gelöst. Nach Beenden der Auflösung wird 5 ml Eisessig zugegeben, die Masse wird mit 1 kg festem Kaliumnitrat in einer grossen Porzellenschale verrieben und das feuchte Salz wird unter vorsichtigem Erhitzen (80°C) und ständigem Umrühren bis zur Trockne eingedampft.

*Diphenylkarbazonlösung:* 0,2 g Diphenylkarbazon wird in 100 ml Alkohol gelöst.

*Methylenblaulösung:* 0,01 g Methylenblau wird in 100 ml dest. Wasser gelöst.

*Brenzcatechinviolettlösung:* 0,5 g Brenzcatechinviolett wird in 100 ml Wasser gelöst.

*Karminsäurelösung:* 0,3 g Karminsäure wird in 100 ml dest. Wasser gelöst.

*Morinlösung:* 0,1 g Morin wird in 100 ml Alkohol gelöst. 0,05 m Metallsalz-Messlösung: Von dem 99,99%-igen metallischen Mangan, Kadmium, Zink, Wismut, Nickel, Blei und Gallium wurde die theoretisch berechnete Menge eingewogen und aufgelöst. Nach dem Auflösen wurde die Lösung in einem Messkolben bis zur Marke aufgefüllt.

*Pufferlösung:* 500 g Ammonazetat wird in 1000 ml dest. Wasser gelöst und nach völliger Auflösung mit 50 ml Eisessig versetzt.

#### DAS VANADIUM(V)KOMPLEXONAT-DIPHENYLKARBAZON INDIKATORSYSTEM<sup>2</sup>

Das fünfwertige Vanadium gibt mit dem Diphenylkarbazon eine lebhaft violettrote Farbreaktion. Bei Zugabe von AeDTA wird der Vanadium-Diphenylkarbazon-Komplex zerstört, das Vanadium bildet mit dem AeDTA einen stabileren Komplex und die Farbreaktion verschwindet. Das Diphenylkarbazon reagiert mit dem Vanadium nicht als ein Redoxindikator, sondern als ein Metallindikator, weil die Bildung des Vanadium(V)-AeDTA-Komplexes durch keine Aenderung des Redoxpotentials begleitet wird. Bei einem pH-Wert unter 5 ist das Diphenylkarbazon farblos, also zeigt bei der direkten Titration im Endpunkt der Titrierung die Lösung einen Farbumschlag von violettrot nach farblos. Oberhalb von pH = 5 ist die Eigenfarbe des Diphenylkarbazons blassrosa. In so einer Lösung tritt ein Farbumschlag des Indikators von violettrot nach blassrosa auf. Um einen scharferen Farbumschlag zu erhalten, kann man neben dem Diphenylkarbazon auch einige Tropfen Methylenblau zugeben. In diesem Fall findet ein Farbumschlag von rotviolett nach hellblau statt.

*Allgemeine Arbeitsvorschrift bei direkten Titration*

Der zur Titration günstige pH-Wert wird mit Ammoniumazetat und Essigsäure eingestellt und die Lösung wird mit dest. Wasser auf 150 bis 200 ml aufgefüllt. Danach wird die Lösung entweder mit ungefähr 1 ml 0,05 m Vanadiumkomplexonatlösung, oder in fester Form mit ungefähr 1 g mit Kaliumnitrat im Verhältnis 40:1 verriebenem Vanadiumkomplexonat versetzt und in Gegenwart von 0,5 ml 0,2%-iger alkoholischer Diphenylkarbazon-Lösung bis zum Farbumschlag des Indikators titriert. Bei Titrationen über pH = 5 wird nach dem Diphenylkarbazon noch 0,5 ml 0,01 %-iger Methylenblaulösung zugegeben. Mit dieser Methode können bei pH = 6–6,5 das Mangan (Tabelle I.), bei pH = 4–6,5 das Zink, Kadmium (Tabelle II.), Nickel (Tabelle III.), Kobalt, bei pH = 3–6 das Wismuth (Tabelle IV) und Blei, bei pH = 3–4,5 das Thorium und die seltenen Erden direkt titrimetrisch bestimmt werden. Das Aluminium kann bei pH = 4,5–6 in 50%-iger alkoholischer Lösung bei 80°C direkt titriert werden, wenn man das Aluminium mit Sulfosalzylsäure als Hilfskomplexbildner in Lösung hält. Das Kalzium kann bei pH = 6,6–6,8 titriert werden, wenn man die Stabilität des Kalzium-AeDTA-Komplexes durch Zugabe von 50%-igem Alkohol erhöht.

TABELLE I.

Zugegebene Mn Menge, mg	Verbrauch an 0,05 m AeDTA Messlösung, ml		Gefundene Mn Menge, mg	mg
	Berechneter	Gefundener		
2,7	1,0	1,05	2,8	+0,1
13,7	5,0	5,1	14,0	+0,3
27,4	10,0	10,1	27,7	+0,3
68,6	25,0	24,9	68,3	-0,3
137,3	50,0	49,8	136,7	-0,6

TABELLE II.

Zugegebene Cd Menge, mg	Verbrauch an 0,05 m AeDTA Messlösung, ml		Gefundene Cd Menge, mg	mg
	Berechneter	Gefundener		
2,8	0,5	0,50	2,8	±0,0
5,6	1,0	1,05	5,9	+0,3
11,2	2,0	2,05	11,5	+0,3
28,1	5,0	5,0	28,1	±0,0
56,2	10,0	9,95	55,9	-0,3
112,4	20,0	19,9	111,8	-0,6
224,8	40,0	39,9	224,2	-0,6

TABELLE III.

Zugegebene Ni Menge, mg	Verbrauch an 0,05 m AeDTA Messlösung, ml		Gefundene Ni Menge, mg	mg
	Berechneter	Gefundener		
2,9	1,0	1,02	2,96	+0,06
5,8	2,0	2,03	5,9	+0,09
14,7	5,0	5,00	14,7	±0,0
29,3	10,0	9,95	29,15	-0,15
58,7	20,0	19,9	58,4	-0,3
117,4	40,0	39,9	117,1	-0,3

*Allgemeine Arbeitsweise beim Rücktitrieren*

Viele Metalle, die bei pH = 3–7 hydrolisieren, werden durch Rücktitrieren bestimmt in Gegenwart des Vanadiumkomplexonat-Diphenylkarbazon Indikatorsystems. In diesem Fall verfährt man folgendermassen: die zu untersuchende Lösung wird mit einem bekannten Anteil der AeDTA-Messlösung (im Überschuss) versetzt und nach Zugabe von ungefähr 1 ml Vanadium(V) Komplexonatlösung oder ungefähr 1 g festem Vanadiumkomplexonat-Kalium-nitrat-Gemisch und 0,5 ml 0,3%-igem Diphenylkarbazon wird der Überschuss des AeDTA mit einer Zink-, Thorium-, Blei-, Mangan- usw. -salzmesslösung bis zum Farbumschlag des Indikators nach rotviolett rücktitriert.

TABELLE IV

Zugegebene Bi Menge, mg	Verbrauch an 0,05 m AeDTA Messlösung, ml		Gefundene Bi Menge, mg	mg
	Berechneter	Gefundener		
5,2	0,5	0,5	5,2	±0,0
10,4	1,0	1,0	10,4	±0,0
20,9	2,0	2,03	21,2	+0,3
52,2	5,0	5,05	52,7	+0,5
104,5	10,0	9,95	104,0	-0,5
209,0	20,0	19,92	208,2	-0,8

Mit dieser Methode kann Aluminium, Titan(IV), Zinn(IV), Antimon(III), Molybden(VI), Chrom(III), Vanadium(V) und Eisen(III) bestimmt werden.

#### DAS VANADIUM(V)-KOMPLEXONAT—BRENCZATECHINVIOLETT INDIKATORSYSTEM

Das Vanadium(V) bildet mit dem Brenzcatechinviolett<sup>3</sup> in Ammonazetathaltiger Lösung einen blaufarbenen Komplex. Diese Farbreaktion kann bei pH = 5–6,5 ebenfalls zur Anzeige des Endpunktes bei den AeDTA-Titrationen dienen. Am Endpunkt der Titration gibt der Indikator einen Farbumschlag von blau nach leuchtend gelb. Diese Methode bietet die Möglichkeit zur weiteren Anwendung des Brenzcatechinvioletts, denn auf diese Weise können mit Brenzcatechinviolett auch solche Kationen titriert werden, die mit Brenzcatechinviolett sonst keine Farbreaktion geben, so z. B. (Tabelle V.) Kadmium, Zink, Blei usw. Das Brenzcatechinviolett kann nur in einem

TABELLE V.

Zugegebene Zn Menge, mg	Verbrauch an 0,05 m AeDTA Messlösung, ml		Gefundene Zn Menge, mg	mg
	Berechneter	Gefundener		
1,6	0,5	0,5	1,6	±0,0
3,2	1,0	1,05	3,35	+0,15
16,3	5,0	5,0	16,3	±0,0
32,7	10,0	9,9	32,4	-0,3
65,4	20,0	19,9	65,1	-0,3
130,8	40,0	39,9	130,5	-0,3

engeren pH-Bereich angewandt werden, als das Diphenylkarbazon. Ausserdem wird es auch durch einzelne Kationen blockiert, also kann mit Brenzcatechinviolett ein weniger universales Indikatorsystem ausgebildet werden, als mit Diphenylkarbazon. Das Brenzcatechinviolett hat aber den grossen Vorteil, dass es wasserlöslich ist und mit trockenem Vanadium komplexonat verrieben in einer Stufe zugegeben werden kann; es ist also nicht nötig, die einzelnen Komponenten des Indikatorsystems gesondert zuzugeben. Wenn man 100 g des wie oben hergestellten festen Vanadiumkomplexonats mit 0,2 g Brenzcatechinviolett verreibt, so erhält man ein monatenlang haltbares Indikatorgemisch.

#### DAS VANADIUMKOMPLEXONAT—KARMINSÄURE INDIKATORSYSTEM

Das Vanadium(V) gibt mit Karminsäure im pH-Bereich 3–6,5 eine violettrote Färbung. Die Eigenfarbe des Indikators ist blassrosa, und die Schärfe des Farbumschlages kann erhöht werden, wenn man neben der Karminsäure auch Methylenblau

zugibt. Da die Karminsäure ebenfalls wasserlöslich ist, kann man eine feste Indikatorermischung herstellen, die alle Komponenten des Indikators enthält. Wenn man 100 g des wie oben hergestellten festen Vanadiumkomplexonats mit 0,1 g Karminsäure und 0,05 g Methylenblau verreibt, so erhält man ein monatenlang haltbares Indikatorgemisch.

#### DAS VANADIUMKOMPLEXONAT—MORIN INDIKATORSYSTEM

Das Vanadium(V) gibt mit einer Morinlösung eine intensiv gelbe Farbreaktion. Die Eigenfarbe der Morinlösung eine blassgelb und am Endpunkt der Titration geht die Farbe des Indikators von intensiv gelb in blassgelb über. Der Farbumschlag kann gut erfasst werden, obwohl er weniger scharf ist, als bei den oben erwähnten Indikatoren.

**Summary**—Quinquevalent vanadium is displaced from its EDTA complex by almost all ions which react with EDTA. The liberated vanadium can then give colour reactions with many dyes, and this can be used to indicate the end-point in a complexometric titration. Many indicator systems can be devised on this basis, and the present paper deals with systems containing vanadium<sup>V</sup>, EDTA and diphenylcarbazone, pyrocatechol violet, carminic acid or morin.

**Résumé**—Le vanadium pentavalent est déplacé du complexe qu'il forme avec l'EDTA par presque tous les ions qui réagissent avec l'EDTA. Le vanadium libéré peut donner des réactions colorées avec de nombreux colorants, qui peuvent être utilisés pour indiquer le point équivalent en complexométrie.

De nombreuses possibilités sont envisagées sur cette base pour les systèmes contenant du vanadium, de l'EDTA, et la diphenylcarbazone, le violet de pyrocatechol, l'acide carminique ou de morin.

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## MICRODETERMINATION OF CYANIDE ION BY RADIOACTIVE PRECIPITATE-EXCHANGE

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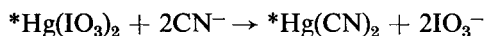
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(Received 14 August 1962)

**Summary**—Small amounts of cyanide ion can be determined by radioactive precipitate-exchange, using mercury<sup>II</sup> iodate with tagged mercury. The accuracy of the method is  $\pm 5\%$ . Chloride and cyanide ions can also be determined in the presence of each other. The cyanide ion is expelled from an acidic solution by heating, or using the formaldehyde reaction.

FOR the determination of small amounts of cyanide only a few methods are known. The basis of most colorimetric determinations is the increase in oxidising ability of copper<sup>II</sup> ions in the presence of hydrogen cyanide, and the measurement of the optical density of products formed during the oxidation.<sup>1-4</sup> Another method is the transformation of hydrogen cyanide to cyanogen halides, which react with pyridine and a condensing agent (like benzidine, pyrazolone or barbituric acid) forming a coloured compound, which can be measured colorimetrically.<sup>5-7</sup>

The present method<sup>8</sup> is based on a new principle. If solid mercury<sup>II</sup> iodate is added to a solution of cyanide, a soluble, non-dissociating complex is formed, comparable with that formed by chloride and bromide ion. If the cyanide-exchange is carried out with mercury<sup>II</sup> iodate, using tagged mercury, the amount of cyanide can be calculated from the activity of the mercury<sup>II</sup> cyanide solution. The amount of mercury<sup>II</sup> which goes into solution is proportional to the amount of cyanide ion.



The actual solubility of the exchanging precipitate can be greatly depressed by the addition of iodate ion, so that the method is fairly suitable for the determination of very small amounts of cyanide. Since cyanide ion can be removed easily from the solution, the method can in addition be applied to the simultaneous determination of chloride and cyanide ions. The radioactive precipitate-exchange of chloride ion has been described elsewhere.<sup>9</sup>

### EXPERIMENTAL

#### Reagents

*Potassium cyanide solutions:* 0.01N and 0.001N: Both were prepared freshly before use by the appropriate dilution and rendering alkaline of 0.1N solutions. The 0.1N solution was standardised in each case according to the Liebig-Denigés method.

*Sodium chloride solution:* 0.01N and 0.001N.

*Sulphuric acid:* 0.1N and 0.01N: these must be free from halides.

*Sodium hydroxide:* 1N: Halide-free.

*Sodium iodate solution:* 1N: For the removal of its halide content this must be shaken with inactive mercury<sup>II</sup> iodate, and filtered.

*Methyl red-methylene blue indicator*

*Water:* Distilled in a glass apparatus from silver nitrate.

*Mercury<sup>II</sup> iodate suspension:* This is tagged with active <sup>203</sup>Hg ( $t_{1/2} = 47$  days). For its preparation take 50 mg of mercury of 6 mC activity or 100 mg of mercury of 20 mC activity, and mix with

about 0.5 g of inactive mercury. (Dilution of the active mercury with inactive mercury is carried out to give a specific activity in the product between 20 and 50 mC/g). Dissolve the sample in nitric acid and boil out nitrous fumes. From the nitrate solution, containing an excess of nitric acid, precipitate active mercury<sup>113</sup> iodate suspension using an excess of potassium iodate, and wash 10 times by decantation with 0.5% nitric acid. The suspension should contain small amounts of free acid, because otherwise basic salt may be formed, and the results are then not reproducible. A small excess of iodate does not interfere.

#### Apparatus

The solution activities were measured with a liquid counter, filled with argon + alcohol and having an Aquadag cathode. An EMG decade scaler (type 1872) was used. According to the activity to be measured counting times were selected so that the errors arising from statistical scattering of the radioactive decomposition would be lower than 1%.

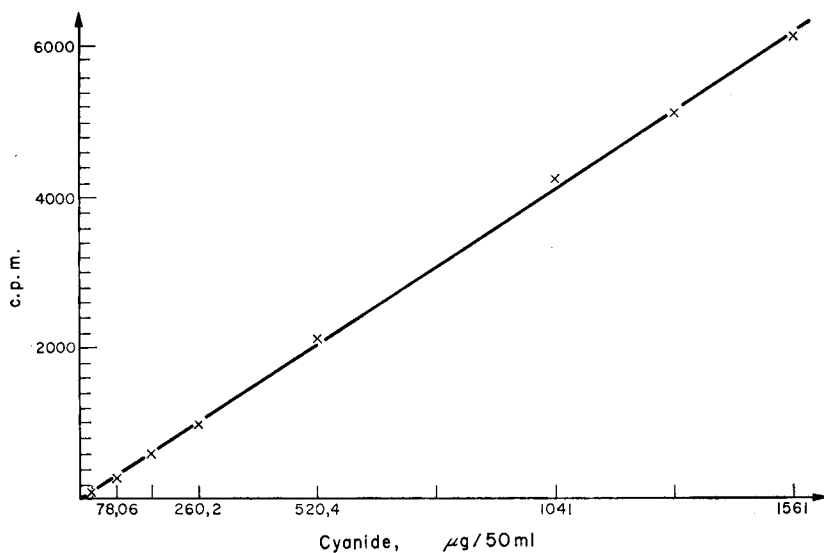


FIG. 1.—Calibration curve.

#### Determination of cyanide ion

Because of the volatility of cyanide ion the following procedure can be suggested.

*Procedure:* Place the sample, containing 26–520  $\mu\text{g}$  of cyanide ion, in a 50-ml volumetric flask, and add to the alkaline solution 1 drop of methyl red-methylene blue indicator and then the acidic active mercury<sup>113</sup> iodate suspension, until excess is indicated by visible amounts of precipitate. If the indicator remains green, add sufficient 0.01N sulphuric acid, dropwise, to turn the colour of the solution just to red. Then add 2 ml of 1N potassium iodate from a pipette, dilute with water to the mark and shake vigorously. After centrifuging for 20 min decant the solution from the precipitate and measure the activity of the mercury<sup>113</sup> cyanide solution. For background use a blank solution, containing the same amount of acid and 2 ml of 1N potassium iodate. If a 10-ml volumetric flask is used, the amount of cyanide should lie between 5.2 and 104  $\mu\text{g}$ , and 0.4 ml of 1N potassium iodate should be added to depress the solubility of the exchanging precipitate. The final volume is determined by the volume of the liquid counter tube.

The correlation between activity and concentration is linear over a wide concentration range (Fig. 1). From the practical point of view the lower part of the calibration curve, *i.e.*, the range of small concentrations, is important.

Some results of cyanide determinations are shown in Table I. The accuracy of measurements, carried out on two different dates with different mercury activities, was within  $\pm 3\%$ ; the standard deviation in the case of 3.12  $\mu\text{g}$  of  $\text{CN}^-/\text{ml}$  is about  $\pm 0.10 \mu\text{g}$ . The measured activities could not be corrected from the radioactive decay law for the time of preparation of the calibration graph, because the active mercury used was contaminated with <sup>197</sup>Hg ( $t_{1/2} = 64$  hr). Instead, two simultaneous experiments with known amounts of cyanide, with activities similar to that of the unknown sample, were carried out. From the concentrations and activities of the reference solutions and the activity of

the unknown solution, the concentration of the latter could be calculated. The calibration curve is only of help in indicating the number of counts to be expected, and must be prepared new for each new suspension.

#### *Simultaneous determination of cyanide and chloride ion*

Since cyanide ion can be easily removed from the solution, cyanide and chloride ions can be determined in the presence of each other, using a similar method. In one aliquot of the sample the activity of cyanide and chloride ions together can be determined. In another aliquot the activity caused by chloride only can be determined after removal of cyanide ion. For the decomposition of cyanide various methods are possible, *e.g.*, the removal of hydrogen cyanide from strongly acidic

TABLE I.—DETERMINATION OF CYANIDE IONS

Cyanide present, $\mu\text{g/ml}$	Cyanide found, $\mu\text{g/ml}$	Deviation, %
0.52	0.56	+7.6
0.52	0.49	-5.7
1.56	1.59	+1.9
3.12	2.93	-6.0
3.12	3.22	+3.2
3.12	3.04	-2.5
3.12	3.10	-0.6
5.20	5.31	+2.1
5.20	5.29	+1.7
5.20	4.95	-4.8
10.40	10.56	+1.5
10.40	10.63	+2.2
10.40	10.84	+4.2
10.40	10.57	+1.6

solutions, treatment with boric acid, oxidation by peroxide in alkaline solution, and decomposition with formaldehyde in alkaline medium.<sup>10-13</sup> Of these methods, the boiling out from acidic solution was chosen, because this method introduces the least amounts of chemicals and thus of contaminations into the solution. The formaldehyde method is also suitable because of its simplicity and rapidity.

*Procedure:* For the removal of hydrogen cyanide by boiling take an aliquot of the solution, acidify with 0.01*N* sulphuric acid to the red colour of the indicator mixture and add a further 20 ml of 0.01*N* sulphuric acid. After boiling the solution for 10 min and cooling, the precipitate exchange can be carried out. The pH of the acid solution is <2.

For the formaldehyde method add to the cyanide-containing sample 0.5 ml of 1*N* sodium hydroxide and 1 ml of 35% formaldehyde, shake the solution well, and neutralise with 0.1*N* sulphuric acid to the red colour of the indicator. The precipitate exchange can then be carried out. The blank value with formaldehyde agrees well with the formaldehyde-free blank.

The determination of both ions can be made with sufficient accuracy only if the number of counts given by the component present in the lesser amount is at least one magnitude greater than the error of the determination of the other component, expressed in counts. If the ratio is poorer than this, only the component present in higher concentration can be determined with an adequate accuracy.

In Table II the results of simultaneous cyanide and chloride determinations are presented. An analytically pure potassium cyanide preparation was also examined for chloride contamination. Agreeing with results of experiments carried out according to the "AnalaR" standard testing methods,<sup>14</sup> it was possible to prove by the radioactive precipitate-exchange method that the chloride content of the preparation was < 0.04%.

TABLE II.—SIMULTANEOUS DETERMINATION OF CHLORIDE AND CYANIDE IONS

Present, $\mu\text{g/ml}$		Found, $\mu\text{g/ml}$		Deviation, %	
$\text{Cl}^-$	$\text{CN}^-$	$\text{Cl}^-$	$\text{CN}^-$	$\text{Cl}^-$	$\text{CN}^-$
			decomposition with acid		
14.18	10.40	14.95	9.80	+5.4	-5.7
14.18	10.40	14.56	10.16	+2.6	-2.3
14.18	1.04	14.61	—	+3.0	—
14.18	1.04	13.90	—	-1.9	—
1.42	10.40	—	10.09	—	-2.9
			decomposition with formaldehyde		
14.18	1.04	15.06	—	+6.2	—

(—: the determination gave erroneous results for the component.)

**Zusammenfassung**—Kleine Mengen von Cyanidionen können mittels radioaktivem Austausch unter Verwendung von markiertem Quecksilberjodat bestimmt werden. Die Genauigkeit der Methode ist  $\pm 5\%$ . Chlorid und Cyanid können bei gleichzeitiger Anwesenheit bestimmt werden. Entfernung der Cyanidionen kann durch Austreiben als Blausäure in kochender saurer Lösung oder mittels der Reaktion mit Formaldehyd erzielt werden.

**Résumé**—De faibles quantités de cyanures peuvent être dosées par radioactivité en utilisant de l'iodate de mercure(II) marqué sur mercure. La précision de la méthode est de  $\pm 5\%$ . Les chlorures et les cyanures peuvent aussi être dosées en présence l'un de l'autre. La décomposition des ions cyanures peut être effectuée en chassant l'acide cyanhydrique par chauffage des solutions acides ou par la réaction au formaldéhyde.

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## NON-AQUEOUS TITRATIONS WITH A STANDARD SOLUTION OF AMIDAZOPHENE—I

### DETERMINATION OF CARBOXYLIC CHLORIDES AND THEIR DECOMPOSITION PRODUCTS

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(Received 14 August 1962)

**Summary**—It is possible to determine directly the hydrochloric acid contamination of acid chlorides in a benzene solution by titration with a standard solution of amidazophene in benzene in the presence of dimethyl yellow. Subsequently, acid chloride is decomposed by methanol, and the equivalent amount of hydrochloric acid liberated by this reaction is measured similarly by titration with a benzene solution of amidazophene. On diluting the solution with methanol, the original content of organic acid in the sample can be measured by titration with methanolic potassium hydroxide in the presence of phenolphthalein. Thus, it is possible to assay a sample of acid chloride from only one weighing, very quickly and simply.

THE analytical assay of acid chlorides of high reactivity presents an extremely difficult task, particularly when, in addition to the content of active acid chloride, also control of the content of free hydrochloric acid and organic acids formed on decomposition is necessary.

In certain methods, the reaction of acid chlorides with ethanol is utilised and the products of this reaction are measured. This reaction may serve also as a basis of a complete analysis of acid chlorides. Namely, subsequent to reacting the substance with anhydrous ethanol, the combined sum of the organic acid from the decomposition of the acid chloride and of the total hydrochloric acid is measured by alkalimetry. During the reaction, an ester forms in an amount equivalent to that of the active acid chloride, and the ester content can be determined on saponification. Subsequently, chloride is determined by argentimetry. From these measurements it is possible to calculate the original content of hydrochloric acid, organic acid and acid chloride of the sample, provided no ester contaminations were originally present.<sup>1</sup>

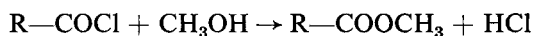
The task can also be carried out in a non-aqueous medium. The amount of free hydrochloric acid from decomposition is measured in a dioxan medium with a standard solution of tributylamine, then, after reaction with ethanol, the amount of hydrochloric acid liberated is measured in a dioxan medium with sodium ethylate. In another portion of the sample, the amount of total acid and acid chloride is measured with sodium ethylate. In this way, the original amounts of the three components can be calculated.<sup>2</sup>

Of the methods suggested for the complete analysis, that of Burger and Schulek<sup>1</sup> is very simple and useful. The fact that, because an indirect calculation is involved, the determination of hydrochloric acid can be carried out only with great error, does not reduce the value of the method. (When the organic acid component of the acid chloride is a weak acid, the total hydrochloric acid can be separately determined by the

two-indicator method, and thus the results will be more precise.) However, it is a serious disadvantage that ester contaminations interfere with this method. Interference was actually experienced in the investigation of a sample of trimethoxybenzoyl chloride where the presence of ester contamination appeared to be rather probable.

In order to eliminate this disadvantage an attempt was made to apply a method originally suggested for determination of the content of free hydrochloric acid and phosgene in chloroform.<sup>3</sup> It was recommended, in order to solve this problem, to carry out the titration with amidazophene in a non-aqueous medium. In the presence of dimethyl yellow indicator, it is possible to measure the content of free hydrochloric acid in chloroform with a solution of amidazophene (dimethylaminophenylpyrazolone). Subsequent to decomposition by ethanol, the amount of hydrochloric acid liberated from phosgene can also be measured. It is possible to prepare a standard solution of accurate titre from amidazophene by simple weighing (this compound can be readily recrystallised).

The method also lends itself to the complete control of acid chlorides. However, instead of chloroform, benzene was applied as solvent because it can be more easily refined and liberated from traces of water. An adequate amount of acid chloride is weighed, dissolved in benzene, and the content of free hydrochloric acid measured by titration with a benzene solution of amidazophene in the presence of dimethyl yellow. The presence of organic acids (including also acetic acid) causes no interference. Because amidazophene as a tertiary amine cannot be acylated, acid chlorides also do not interfere with the measurement, and they do not decompose. In the next step, acid chloride is decomposed by heating with methanol:



and the amount of hydrochloric acid liberated is measured similarly with a benzene solution of amidazophene. (The methanol content of the solution must be kept strictly within the prescribed range because otherwise methanol interferes with the end-point detection.) The solution is then diluted with methanol, and the combined sum of the original organic acid and of the amount of hydrochloric acid already titrated earlier is measured by titration with a methanolic solution of potassium hydroxide in the presence of phenolphthalein. In the given medium, the esters formed in the reaction of acid chloride with methanol do not saponify in the cold, *i.e.* they do not interfere. Amidazophene (as a weak base), previously applied as a standard substance, also does not interfere in the presence of the given indicator. Thus, it is possible to determine the three components quickly and accurately from one weighing, by using two (eventually three) simply preparable standard solutions.

Ester contaminations do not interfere with the method. Moreover, the quantity of this contamination can also be determined in a further step or by saponification carried out in the way already cited.<sup>1</sup> The method lends itself mainly to the complete assay of acid chlorides of moderate activity.

## EXPERIMENTAL

### Reagents

*Anhydrous benzene:* analytical grade.

*0.1 and 0.01M Solutions of amidazophene:* Dissolve 2.314 and 0.2314 g, respectively, of pure amidazophene or of that material recrystallized from ethanol, in benzene in a 100-ml volumetric flask, and make to the mark with benzene. This solution can be stored without any decomposition

TABLE I

Analysed sample and its amount weighed, mg	Content of hydrochloric acid				Content of carboxylic acid				Content of acid chloride			
	single	tests	average	%	single	tests	average	%	single	tests	average	%
	mg	%	%		mg	%	%		mg	%	%	
49.1	0.0265	0.054			4.988	10.16			42.98	87.54		
40.7	0.0199	0.049			4.098	10.07			36.00	88.45		
59.2	0.0355	0.060			6.329	10.69			51.52	87.03		
54.3	0.0331	0.061			5.829	10.66			47.22	86.97		
43.0	0.0232	0.054			4.481	10.42			37.22	86.55		
47.4	0.0266	0.056	0.055		4.830	10.19	10.40		42.02	88.65		87.57*
32.3	0.0168	0.052			3.262	10.10			28.48	88.18		
40.7	0.0236	0.058			4.151	10.20			35.94	88.11		
29.6	0.0148	0.050			3.182	10.75			25.94	87.64		
45.7	0.0265	0.058			4.744	10.38			39.91	87.33		
32.0	0.0179	0.056			3.446	10.77			27.15	86.84		
38.5	0.0343	0.087			0.671	1.74			38.09	98.95		
69.5	0.0639	0.092	0.088		1.161	1.67	1.72		68.20	98.13		98.48
65.6	0.0545	0.085			1.164	1.77			64.52	98.35		
52.9	0.0476	0.090			0.894	1.69			52.09	98.47		
37.6	0.0132	0.035			0.135	0.36			37.53	99.80		
23.4	0.0101	0.042	0.036		—	0.00	0.27		23.50	100.4		100.2
40.9	0.0163	0.040			0.123	0.30			41.10	100.5		
27.6	0.0077	0.028			0.116	0.42			27.68	100.3		

\* Calculated on the basis of the chloride content (neglecting the content of free hydrochloric acid), the sample proved to be of 87.45% grade.

for a few days in the bulb of a micro burette sealed with a trap filled with benzene. The ground joints of the burette should be smeared with glycerol containing starch.

#### *Anhydrous methanol*

*0.1M Methanolic potassium hydroxide solution:* Dissolve 0.60 g of potassium hydroxide in methanol in a 100-ml volumetric flask, make to the mark with methanol, and keep in the bulb of a micro burette sealed with a gas trap filled with methanolic potassium hydroxide. The titre of the solution is determined in the presence of phenolphthalein indicator with a 0.1M aqueous solution of hydrochloric acid of known titre (diluted with neutral methanol).

#### *Procedure—0.1% Solution of dimethyl yellow in benzene.*

*1% Solution of phenolphthalein in ethanol.* Weigh a sample of about 0.2 mg equiv of the acid chloride and dissolve in 1 ml of benzene in a 25-ml round-bottom flask attached to a reflux condenser with a ground joint. Add 1 drop of dimethyl yellow indicator and titrate the solution at a high speed with a 0.01M solution of amidazophene till a lemon-yellow tint appears: 1 ml of 0.01M standard amidazophene solution  $\equiv$  0.3647 mg of hydrochloric acid.

Now add 0.5 ml of anhydrous methanol to the yellow solution, attach the flask to the reflux condenser and heat for 10 min at 60–65°. Cool, and rinse the reflux condenser with 10–15 ml of benzene. Subsequently, add 1–2 drops of dimethyl yellow solution to the red solution which should not contain more than 5% of methanol, and titrate with a 0.1M solution of amidazophene till a yellow colour appears: 1 ml of 0.1M amidazophene solution  $\equiv$  0.1 mg equiv of acid chloride.

Finally, rinse the mixture with 10–15 ml of methanol into a 50-ml flask, and determine the total acid content by titration with methanolic potassium hydroxide in the presence of phenolphthalein. On subtracting the volume of 0.1M amidazophene solution consumed in the first two titrations from the consumption in the last titration, one obtains the volume of titrant consumed by the original content of free organic acid in the tested sample of acid chloride: 1 ml of 0.1M potassium hydroxide solution  $\equiv$  0.1 mg equiv of free organic acid.

Some samples of acid chlorides were investigated by the method presented, and the results obtained are given in Table I.

**Zusammenfassung**—Es ist möglich die Verunreinigung von Säurechloriden durch Salzsäure durch Titration mit Amidazophen in Benzol unter Verwendung von Dimethylgelb als Indicator direkt zu bestimmen. Anschliessend können die Säurechloride durch Methanol zersetzt werden und die in äquivalenter Menge frei gewordene Salzsäure wird in gleicher Art titriert. Bei Verdünnung der Lösung mit Methanol kann auch der ursprüngliche Gehalt an organischer Säure in der Probe durch Titration mit methanolischer Kalilauge gegen Phenolphthalein titriert werden. So ist die Kontrollbestimmung von Säurechloriden aus einer Einwaage sehr schnell und einfach möglich.

**Résumé**—Il est possible de doser directement la contamination en acide chlorhydrique des chlorures d'acide en solution dans le benzène, par titrage au moyen d'une solution étalon d'amidazophène dans le benzène en présence de jaune de diméthyle. A la suite de ce dosage, la chlorure d'acide est décomposée par le méthanol, et la quantité équivalente d'acide chlorhydrique libéré par cette réaction est dosée par titrage au moyen d'une solution benzénique d'amidazophène. Lors de la dilution de la solution par le méthanol, la teneur initiale de l'échantillon en acide organique peut être déterminée par titrage au moyen d'une solution de potasse dans le méthanol en présence de phénolphtaléine. Par suite, il est possible de contrôler très simplement et très rapidement la teneur d'un échantillon de chlorure d'acide au moyen d'une seule pesée.

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## USE OF A PLATE ELECTRODE FOR THE SPECTRO-CHEMICAL ANALYSIS OF SOLUTIONS

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(Received 14 August 1962)

**Summary**—A carbon electrode, with three thin plates on one end, has been developed. With this "plate electrode," the ultramicro analysis of solutions can be carried out using d.c. arc excitation.

RECENTLY a type of electrode which seems to be suitable for various spectrochemical purposes has been developed by the author. In this paper the principles of development of this electrode are discussed as well as measurements carried out with light sources consisting of this electrode, using d.c. arc excitation.

### THE PLATE ELECTRODE

In those spectrochemical analyses of solutions where a high absolute sensitivity is required, it is essential to concentrate the solution on a small part of the electrode. If carbon and graphite electrodes are used, the concentration is prohibited by the porous surface of the substance. This porous structure has an unwanted action, firstly in the absorption of the solution and secondly during the operation of the light source. When the solution becomes sucked into the electrode, a chromatographic separation takes place. During the operation of the light source, some of the metal vapours, formed on the surface, diffuses into the electrode and condenses there on the colder parts. The latter process becomes considerable if excitation is made with a continuous arc.

To inhibit the suction of the solution there are three methods to be found in the literature. The first of these is the production of a hydrophobic surface by impregnation.<sup>1</sup> According to the second method the solution must be dropped on the surface of a heated electrode to remove the solvent rapidly.<sup>2,3</sup> The former method has the disadvantage that the adhesion of the substance to be analysed is incomplete, while in the latter case the taking up of the solution is uncertain. Haftka<sup>4</sup> carried out surface concentration on the basis of the ring oven method, which is well known in micro-analysis. In this method the solution to be analysed is concentrated on the end surface of a separate small carbon rod. On continuous arc excitation the rod becomes hot in its whole mass, and therefore the possibility of internal condensation of metal vapours is small. Haftka thus gained a  $10^2$ – $10^3$ -fold increase in absolute sensitivity in some cases, which is an extremely high efficiency. About the quantitative use of the method there is yet no information. The porosity of the carbon rod plays an important role in this problem.

For the surface concentration of the solution a special form of electrode, seen in Fig. 1, has been developed by the author.

The plate electrode, made from carbon, must be rendered hygroscopic by pre-heating. On the upper plate about 0.01 ml of solution can be taken up without a

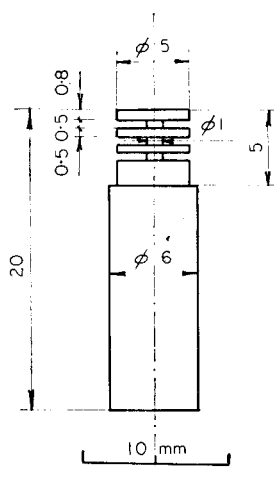


FIG. 1.—Plate electrode.

considerable suction of the solution over the plate. After drying of the electrode, further portions of the solution can be taken up, until the pores of the upper plate become saturated with the solution. In this way about 1 mg of metallic nickel can be taken up in its dissolved form. On continuous arc excitation the vapours migrate towards the electrode, then change their direction towards the plasma or condense on the lower plate. The evaporation of the condensed substance takes place after the combustion of the upper plate.

#### USE OF PLATE ELECTRODE FOR CONTINUOUS D.C. ARC EXCITATION

The behaviour of the plate electrode has been studied up to now with a d.c. arc. Two types of light source were developed for use with this electrode (see Fig. 2). Investigations were always made so that all three plates were combusted. The light source in Fig. 2(a) can be termed "total combustion" (TC) and that in Fig. 2(b) "buffered total combustion" (TCB) excitation.

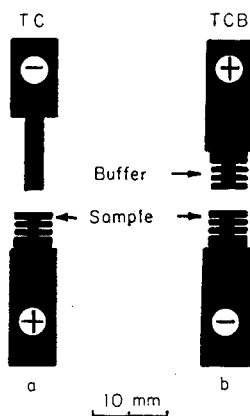


FIG. 2.—Electrode systems for d.c. arc.

## EXPERIMENTAL

*Excitation:* 220 V, d.c. arc, with 6 A (TC) and 7 A (TCB) effective currents; arc width: 3 mm.

*Spectrograph:* Zeiss Q 24 quartz spectrograph with 15- $\mu$  slit width, internal focusing, using the middle two thirds part of the arc column.

*Lighting time:* Until complete combustion of the plates occurred [about 100 sec (TC) or 180 sec (TCB)].

*Photography:* AGFA Blau Extrahart Spektral Platten, Kodak D 19 developer, 18°, 5 min, interruption bath.

*Photometry:* Zeiss Schnellphotometer; emulsion calibration with step light filters.

The plate electrodes were prepared with special knives on a lathe, and they were preheated in the case of the TC method for 30 sec. The solution was transferred to the upper plate of the cold electrode with a micrometer syringe. Glass instead of steel capillaries were used with the syringe. A volume of 0.01 ml of solution could be taken up with a relative error of  $\pm 2.1\%$ .

Using the TCB method on the "buffer electrode" so much lithium nitrate solution (0.25 g of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}/\text{ml}$ ) was taken up from a capillary that it just filled the spaces between the plates, then the electrodes were dried. Excitation was interrupted after 1 min, and the electrode was freshly impregnated with the buffer solution.

It is important to emphasise that the buffer electrode operates normally only if it is made of carbon and not of graphite.

## RESULTS

Time studies were made with the TC and TCB light sources. Experimental results are shown in Figs. 3, 4 and 5. As ordinates  $\log IK = Y$  values of the line and the  $\Delta Y$  values of the line pairs are plotted.

Evaporation maxima, seen in Fig. 3, are from the combustion of the single plates. Using the TC method the first evaporation maximum is much higher, because of the rapid temperature rise. The second evaporation maximum of lithium is the result of the taking up of the second portion of the buffer. Figs. 3 and 4 show results when 100  $\mu\text{g}$  and 1000  $\mu\text{g}$ , respectively, of nickel were taken up. The TCB method, in each case, shows more uniform evaporation. The variation of spectrum characteristics was followed (Fig. 4) by measurement of the intensities of ionic and atomic lines of vanadium.<sup>5</sup>

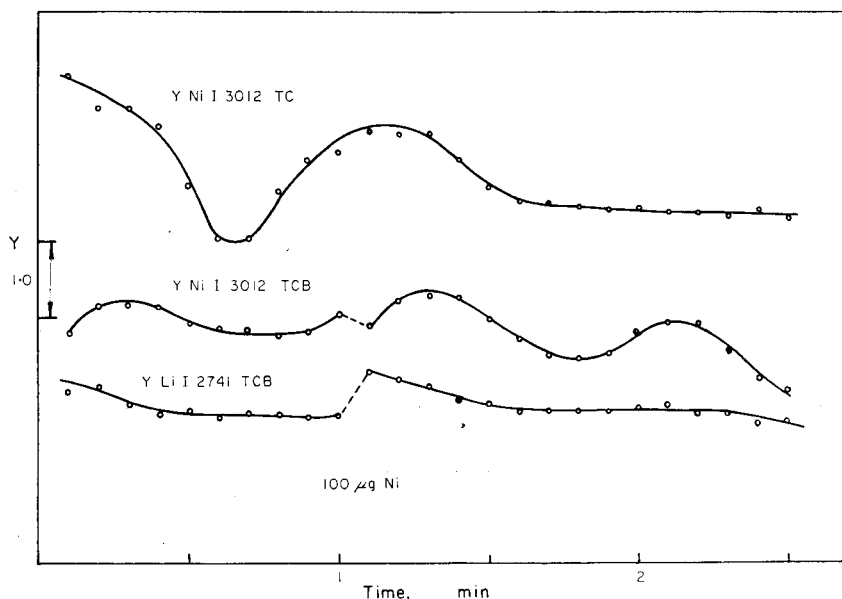


Fig. 3.—Time studies of TC and TCB methods.

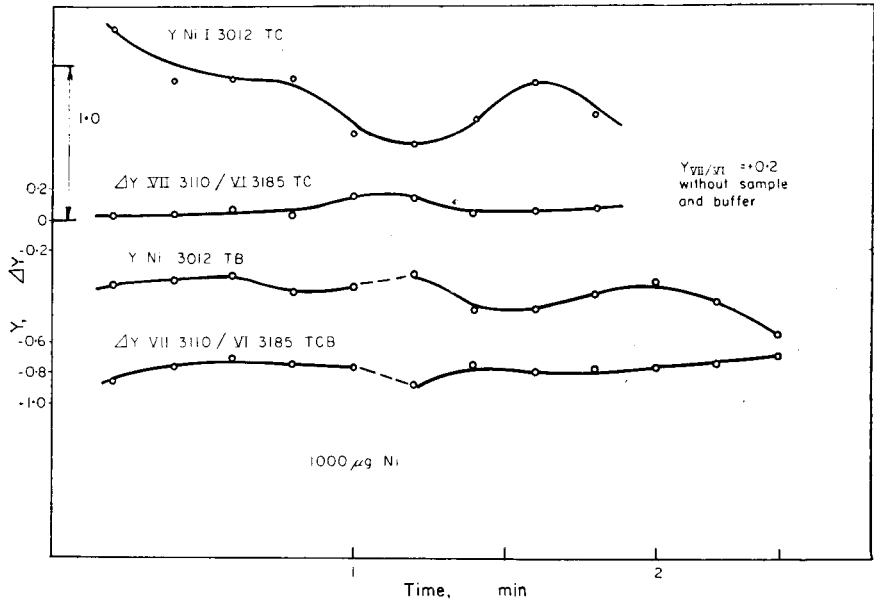


FIG. 4.—Time studies of TC and TCB methods.

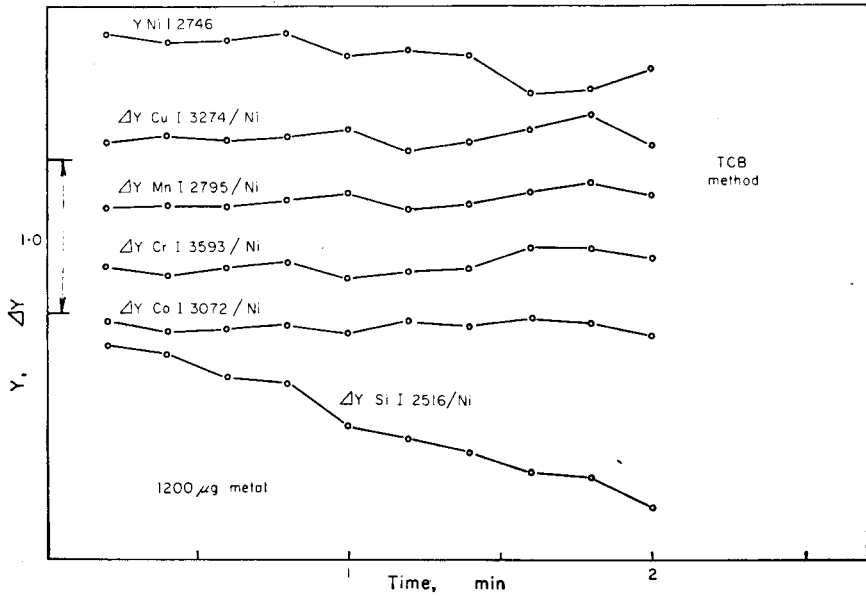


FIG. 5.—Time studies of TC and TCB methods.



In Fig. 5 the  $\Delta Y$ -time curves of a nickel alloy were obtained by the TCB method. The curves gained with the TC method show irregular and strongly varying shapes after 30 sec of excitation.

#### *Precision and sensitivity of the TC and TCB methods*

*Precision* can be characterised by the coefficient of variation, which was calculated for the analysis of two components of a nickel alloy from the results of fourteen parallel measurements. These data are shown in Table I. The values of the coefficients of variation correspond to 1% of cobalt and 0.1% of manganese (in percentage of the nickel alloy).

TABLE I.—REPRODUCIBILITY OF TC AND TCB METHODS

Anal. line/Ref. line, $\text{\AA}$	Coefficient of variation, %	
	TC	TCB
Co I 3072.3/Ni I 2746.8	8.3	5.2
Mn I 2801.1/Ni I 2746.8	*	3.7
Mn II 2576.1/Ni I 2746.8	8.7	6.4

\* Wide self-reversal

*Sensitivity* can be characterised according to Harvey<sup>6</sup> with a  $k$  "sensitivity factor". The  $k$  factors express the absolute value of the sensitivity only with a small accuracy but are especially adequate for the comparison of sensitivities of various analytical methods. The  $k$  factors can be calculated by the following equations:

$$k = c/2I_{1/b}$$

and

$$I_{1/b} = [I_{\text{line+backg.}}/I_{\text{backg.}}] - 1$$

where  $c$  is the concentration, and  $I$  is the intensity. Harvey expressed the sensitivity of his TC methods in percentages of 10-mg sample ( $k$ [%]). These have now been recalculated according to the equation  $k[\mu\text{g}] = 100 \cdot k$  [%], and are shown together with the present results in Table II.

TABLE II.—SENSITIVITY OF TC AND TCB METHODS

Anal. line, $\text{\AA}$	$k$ [ $\mu\text{g}$ ]		
	TC	TCB	Harvey (in carbon)
Co I 3453.5	0.85	0.16	0.2
Co I 3044.0	0.58	0.18	1.8
Mn I 2794.8	0.31	0.017	0.3
Mn II 2576.1	0.14	0.024	0.14
Ni I 3414.8	0.88	0.12	0.25
Ni I 3002.5	0.16	0.12	0.31
V I 3185.4	2.9	0.098	0.70
V II 3110.7	1.6	0.85	—

#### DISCUSSION

The TCB method fulfils the requirements of an ultramicro quantitative method. It makes possible the direct determination of 0.1 to 0.01% amounts of elements in 1 mg of sample, transferred to the upper part of the electrode.

The plate electrode, as "buffer electrode," is a step towards complete combustion and continuous buffering. Using this light source of constant temperature, development of an analytical method independent of matrix effects can be expected.

*Acknowledgement*—The author wishes to express his thanks to Professor L. Erdey, Head of the Institute, and to M. T. Vándorffy for their help in this work.

**Zusammenfassung**—Eine Kohlenstoffelektrode mit drei dünnen Scheiben an einem Ende wurde konstruiert. Mit dieser sogenannten "Plattenelektrode" kann die Ultramikroanalyse von Lösungen unter Verwendung eines Gleichstrombogens durchgeführt werden.

**Résumé**—L'auteur a mis au point une électrode de carbone terminée par trois disques de faible épaisseur. Avec cette électrode il est possible d'effectuer de l'ultramicro analyses de solutions en utilisant un arc alimenté en courant continu.

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# AUF DEN SCHWÄRZUNGSUNTERSCHIEDEN DER MANGANLINIEN BERUHENDE NEUE QUALITATIVE AUSWERTUNGSMETHODE, ZUR BESTIMMUNG DES MANGANGEHALTES DER ALUMINIUMLEGIERUNGEN—I

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(Eingegangen am 14 August 1962)

**Zusammenfassung**—Diese Arbeit berichtet über solche bisher unbekannt für quantitative Bestimmung geeigneten Zusammenhänge, die die mengenmässige Analyse der Mangan-Aluminium-Legierungen auf Grund der auf den Legierungslinien gemessenen Schwärzungsunterschiede ermöglichen. Laut diesem Verfahren werden die Aufnahmen mit einem Feussner-Erreger von 15 kv Spitzenspannung 5000 pf und 12,8 mH Selbstinduktion gemacht. Bei dem Abfunken sind 99,99%-tige Aluminiumelektrode 4 mm Elektrodenabstand und Zwischenabbildung zu verwenden. Wir führen das Licht aus der vor dem untersuchendem Material vorhandenen 1,3 mm dicken Schicht des Funkenstrecke in den Spektrograph ein. Das Photographieren der Aufnahmen geschieht auf "Agfa blau extrahart" Platte mit 20  $\mu$  Spaltbreite und mit 60 Sek Beleuchtung. Die Schwärzung der für das Messen angewandten Linienpaare—Mn 3547,79/Mn 2798,27 und Mn 3547,79/Mn 2576,10—muss man mithilfe der Verwendung der *Seidel'schen "W"-Transformation* bestimmen.

## EINLEITUNG

DIE Messergebnisse der früher mit Erregern kleiner Energie durchgeführten Aufnahmen zeigten, dass die transformierten Schwärzungsunterschiede der Zusatzlinien von der Konzentration des vorliegenden Legierungselementes abhängen. In Betracht nehmend, dass es uns im Falle von Erregung mit kleiner Energie auch bei den zur Selbstabsorption am besten neigenden Linien keine Selbstabsorption beobachten gelang, schien die Hypothese zutreffend, dass einige Zusatzlinien unter entsprechenden Versuchsumständen auch sich selbst-für die qualitative Auswertung geeignet sind. In der Literatur ist bekannt ein Verfahren, welches für die qualitative Bestimmung auf Grund der voneinander abweichenden Selbstabsorption zweier Linien geeignet ist. Dieses Verfahren verbreitete sich nicht, weil die Selbstabsorption durch viele "in der Hand schwer haltbaren" Umstände beeinflusst sein kann. Die unten zur Darlegung kommenden Untersuchungen deweisen es, dass man auch ohne Selbstabsorption die Auswertungslinien zur Bestimmung des Mangans in Aluminium abfassen kann. Das Ziel dieser Versuche war die für die qualitative Bestimmung geeignetsten Linien zu forschen, die zur qualitativen Bestimmung'entsprechendsten Versuchsumstände in jenem Fall festzulegen, wenn die Legierung nur Mangan enthält.

## DIE VERSUCHSUMTÄNDE

Der Mangangehalt der zu den Untersuchungen gebrauchten siebengliedrigen Legierungsreihe änderte sich von 0,13% bis 3,0%. Ich hatte für die Herstellung dieser Aluminium von 99,99% und elektrolytisches Mangan verwandt, so gelang es die Gesamtmenge der Verunreinigungen unter 0,02% zu halten und damit den Effekt des dritten Elements praktisch zu beseitigen.

Ich hatte die Aufnahmen mit einem Spektrograph Qu 24, bei Zwischenabbildung mit einer Spaltbreite von  $20\ \mu$  gemacht. Die Anregung führte ich mit einem Erreger von System Feussner bei Spitzenspannung 15 kv und mit einem unterbrechenden Bogenerreger von Wechselstromspannung 220 v bei einer Stromstärke 1,5 A durch. Die Entladung des Kondensators von 5000 pf des Feussner-Erregers dämpfte ich mit Einschaltung der Selbst-induktionen 12,8, 3,2 und 0,8 mH. Die 6 mm dicken zylindrischen Elektroden beendeten sich in einem Zapfen von 3 mm Durchmesser und 6 mm Länge. Zur Anregung verwandte ich Gegenelektroden aus 99,99% Aluminium mit dem untersuchten Material gleichen Massen und einen 3 mm gross Elektrodenabstand. Das in den Spektrograph eingeführte und aufgelöste Licht stammte aus der 1,3 mm dicken Schicht des Elektrodenzwischenraumes über dem untersuchten Material, also die Aufnahmen geben Auskunft über den in diesem Raumteil sich ausgestalteten Zustand. Die Spektren wurden während einer Beleuchtungszeit 60 Sek bei Anwendung des Funkenerregers, hingegen während 45 Sek bei Anwendung des Bogenerregers auf "Agfa blau extrahart Platte" ohne Vorfunken erzeugt.

#### DIE VERSUCHSERGEBNISSE

Von den Aufnahmen aus hatte ich die Seidel-sche transformierte Schwärzung vieler Manganlinien gemäss der gestellten Aufgabe gemessen. Zwischen den für die Auswertung geeigneten sechs Zusatzlinien, bei drei Linien wächst die Schwärzung in grossem Masse mit der Zunahme der Konzentration der Zusatz während man bei den anderen drei-im Vergleich zu den Vorigen-ein weit minder Schwärzungswachstum in Abhängigkeit der Manganmenge erfahren kann. Auf Grund der Erwähnten können wir die Mn 2933,06, Mn 3547,79 und Mn 3441,98 als "Zusatzlinien"-, die Mn 2576,10, Mn 2798,27 und Mn 2801,06 als "Grundmateriallinien" auffassen, deshalb ich aus den Messergebnissen der in unterschiedenen Anregungsumständen gefertigten Bleche neun Schwärzungsunterschiede gezählt und in der Funktion des Mangangehaltes dargestellt hatte. Die neun Linienpaare und die Konzentrationsabhängigkeit der Schwärzungsunterschiede der Linienpaare darstellenden Kurven hatte ich der Einfachheit halber mit laufender Nummer versehen. Die laufenden Nummer der Linienpaare und die Wellenlänge deren Glieder hatte ich in Tafel I. zusammengestellt.

TAFEL I

I.	Mn 2933,06/Mn 2576,10
II.	Mn 2933,06/Mn 2798,27
III.	Mn 2933,06/Mn 2801,06
IV.	Mn 3547,79/Mn 2576,10
V.	Mn 3547,79/Mn 2798,27
VI.	Mn 3547,79/Mn 2801,06
VII.	Mn 3441,98/Mn 2576,10
VIII.	Mn 3441,98/Mn 2798,27
IX.	Mn 3441,98/Mn 2801,06

Von den viererlei Anregungsumständen entsprachen dem gesetztem Ziel die mit 12,8 mH Selbstinduktion gedämpften Funkentladungen. Auf den solcherweise erzeugten Blechen kann man die Mn 2933-Linie auf allen Aufnahmen auffinden, während die Mn 3547 und Mn 3442 nur bei einem Mangangehalt 0,34% erscheint. Unter den Kurven sind I. und III. gerade, während die Kurve II. bei grösserem Mangangehalt gewölbt (konvex) ist. Die Steilheit der Kurven annähernd gleich ist und kleiner als jene der im Praxis als gut genannten Auswertungskurven. Die Kurven IV. und V. sind in ihrer ganzen Länge linear und mehr steiler als die vorigen, während die VI. bei kleinen Konzentrationen konkav ist. Zwischen den die Schwärzungsunterschiede der auf die dritte Konzentration empfindliche Manganlinie enthaltenden Linienpaare

darstellenden Kurven ist nur die VIII. gerade, die anderen zwei sind bei kleinen Konzentrationen verflachend. Die Steilheit der Kurven ist gross, diese sind also für qualitative Auswertung in diesem Hinsicht geeignet (ABB. 1.).

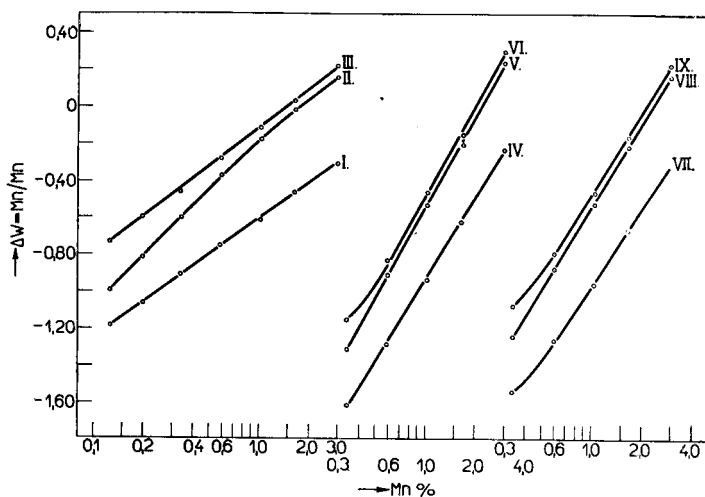


ABB. 1

Die Abnahme der Dämpfung der Anregung ergibt die Verzerrung und Abnahme der Steilheit der Auswertungslinien, wie die Messergebnisse der mit Selbstinduktion 3,2 mH gefertigten Aufnahmen dieses zeigen. Von den aus diesen Aufnahmen bekommenen Kurven weist nur die mit "I." bezeichnete entlang ihrer vollen Länge einen linearen Zusammenhang, flächerer als die Vorigen auf. In der Kurve II. kann man eine Brechung finden, während die III. bei den kleinen Konzentrationen konkav ist. Durch die funkenmässige Anregung veranlasst, die Linie Mn 3547 hat schon bei Mangengehalt 0,2% eine messbare Schwärzung. Der Neigungswinkel der mit Anwendung dieser Linie hergestellten Kurven ist kleiner als bei Dämpfung von 12,8 mH und bei kleinen Konzentrationen ist verflachend. Auch die dritte Gruppe der Kurven ist von kleinerer Steilheit und gegen die kleinen Konzentrationen verflachend ist. (ABB. 2).

Den induktiven Widerstand des Entladungskreises des Erregers weiter abnehmend, die in obigen dargestellten Erscheinungen in gesteigertem Masse sich melden. Die Linie der Mn 3547 meldet sich nochmals nur bei Legierungsgehalt 0,34% mit messbarer Stärke, die anderen zwei zeigen eine gut messbare Schwärzung zwischen den versuchten Grenzen, weist aber der Schwärzungsunterschied der mit denen beschaffenen Linienpaare nur bei grösserem (0,60%) Legierungsgehalt einen linearen Zusammenhang mit der Konzentration auf. (Abb. 3).

Die von den mit Bogenanregung erzeugten Aufnahmen erhaltenden Schwärzungsunterschiede untersuchend, kann man sehen, dass diese Anregungsmethode nicht günstig im Betracht der Auswertungskurven ist. Alle Analysenlinie erscheinen schon beim Mangengehalt von 0,13%, ist aber die Hauptmasse der Auswertungskurven praktisch ganz unbrauchbar. In der erste Gruppe der Kurven sind II. und III. bei den kleinen Konzentrationen konkav, bei den grossen konvex. Die Kurve I. ist gerade zwischen 0,34% und 3,0%, jedoch ihr Neigungswinkel sehr klein ist. Von den mit der

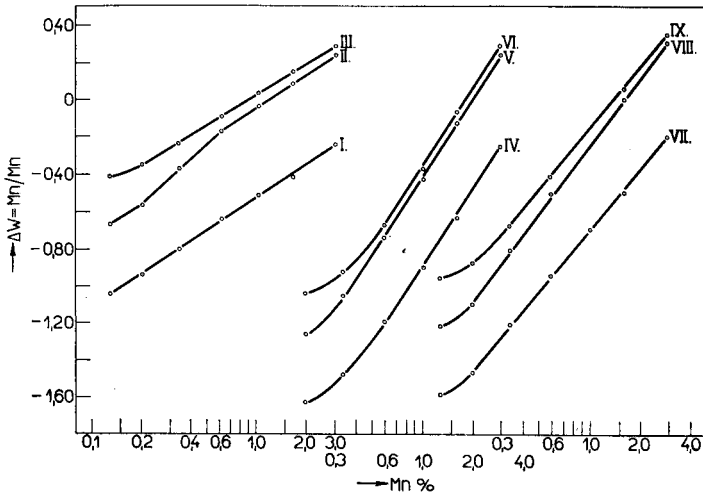


ABB. 2

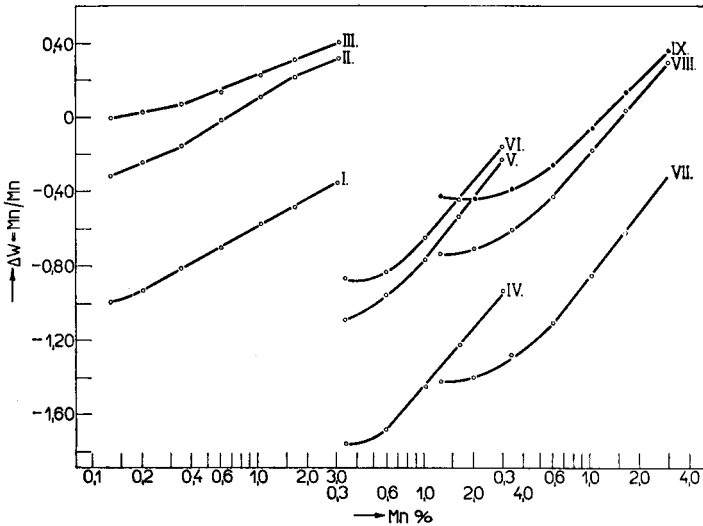


ABB. 3

Linie Mn 3547 hergestellten Kurven zeigt nur die Nr. IV. einen linearen Zusammenhang zwischen 1,0% und 3,0%, die anderen zwei haben eine stark gestreckte S-form. Die Kurve VII. ist die einzige der mit Bogenerreger erzeugten Auswertungslinien, bei deren man eine lineare Zusammenhang zwischen den Legierungsgehalt und Schwärzungs unterschied der Legierungslinien erfahren kann. (Abb. 4)

#### DIE FOLGERUNGEN

Die dargestellten Untersuchungen beweisen, dass man auf Grund der auf den Legierungslinien messbaren Unterschiede eine qualitative Bestimmung in einem verhältnismässig grossen Konzentrationsbereich durchführen kann. Zur Entscheidung, dass ob die dargestellten Zusammenhänge die Folgen der unterschiedlichen Absorptionsfähigkeit der Legierungslinien sein sollen, oder handelt es um eine davon unabhängige

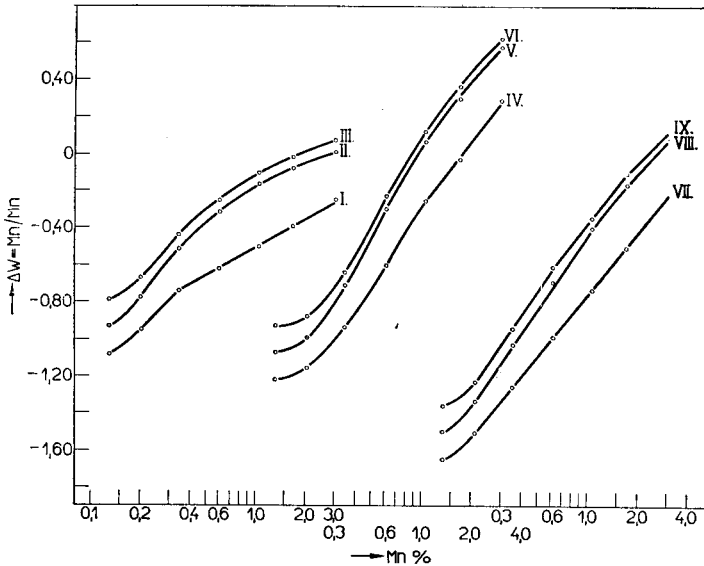


ABB. 4

Erscheinung, schien es zweckmässig die Abbildung der den Konzentrationsabänderungen empfindlichen Manganlinien und der Schwärzungsunterschiede einer gemäss den praktischen Erfahrungen absorptionfreien Grundmateriallinie in der Funktion der Konzentration durchzuführen. Zu dieser Vergleichung wählte ich die Linie Al II 3064,30 aus. Mit Verwendung dieser gebildete Schwärzungsunterschiede stellte ich in Abbildungen 5,6,7. und 8. unter unterschiedlichen Anregungsumständen vor.

Das Buchstabenzeichnen der Kurven in den Abbildungen ist das Folgende:

a = Mn 2933,06/Al 3064,30

b = Mn 3547,79/Al 3064,30

c = Mn 3441,98/Al 3064,30

Gemäss den Erfahrungen, die ausgewählte Aluminiumlinie hat keine Selbstabsorption, so wird der Schwärzungsunterschied der mit ihr hergestellten Linienpaare in jenem Fall die lineare Funktion der Legierungsgehaltenes sein, wenn auch das andere Glied des Linienpaares keine Selbstabsorption zeigt. Von den mit 12,8 mH erzeugten Aufnahmen zusammengestellten Kurven wie wir es schon in den vorhergehenden gesehen hatten fasst einen Zusatzbereich von 0,13 % bis 3,0 % um die anderen zwei kann man nur von den Spektren der Zusatzmenge 0,34 % und grösserer als diese messen. Eine von den Kurven mit Zeichen "b" ist in voller Länge gerade. Die mit "a" bezeichnete zeigt eine scharfe Brechung bei 0,34 % und 0,60 % und eine mindere Steilheit nach der Brechung. Auf der Kurve "c" kann man bei 0,60 % eine mässige Brechung erfahren. Diese Brechungen sind wahrscheinlich die Folgen der Erscheinungen der Metallographie und der Selbstabsorption (Abb. 5).

Das mehr und mehr Funkengemässwerden der Erregung verursacht keine wesentliche Abänderungen in der Form der Kurven, wie es in Abb. 6. sichtbar ist. Die Kurve "b" fasst grösseren (0,20 % — 3,0 %) Legierungsbereich um und in ihrer vollen Länge ist gerade und ihre Steilheit ist unverändert.

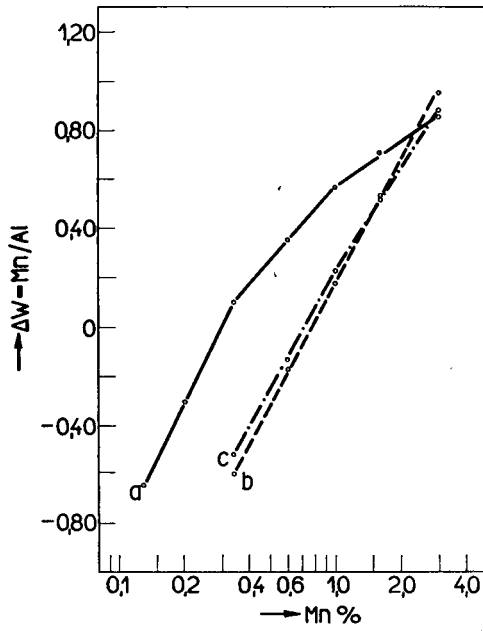


ABB. 5

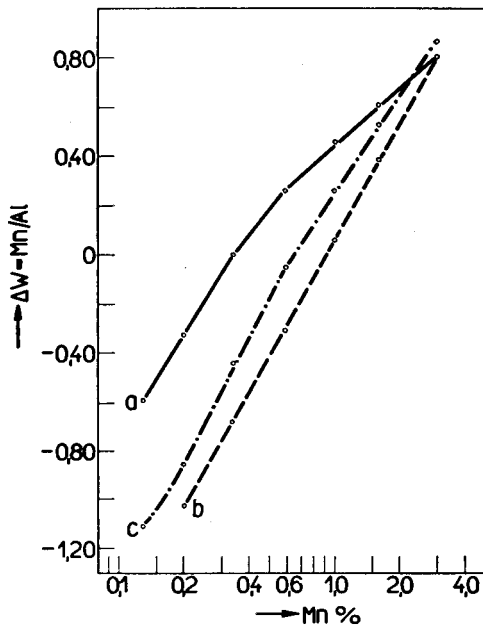
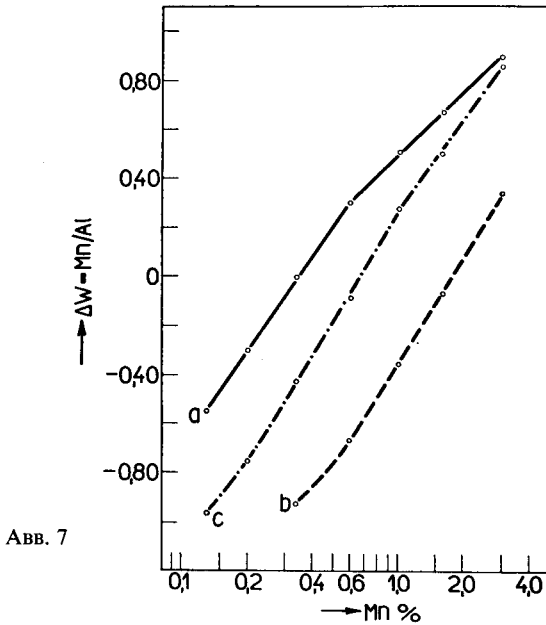


ABB. 6



Auch die aus den mit Dämpfung 0,8 mH hergestellten Aufnahmen bestimmten Kurven "a" und "c" zeigen keine wesentlichen Abänderungen im Vergleich mit den Vorigen. Der Neigungswinkel der Kurve "b" nimmt ab und bei kleiner Konzentration verflachend ist, die Selbstabsorption der Manganlinie kann man aber noch auch hier nicht beobachten (Abb. 7).



Die aus den mit Bogenanregung erzeugten Aufnahmen stammenden Kurven lassen darauf schließen, dass die untersuchten Manganlinien alle unter solchen Anregungsumständen Selbstabsorption haben (Abb. 8).

Die obenerwähnten beweisen, dass solche Manganlinien bestehen, die bei der Anwendung geeigneter Anregungsmethode keine Selbstabsorption haben und so die zwischen ihnen befindlichen Schwärzungsunterschiede sind von der Selbstabsorption unabhängig, deshalb beeinflusst diese sehr schwer reproduzierbare Erscheinung nicht die mit Hilfe solcher Linien durchgeführte qualitative Bestimmung.

Auf Grund der aus den unter verschiedenen Anregungsumständen aufgenommenen Spektren stammenden Messergebnisse fanden wir es so, dass die geeignetste Anregungsmethode die bei einer Spitzenspannung 15 kv gedämpfte Funkenanregung ist, die wir mit Anwendung der Kondensatorkapazität 5000 pF und der Selbstinduktion 12,8 mH herstellen können. Bei der Anwendung der Aluminium-Gegelektroden, zur Beleuchtung des Spektrographes müssen wir über der untersuchten Probe liegende 1,3 mm dicke Schicht benutzen. Für das Messen sind die Linienpaare Mn 3547,79/Mn 2798,27 und Mn 3547,79/Mn 2576,10 gleichermaßen gut anwendbar. Die obengenannten Linienpaare liefern mit dem Linienpaar Mn 3547,79/Al 3064,30 gleicher Steilheit und eine für qualitative Bestimmungen vorzüglich geeignete Kurve. Die Linienschwärzungen und damit auch die Schwärzungsunterschiede gut reproduzierbar sind, was das wichtigste Erfordernis bei der qualitativen Spektralanalysen ist.

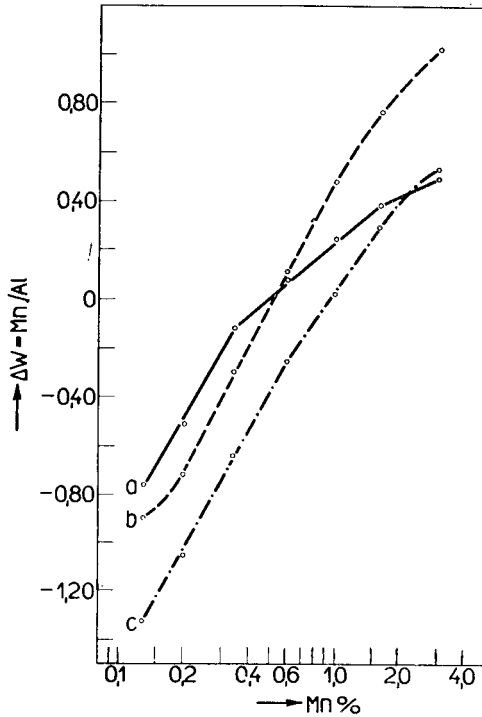


ABB. 8

Bei der Verfertigung der Aufnahmen muss man auf die pünktliche Einstellung der Elektroden achten, weil der Manganinhalt gemäss den Erfahrungen entlang der Funkenstrecken veränderlich ist. Im Falle unpünktlicher Elektrodeneinstellung kann dieser Umstand die Ergebnisse der Messen stark zerstören.

**Summary**—A new method is described for the analysis of Mn-Al alloys, based on the difference in line intensities. Feussner excitation is used with 15 kv kick voltage, 5000 pf, and 12.8 mH induction. Aluminium electrodes (99.99% pure) 4 mm apart are used. The spectrum is photographed on "Agfa blau extrahart" using a 20- $\mu$  slit width and 60 sec exposure time. The intensities of the pairs of manganese lines 3547.79-2798.27 and 3547.79-2576.10 are evaluated by Seidel's "W" transformation.

**Résumé**—L'auteur décrit une nouvelle méthode d'analyse des alliages Mn-Al, basée sur la différence d'intensité des raies. Une excitation Feussner est utilisée, avec une tension de 15 kV, 5000 pF et une induction de 12,8 mH. Des électrodes d'aluminium pur à 99,99% à une distance de 4 mm l'une de l'autre sont utilisées. La lumière est envoyée dans le spectrographe et photographiée sur "Agfa bleu extra dur" en utilisant une épaisseur de 20 $\mu$  et un temps d'exposition de 60 sec. L'intensité de la paire de raies—Mn 3547,79/Mn 2798,27 et Mn 3547,79/Mn 2576,10—est évaluée par une transformation "W" de Seidel.

## SPECTROGRAPHIC INVESTIGATION OF HUNGARIAN ARCHEOLOGICAL FINDS FROM THE COPPER AND BRONZE AGE

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(Received 14 August 1962)

**Summary**—A method has been evolved for the spectrographic investigation of copper-base archeological finds. Drillings from the specimens are placed in the cup of a carbon electrode and excited by an a.c. arc of anodic polarisation. The spectra are established using a special slit distributor with a two-step filter. Evaluation of spectra is carried out by visual comparison with spectra established with standards. The evolved method makes possible the classification of the archeological finds and, hence, conclusions to be drawn as regards their origin, age, etc.

### INTRODUCTION

Two of the authors (K. Z. and Z. L. Sz.) were charged by the Hungarian National Museum, Budapest, with a systematic spectrographic investigation of Hungarian finds from the early Bronze Age, particularly those of the Copper Age. Classification by typological examination alone is not of unequivocal validity. In many cases, even the site of the find is not authentic or the origin of the museum object is rather uncertain (booty, prehistoric merchandise, etc.).

A correct knowledge of the sites of preparation of prehistoric objects and of the accompanying elements of the ores and metals used for their preparation may serve as an important guide in detecting the origin and age of archeological subjects. In this respect, spectrographic analysis appears to be an ideal method of investigation.

### EXPERIMENTAL

#### *Sampling*

The actual composition of the surface layer of archeological finds essentially deviates from the original composition of the metallic object because of the effect of corrosion over many centuries and of the reactions with soil components. The inner substance of specimens is not homogeneous because prehistoric metallurgical procedures were rather primitive. Because archeological finds are works of art, however, detrimental effects, particularly destruction of their surface, must be avoided.

Direct excitation after removal of the superficial oxide layer cannot be applied unless a comparatively large surface area of the specimen is carefully cleaned for this purpose. However, this cannot be permitted in the case of works of art. Besides, in the case of certain copper finds, it would be rather difficult to find a flat surface of appropriate size. Furthermore, heat conductance varies to a considerable extent because of essential differences in the dimensions of the specimens. In such cases the results obtained for the individual specimens cannot be compared with each other because of deviations in their evaporation.

Taking into account the afore-mentioned facts, samples were taken from the archeological objects with a steel drill of 2.5-mm diameter. In this way, the samples were to a certain extent in the nature of an average sample. Subsequently, the hole in the specimen could readily be filled and the specimen restored. In order to avoid any contamination of the sample by the substance of the drill, the samples withdrawn by the drill were subjected to magnetic separation.

### Excitation

In respect of the inhomogeneity of the sample and of the not negligible differences in the composition of specimens authentically originating from the same sites, no accurate quantitative determinations were necessary. Regarding the requirements of accuracy of the analyses, it can be mentioned that the scattering of concentration values belonging to various points of the objects examined ranges at least 10%, and in general 20-50%, sometimes disclosing even fluctuations of over 100%.<sup>1</sup>

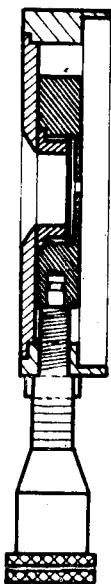


FIG. 1

In choosing an adequate method of excitation and exposure, the following aspects were taken into account:

1. The method must possess a sensitivity satisfactory for the detection of trace elements, though it is not necessary to detect contaminants below 0.001%.

2. The method should make it possible to assess the order of magnitude of the alloying elements present in greater quantities.

3. In order to save the archeological finds and to facilitate the rapid investigation of samples, all components of a specimen should be determined by only one exposure.

4. The preparatory operations should not be cumbersome.

5. The method should yield results reproducible to a satisfactory extent.

In order to meet these requirements a.c. arc excitation with anodic polarisation was employed, because it possesses satisfactory sensitivity and fair reproducibility. In the lower and higher concentration range, evaluation can be carried out on the basis of only one exposure. Spark excitation,<sup>2,3</sup> often used in other cases for the investigation of bronzes, and d.c. arc excitation,<sup>4,5</sup> proved to be less suitable for our purposes. Thus, the sensitivity of spark excitation is unsatisfactory while with d.c. arc excitation, the sensitivity is superfluously high and this leads to difficulties in evaluating data in higher concentration ranges. Application of the solution method,<sup>6</sup> the copper oxide method<sup>5,7</sup> or the globule method<sup>1,5,8</sup> was not considered because of the lengthy preparatory operations.

### Conditions of investigation

On excitation, a current intensity of 6 A was applied. Higher intensities proved to be impracticable in that they raised the background radiation without increasing the sensitivity proper.

The spectra were established with a quartz spectrograph ISP 22 of middle dispersion, applying the illumination-type Zeiss ("Zwischenabbildung").

The arc was generated between a carbon electrode RW 1 extra (Ringsdorff Werke, Bad Godesberg; 4 mm height and 4 mm diameter), placed in a pin and containing the copper drillings in a cup (2.5 mm diameter and 3 mm deep), and a graphite counter electrode of identical type and dimensions but without any cup. In each test, 30 mg of drillings were used. In this case the reproducibility of results

was quite satisfactory. The specimen serving as an anode is locally better heated, and thus a satisfactory amount of substance evaporates, leading to an adequate sensitivity.

The electrode distance ranged 2 mm, and ignition took place at the maximum voltage. No pre-arc was applied. In this way it was easier to detect the more volatile components and, as proved by preliminary tests, the reproducibility did not decrease to any perceptible extent. Rather short pre-arc used to be applied, in general, in quantitative analysis.<sup>1</sup> The exposure ranged 2 min. In order to avoid the occurrence of line coincidences, a 15- $\mu$ m slit width was applied. Agfa Spektral-Platten blau extrahart were used. The plates were developed for 5 min at 19° in Agfa 1 developer.

#### *Application of a slit attachment with step filter*

For the evaluation of specimens on the basis of one spectrum, the use of a step filter was necessary. In the case of spectra established in two steps, evaluation in the range of higher wavelengths took place at a weaker step because of the higher sensitivity of the plate, while below 320 nm the unweakened step was used. In respect of the varying composition of specimens, spectral atlases were necessary for the reliable identification of weak or poorly visible lines. For this purpose, using a step slit, the spectrum of iron must be photographed under the actual spectra of specimens tested.

Both of these requirements were met by the application of a slit attachment with step filter evolved by Szakács.<sup>9</sup> This attachment comprises filters of a transmittance of 100/20%. With the aid of a micrometer screw, the filter can be moved along the slit, and thus it is possible to photograph the spectrum of the specimen and of iron in two steps below each other. The height-limiting slit before the two-step filter, and the rise of the micrometer screw ranges 1 mm. Consequently, the height of a step before the slit is 0.5 mm, while on the plate it ranges 0.7 mm in the case of a spectrograph ISP 22 at an average enlargement of 1.4. The height of the slit before the filter and the rise of the micrometer screw are identical within 0.01 mm, so the spectrum of iron and that of the specimen are in contact in the spectrum projector within 0.2 mm at an enlargement of 20. Without moving the plate cassette, it is possible to establish the spectra of 8 specimens. In order to save plates and because the major lines of spectra were identical, only one iron spectrum was photographed for each set of individual test spectra.

## RESULTS AND DISCUSSION

Of the conventional alloying and contaminating elements of copper and bronze objects, the following 11 elements proved to be characteristic: silver, arsenic, gold, bismuth, iron, nickel, lead, antimony, tin, tellurium and zinc, while cobalt and, in general, chromium and manganese were not detectable. The presence of alkali and alkaline earth metals and also of silicon and aluminium may arise partly from the primitive pre-historic methods of metallurgy and partly from contamination by various soil components during the reactions occurring there. However, these latter elements are of negligible importance from the aspect of detection and identification of the site of finds. Among the other elements listed above, iron and nickel are also not important.

In the assessment of the orders of magnitude of concentrations on the basis of the blackenings at the spectral lines of alloying elements of highest sensitivity, the copper alloy standards of Johnson-Matthey Co. were used. The spectra of these standards were established under conditions completely identical with those applied when testing the specimens. However, no gold-containing standards were available. Gold occurred in our specimens rather rarely, and no assessments were necessary in these cases. When the specimens contained tellurium in addition to gold, this was taken as a proof of the Transylvanian origin of the specimen tested.

In the assessment of the orders of magnitude on the basis of a visual assay, the following notations were applied: a concentration of the element in question corresponding to the limit of detectability was denoted by a + sign, with blackenings above this extent by increasing numbers. In general, differences of two numbers corresponded to a difference of one order of magnitude of concentration. On establishing the relative blackenings of lines, differences in the total intensity of the single spectra were taken into account by comparing them with the blackenings of the

TABLE I

Element	Order of magnitude of concentration, %	Relative intensity of analytical lines
Ag	0.0001	1
	0.001	3
	0.01	5
	0.1	8
Fe, Pb, Sn	0.001	2
	0.01	4
	0.1	6
Ni, Sb	0.001	1
	0.01	3
	0.1	6
As, Te, Zn	0.01	2
	0.1	4

copper lines adjacent to the analytical lines. In Table I values pointing to the orders of magnitude of concentration of some elements are given.

It must be noted that the assessment of the orders of magnitude obtained on using the standards were completely in accordance with the results of the quantitative spectral analyses obtained earlier by German authors in the laboratory of the Württembergisches Landesmuseum (Stuttgart) with 10 specimens examined now also by us. However, the German authors were unable to detect the trace elements because of the low sensitivity of their method.<sup>10</sup>

On the basis of the results obtained by spectrographic analysis and without any other knowledge, the finds could only be classified when the scattering of the analytical data within the single groups was so low that any possibility of overlapping between various groups could be excluded. Accurate classification could be carried out by statistical methods.

Considering the results of spectrographic analyses and applying frequency analysis as well, we succeeded in establishing the characteristic composition of the single

TABLE II

No. of spectrum	File number	Object	Ag	As	Sb	Bi	Pb	Sn	Au	Te	Zn	Ni	Fe
53	74/1899-2	Fokos (small axe on long helve)	3	+	+	-	1	-	-	-	-	+	2
54	94/1910	Pick	3	1	+	-	1	-	-	-	-	+	+
60	581	Flat hatchet	4	+	+	-	2	-	-	-	-	1	1
69	B 673	Hatchet	4	-	1	+	2	-	-	-	-	+	2
17	121/1883-2	Flat hatchet	7	-	7	7	1	-	-	-	+	+	1
18	121/1883-3	Chisel	6	-	6	7	1	-	-	-	-	+	-
22	129/1883-4	Flat hatchet	6	-	7	6	+	-	-	-	-	+	-
24	116/1884-1	Flat hatchet	4	6	4	4	5	3	-	-	3	3	3
32	82/1889-6	Flat hatchet	3	5	4	3	4	2	-	-	2	4	2
7	20/1883	Axe	6	4	4	3	5	4	2	2	1	2	1
41	51/1883-5	Axe	6	4	5	4	4	6	2	1	-	2	3

groups and in classifying the overwhelming majority of the examined archeological objects into the established groups. Some characteristic types of the obtained results are presented in Table II. The first four objects are typical Copper Age finds, presumably of the Bodrogkeresztúr culture. The next three items belong to another group, while the third group is characteristic of the early Bronze Age type, presumably pertaining to the Vučedol culture. The last two specimens are probably of Transylvanian origin, typical items of the Bronze Age.

On comparing our results with the available data in respect of site and typological features, we succeeded in evolving a better method of classification of Hungarian finds of the Copper and Bronze Age, based on more correct scientific knowledge. In establishing the archeological aspects and typological classification of the finds, we enjoyed the help of Dr. P. Patay of the Hungarian National Museum. Further examination of Hungarian archeological objects and the development of an informative quantitative method is in progress.

**Zusammenfassung**—Für die Übersichtsanalyse archäologischer Funde aus der Kupfer und Bronzezeit wurde eine spektrographische Methode entwickelt. Aus der Probe entnommene Bohrspäne wurden in der Bohrung einer Kohlenelektrode im anodisch polarisierten Wechselstrombogen angeregt. Mit einem mit Stufenfilter versehenen Spaltaufsatz konnten die Probenspektren und ein Eisenspektrum in zwei Intensitätsstufen untereinander aufgenommen werden. Die Auswertung erfolgte durch visuellen Vergleich mit den Aufnahmen von Standardproben. Durch Gruppierung der Proben ermöglicht die Methode eine Folgerung an die Herkunft und Alter der Funde.

**Résumé**—Les auteurs ont mis au point une méthode pour l'étude spectrographique des pièces archéologiques à base de cuivre. Des parcelles de spécimen ont été placés dans la coupelle d'une électrode de carbone excitées par un arc à courant alternatif de polarisation anodique. Le spectre a été obtenu en utilisant une fente spéciale et un filtre à 2 étages. Il a été étudié par comparaison visuelle avec des spectres établis à partir d'étalons. La méthode permet la classification des pièces et par suite, de tirer des conclusions sur leur origine, leur âge, etc.

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## SPECTROGRAPHIC DETERMINATION OF 0.1–1.0% OF COPPER IN ALUMINIUM ALLOYS

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(Received 14 August 1962)

**Summary**—A method has been developed for the spectrographic determination of 0.1–1.0% of copper in aluminium alloys. For this purpose, the lines of the spark spectrum of copper in the region below 2300 Å prove to be most suitable. Low-voltage spark excitation is applied. In establishing the spectra in the region of short wavelengths, spectral plates previously sensitised with an ethanolic solution of sodium salicylate are used. In the process of evaluation, P-transformation is applied. Because of the high  $\gamma$  values and the absence of self-absorption of the applied spectral lines, the analytical accuracy of the method markedly exceeds that obtained when using atomic lines.

### INTRODUCTION

IN the literature a great number of communications deal with the spectrographic determination of copper contents below 0.1% and above 1.0% in aluminium. However, almost no data is available in respect of the determination of moderate copper contents. This is because, on the one hand, analytical requirements in this range occur only rarely in practice and, on the other hand, even in the medium ultraviolet range, which can be easily photographed, no copper lines are to be found which would lend themselves to the accurate determination of the concentrations of copper desired.

#### *Choice of lines*

The two major lines (3247.54 and 3273.96 Å) of the atomic spectrum of copper generally applied in trace analysis are extremely sensitive resonant lines. On using these lines, for example, with a high-voltage spark excitation, linear calibration curves are obtained from 0.0001% up through three full orders of magnitude. However, over the concentration range of 0.1–0.2%, the calibration curve shows an abrupt fall because of self-absorption of the lines and, thus, this section becomes unsuitable for the purposes of an accurate analysis. The resonant copper lines, similarly to the phenomenon observable in the case of the other elements in the first column of the Periodic Table, possess intensities higher by several orders of magnitude than those of the other lines of copper. Consequently, the otherwise applicable lines (2824.37 and 2369.89 Å) can only be used at copper contents above 1%, and even in this case a background correction must be applied.



Instead of the unsuitable lines of atomic spectra a great number of very intensive lines of spark spectra free from interfering effects and free from self-absorption can be found in the region below 2300 Å, e.g., 2247.00, 2242.61, 2228.86, 2218.10, 2210.26, 2192.26, 2189.62, 2179.40, 2148.97, 2135.98 and 2126.03 Å.

The use of the otherwise rather favourable lines of the spark spectra is impeded by the fact that the types of emulsion generally used in spectral analysis are unsuited for application below 2300 Å. The absorption of gelatin rises rapidly with a decrease of wavelength of the light source applied and, thus, the intensity of light affecting the silver halide particles diminishes, leading to a rapid decrease of the sensitivity and gradation of the emulsion. Certainly this is responsible for the fact that only few authors mention in the literature the use of lines of spark spectra, and then mainly in a higher concentration range (2–5%).<sup>1,2,3</sup>

## EXPERIMENTAL

### *Technique of determination*

Details of the technique of operation developed are as follows:—

Excitation: low-voltage spark excitation

Maximum voltage: 500 V

Capacitance: 2.5 or 5.0 μF

Inductance: 1 mH

Shape of electrodes: electrode of 6 mm diameter, with a pin of 3 mm diameter, and with flat front surface

Electrode distance: 2 mm

Pre-sparking: 1 min

Exposure: 2 min

Projection of light source: intermediate

Spectrograph: Zeiss Qu 24

Slit width: 20 μm

Three-step filter: 100/50/10% (steps denoted by a, b, c)

Emulsion: Agfa Spektral blau extrahart, sensitised by a saturated ethanolic solution of sodium salicylate with respect to ultraviolet radiation

Processing of plates: Developer Agfa 1 at 18° for 4 min, interrupting bath of 1% acetic acid, then acidic fixation by thiosulphate

Pair of lines: Cu<sup>b</sup> 2247.00, \* Al<sup>a</sup> 2319.07 or Al<sup>b</sup> 2321.57

Photometer: Zeiss rapid photometer

Evaluation: Determination of ΔP, using transformation constant  $\kappa = 1.3$ .

### *Critical investigation of the method*

Comparative investigations were carried out with the lines Cu 3247, Cu 2824 and Cu 2247 under the given experimental conditions. Obviously, in the first two cases "extrahart" emulsions without any sensitisation were applied, while with the third copper line a background correction was also necessary. The calibration curves obtained are shown in Fig. 1. Because of self-absorption, the Cu 3247 line proved to be completely unsuited for use. The Cu 2824 line, because of its low intensity, is similarly unsuitable in the concentration range in question, even on using a background correction, and in the case of higher concentrations its curve is much flatter than that of the Cu 2247 line. This latter is because of the high value (2.5) of  $\gamma$ . The Al 2321.57 line is of higher intensity than the Al 2319.07 line, but the intense Ni 2321.38 line interferes with it.

On comparing the sparking-off curves in Fig. 2, obtained with the pairs of lines Cu 3247/Al 3050 and Cu 2247/Al 2319, very interesting conclusions can be drawn. These curves refer to the same sparking process. It can be observed, however, that on using the Cu 2247 line a much steadier curve is obtained than with the Cu 3247 line. This is certainly because of periodical changes in the tension of absorbing cold vapours, which in addition also increase the scattering of the analytical results. Lastly, it was proved that 1 min of pre-sparking, as stated in *Technique of determination* is satisfactory.

The accuracy of the suggested analytical method was subjected separately to investigations. The Gauss quadratic mean error values in the case of a copper content of 0.46% ranged  $\pm 9.0\%$  using

\* The method is also suitable for the determination of copper contents above 1%. In this case it is practical to use the Cu 2242.61 line of lower intensity.

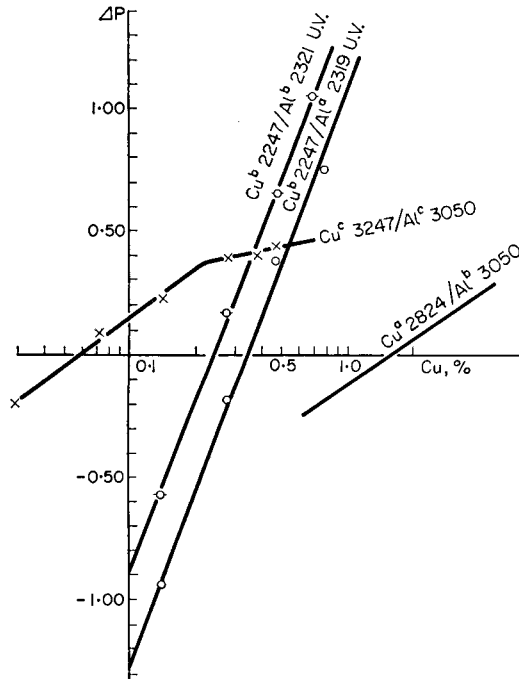


FIG. 1.—Calibration curves

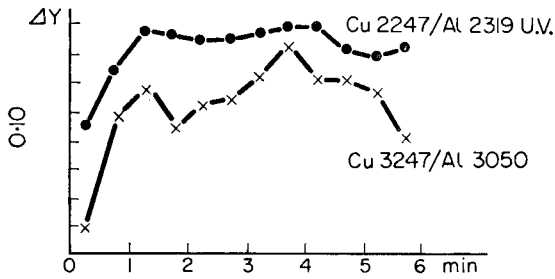


FIG. 2.—Sparking-off curves

the pair of lines Cu 2247/Al 2321, and  $\pm 57.1\%$  with the pair of lines Cu 3247/Al 3060. In the case of a sample of 2.5% copper content, the error was  $\pm 8.2\%$ . Although the accuracy of the new method appreciably exceeds that of the earlier procedure where the 3247 line is applied, the observed scattering of  $\pm 8.2-9.0\%$  ranges over the conventional error limits of  $\pm 3-5\%$  of the analyses carried out with commercial spectral emulsions not sensitised with respect to the deep ultraviolet domain. This is certainly because so far it was still not possible to transfer the sensitiser on the emulsion in a satisfactorily homogeneous layer. This presumption is also supported by our photographic experiments in respect to scattering. Namely, these experiments proved that the error of analytical results from the photographic procedure amounts to  $\pm 2.8-4.7\%$ . On taking into consideration the slope of the calibration curve, these values can be rather high photographic scatterings, in comparison to the unsensitised plates.

**Zusammenfassung**—Zur spektrographischen Bestimmung von Kupfergehalten von 0.1 bis 1.0% in Aluminiumlegierungen wurde eine Methode entwickelt. Für diesen Zweck sind die Linien des Funkenpektrums des Kupfer im Bereich unter 2300 Å die geeignetsten. Die Anregung erfolgte durch Niederspannungsfunken. Beim Photographieren des Kurzwellenbereiches wurden mit einer Äthanol-Lösung von Natriumsalicylat sensibilisierte Spektralplatten benützt. Bei der

Auswertung wurde P-Transformation angewandt. Infolge der hohen  $\gamma$ -Werte und der Anwendung selbstabsorptionfreier Spektrallinien übertraf die durch diese Methode erreichte analytische Genauigkeit die der auf Atomlinien beruhenden Analysen wesentlich.

**Résumé**—Les auteurs ont mis au point une méthode pour le dosage spectrographique du cuivre dans les alliages d'aluminium de 0,1 à 1 % de cet élément. A cet effet les raies du spectre d'étincelle du cuivre de longueur d'onde inférieure à 2300 Å ont été jugées les plus utiles. Une excitation par étincelle sous faible tension a été appliquée. Pour l'enregistrement des spectres dans le domaine des courtes longueurs d'ondes, des plaques photographiques préalablement sensibilisées avec une solution de salicylate de sodium dans le éthanol, ont été utilisées. Lors de l'étude du spectre, une transformation P a été effectuée. En raison de  $\gamma$ -valeur élevée et l'absence d'autoabsorption des raies spectrales utilisées, la précision de la méthode est très notablement supérieure à celle obtenue en utilisant les raies atomiques.

*Acknowledgements*—Thanks are due to Mrs. P. Dominák and to Mrs. L. Buzás for their assistance in carrying out the preparation of spectra and part of the measurements.

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## THE ACCURACY OF ZINC DETERMINATION BY ATOMIC ABSORPTION METHODS

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(Received 14 August 1962)

**Summary**—The best experimental conditions for zinc determinations by atomic absorption spectrophotometry, air pressure, slit width and concentration limits have been established. The precision of the method is calculated on the basis of error calculus of absorption measurements. If solutions containing 30–120 ppm of  $Zn^{2+}$  are measured, the relative errors are lower than  $\pm 0.5\%$ . Interferences of anions and cations have been investigated, and found in most cases to be negligible.

ATOMIC absorption spectrophotometric methods are used more and more frequently in practical analysis. Their selectivity seems to be a great advantage over other methods. Numerous papers<sup>1–26</sup> have already been published in this field, mostly concerned with practical ends. Systematic investigation of the best experimental conditions, and of the selectivity and precision of the methods are, however, still lacking. We therefore decided to test these methods first of all for their maximum attainable accuracy, and then to increase the concentrations of solutions to be determined, so as to permit the determination of main constituents in analytical samples.

Zinc was the first choice for this work, since the method seems to be most suitable for zinc determinations. Although other workers<sup>5,14</sup> have reported on the determination of zinc, they did not determine the most satisfactory concentration limits or experimental conditions.

### EXPERIMENTAL

#### *Reagents*

*ZnSO<sub>4</sub> standard solutions:* Prepared from analytically pure  $ZnSO_4 \cdot 7H_2O$ . Their concentrations were controlled by complexometric titrations.

*Solutions used for investigation of interferences:* Prepared from analytically pure reagents; their concentrations, however, were adjusted by weighing, but were not controlled by independent determinations.

#### *Apparatus*

The Hilger Uvispek 700 spectrophotometer was used with its atomic absorption attachment. Its atomiser, however, was replaced by an atomiser used in Zeiss-type flame photometers. This called for a separate control of air pressure with a fine manometer. Illuminating gas was introduced directly into the burner from a laboratory gas tap. Its pressure seems to be constant and has a value of about 40 mm of water.

Zinc determinations were made on the 2138 Å zinc resonance line, using the hollow cathode lamp of the instrument. The lamp current was kept at 40 mA according to the instructions of the makers.

### INVESTIGATION OF EXPERIMENTAL CONDITIONS

#### *Air pressure*

Preliminary experiments established that a concentration of 50 ppm of  $Zn^{2+}$  is in the middle of the best concentration range. Solutions containing 50 ppm of  $Zn^{2+}$  were therefore sprayed into the flame with various air pressures using a slit width of

0.30 mm. In each case six optical density readings were made, and standard deviations were calculated. Results are summarised in Table I. From these results it can be seen that an excess air pressure of 0.30 atm seems to be most adequate for the measurements, although pressures of 0.4–0.5 atm also yield satisfactory precision.

TABLE I.—VARIATION OF AIR PRESSURE

Excess air pressure, atm	Optical density (mean of 6 readings)	Standard deviation, $\pm\%$
0.15	0.037	5.13
0.20	0.160	1.43
0.25	0.269	0.59
0.30	0.362	0.41
0.35	0.425	0.73
0.40	0.471	0.54
0.45	0.547	0.35
0.50	0.613	0.56

### Concentration limits

Atomic absorption measurements, if optical densities are measured against water (or solvent), are analogous to ordinary spectrophotometric measurements. The relative error of the concentration determination can be deduced from Beer's law, and can be expressed as follows:<sup>27</sup>

$$\frac{\Delta c}{c} = \pm \frac{0.4343}{\frac{I}{I_0} \left( \log \frac{I}{I_0} \right)} \Delta \frac{I}{I_0}$$

where  $I/I_0$  is the transmittance of the aerosol in the flame, and  $\Delta(I/I_0)$  is the error (standard deviation) of transmittance readings. If  $\Delta(I/I_0)$  is regarded as constant and equal to the unit, from various  $I/I_0$  values the error function can be calculated and drawn up.<sup>27</sup> This function shows a minimum at 36.8% transmittance (optical density 0.4343), and acceptably low errors can be expected only if transmittances are between 20–60% (optical densities between 0.8 and 0.2). Such readings were obtained over the range 30–120 ppm of  $Zn^{2+}$ . This concentration range lies somewhat higher than those recommended in the literature.<sup>5,14</sup> A further increase of concentration can be obtained if a differential technique is used, and work on this aspect is at present in progress.

### Slit width

The choice of the correct slit width is necessary to obtain satisfactory results. Too wide a slit, especially in the presence of foreign ions, may result in interferences arising from poor monochromatic character, while a too narrow slit produces high scattering in extinction readings. Experiments were made with solutions containing 50 ppm of  $Zn^{2+}$ , at various slit widths, and with the other experimental conditions the same as before. Six optical density readings were made in each case, and the standard deviations were calculated. Results are presented in Table II. On the basis of these results a slit width of 0.30 mm was chosen in further work.

TABLE II.—VARIATION OF SLIT WIDTH

Slit width, <i>mm</i>	Optical density (mean of 6 readings)	Standard deviation, ± %
0.150	0.333	5.43
0.175	0.343	0.91
0.200	0.336	0.48
0.225	0.334	1.61
0.250	0.341	1.99
0.275	0.346	0.69
0.300	0.341	0.33
0.350	0.343	0.38
0.400	0.341	0.76

### Precision

The most satisfactory conditions for the determination of zinc are summarised in Table III. The precision of the method can be evaluated on the basis of the error function mentioned above. For this purpose measurements were made between 30–120 ppm of  $Zn^{2+}$  at various concentrations. At each concentration six readings were made, and both transmittances and optical densities were recorded. The standard deviations of transmittance readings  $\Delta \frac{I}{I_0}$  were calculated, and were multiplied by the corresponding value of the theoretical error function.

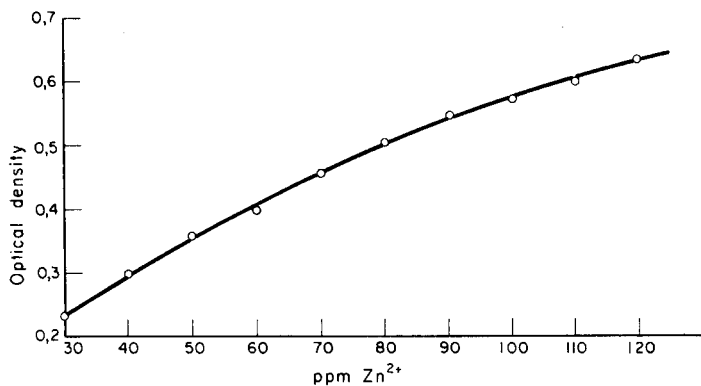


FIG. 1

TABLE III.—BEST CONDITIONS FOR DETERMINATION OF ZINC

Line: 2138 Å, Zn resonance line.  
 Lamp current: 40 mA.  
 Air pressure: 0.30 atm (excess pressure).  
 Slit width: 0.30 mm.  
 Concentration limits: 30–120 ppm of  $Zn^{2+}$ .

This standard deviation, given in %, represents the practically attainable precision of the method. Results of measurements and calculations are presented in Table IV, and the optical density *vs.* concentration graph is shown in Fig. 1. From the last column of Table IV it can be seen that the percentage standard deviation for the determination of concentration, with the exception of the first value, does not exceed

$\pm 0.5\%$ . This permits zinc to be determined as a main constituent in samples with a satisfactory precision. If the apparatus is in use, only a short time (5 min) is needed after the dissolution of the sample for the completion of an analysis. This presents a great advantage over other methods.

TABLE IV.—PRECISION OF ZINC DETERMINATION

Zn concentration, ppm	Optical density	$\frac{I}{I_0}$ , %	$\pm \Delta \frac{I}{I_0}$ , %	$\frac{0.4343}{I_0} \cdot \log \frac{I}{I_0}$	$\pm \frac{\Delta c}{c}$ , %
30	0.227	59.20	0.27	3.2	0.86
40	0.297	50.04	0.02	2.9	0.06
50	0.357	43.88	0.10	2.8	0.28
60	0.397	39.96	0.09	2.7	0.27
70	0.455	35.06	0.13	2.7	0.35
80	0.507	31.24	0.17	2.8	0.48
90	0.547	28.33	0.08	2.8	0.22
100	0.574	26.66	0.08	2.9	0.23
110	0.599	25.03	0.01	2.9	0.03
120	0.639	22.88	0.11	3.0	0.30

## EFFECT OF FOREIGN IONS

One of the most important advantages of atomic absorption spectroscopic methods is the relative lack of effect of foreign ions. In the systematic investigation of interfering effects measurements were first carried out in the presence of various amounts of anions. The solutions contained in all cases 50 ppm of  $Zn^{2+}$ , and various amounts of anions. Two sets of determinations were made, the anion being introduced once

TABLE V.—EFFECT OF ANIONS ON THE ACCURACY OF ZINC DETERMINATIONS

Anion	Mole ratio, anion: $Zn^{2+}$						
	0.25:1	0.50:1	0.75:1	1:1	2:1	3:1	5:1
	Relative error caused by the anion, %						
$Cl^-$	$\pm 0.00$	+0.45	$\pm 0.00$	$\pm 0.00$	+0.40	+0.32	+0.41
$NO_3^-$	+0.25	$\pm 0.00$	+0.41	+0.52	+0.41	+0.24	+0.37
$SO_4^{2-}$	+0.15	+0.28	+0.40	-0.28	-0.17	+0.17	+0.34
$PO_4^{3-}$	$\pm 0.00$	+0.45	+0.84	+0.42	+0.30	+0.42	+0.40
$CH_3COO^-$	+0.17	+0.34	+0.17	$\pm 0.00$	+0.49	+0.34	+0.34
$BO_3^{3-}$	$\pm 0.00$	+0.20	+0.40	+0.25	+0.35	+0.35	+0.45
$I^-$	+0.20	+0.30	+0.25	+0.40	+0.30	+0.20	$\pm 0.00$
$Br^-$	+0.35	+0.21	+0.21	+0.42	+0.21	+0.42	+0.42

in the form of the corresponding acid, and once as the ammonium salt (with the exception of bromide and iodide, which were added only as ammonium salts). Since no essential differences were found between the results of these two sets of experiments, in Table V only one result is given in each case. These results indicate, that within relatively wide concentration ranges, the errors caused by the presence of anions are less than lower 0.5%; that is, the results fall within  $\pm 0.5\%$  of the true value, as defined by the standard deviation.

TABLE VI.—EFFECT OF CATIONS ON THE ACCURACY OF ZINC DETERMINATIONS

Cation	Weight ratio, cation: Zn <sup>2+</sup>					
	5:1	10:1	15:1	20:1	25:1	30:1
Relative error caused by the cation, %						
Ag	+0.2	+0.3				
Cd	±0.0	+0.3	+0.6	+0.9	+1.3	+1.7
Co <sup>II</sup>	±0.0	+0.3	+0.7	+0.9	+1.2	+1.6
Cr <sup>III</sup>	-0.4	-0.5	-0.8			
Cu <sup>II</sup>	+0.2	+0.3	+0.5	+0.7	+1.0	+1.2
Fe <sup>III</sup>	-0.3	-1.5	-2.4			
Hg <sup>II</sup>	-0.7	+0.4				
Mn <sup>II</sup>	-0.3	+0.9	+1.4			
Ni <sup>II</sup>	±0.0	+0.8	+1.2			
Bi <sup>III</sup>	-0.7	-1.3	-2.7			

The optical densities of sprays from solutions containing 50 ppm of Zn<sup>2+</sup> and various amounts of cations were then measured. The concentrations of the latter were relatively higher than in case of the anions. From the results presented in Table VI, it can be seen that up to a 5:1 weight ratio the interferences are in most cases negligible. Even if extremely large amounts of foreign cations are added, the errors are not particularly high, and for practical analyses the method can be reliably used.

**Zusammenfassung**—Die optimalen Bedingungen zur Bestimmung von Zink durch Atomabsorptionsspektrophotometrie wurden untersucht. Optimaler Luftdruck, Spaltweite und Konzentrationsbereich wurden ermittelt. Die Präzision der Methode wurde aufgrund der Fehlertheorie von Absorptionsmessungen berechnet. Wenn Lösungen mit 30–120 ppm Zink gemessen werden, beträgt der relative Fehler weniger als ±0.5%. Störungen durch andere Kationen sowie Anionen wurden untersucht und es wurde gefunden, dass sie in den meisten Fällen vernachlässigt werden können.

**Résumé**—Les conditions expérimentales optimales du dosage du zinc par spectrophotométrie d'absorption atomique ont été étudiées. La pression d'air, la largeur de fente optimales, les concentrations limites ont été déterminées. La précision de la méthode a été calculée sur la base des erreurs sur les mesures d'absorption. Si 30 à 120 ppm de Zn<sup>2+</sup> sont dosés, l'erreur relative est inférieure à ±0,5%. L'interférence des anions et des cations a été étudiée; elle est dans la plupart des cas négligeable.

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## THE ROLE OF RATE OF ATOMISATION IN FLAME PHOTOMETRY

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(Received 14 August 1962)

**Summary**—It is established that if concentric atomisers are used, the surfacial pressure component of the pressure from Hagen-Poiseuille's law changes according to the grade of turbulency of the turbulent gas current. The amount of liquid passing through the capillary is influenced, therefore, by the viscosity of the solution, and more or less, as pointed out before, by the surfacial tension. If the atomiser is non-concentric, the surfacial tension has no influence on the rate of atomisation. In the case of concentric atomisers, the results can also be explained quantitatively.

AMONG factors influencing flame photometric emission, the amount of substance taken into the flame in unit time seems to be fairly important. Methods used nowadays transfer the substance through atomisers into the flame. Either concentric<sup>1</sup> or non-concentric<sup>2</sup> atomisers are used, and the liquid to be atomised must pass through the capillary of the atomising unit. The amount of liquid passing through the capillary is determined by the characteristics of the solution and capillary.

The flow of the liquid through the capillary can be described by the Hagen-Poiseuille law. According to this, the amount of liquid passing through the capillary in unit time is

$$V_e = \frac{P\pi r^4}{8l\eta}$$

where  $r$  is the radius of the capillary,  $l$  is its length,  $\eta$  is the viscosity of the solution and  $P$  is the pressure causing the flow of the liquid.

The pressure in the equation is the resultant of two pressures. The first one is the pressure drop at the end of the capillary, formed according to the Bernoulli law, while the second one is the capillary pressure of the liquid surface, being connected with the liquid flowing out from the capillary, which acts against the first type of pressure.

To establish the role of capillary pressure at atomisers used in practice today, we have made investigations with alcoholic solutions. In the case of alcoholic solutions the surfacial pressure shows a monotone, while the viscosity shows a maximum function with increase of alcohol concentration.<sup>3</sup> The choice of alcoholic solutions is adequate also because more scientists are using alcohol-containing systems in flame photometric practice.<sup>4</sup>

We have made investigations both with concentric direct atomisers and non-concentric indirect atomisers. The diameter of the concentric atomiser-capillary was 0.5 and 0.8 mm, while that of the non-concentric atomisers was 0.4 and 0.6 mm. In the first part of our investigations we measured the time needed for atomisation of the same amount of solution at various alcohol concentrations. In the case of the concentric atomiser, atomisation was made from a glass vessel in which the volume between two

marks was 0.33 ml. In the case of the Zeiss-type atomiser, the atomisation time needed for 5 ml of solution was measured. The pressure on the liquid moving in the capillary was varied by the gas flow rate, and in the case of similar flowing cross-sections by varying the pressure of the gas. The pressures were varied at concentric atomisers between 0.8 and 1.4 atm and in the Zeiss-atomiser between 0.2 and 1.0 atm.

TABLE I.—TIME REQUIRED FOR ATOMISATION OF 0.33 ml OF SOLUTION, REFERRED TO AQUEOUS SOLUTIONS AS UNITS AT VARIOUS ALCOHOL CONCENTRATIONS, USING DIRECT ATOMISATION WITH A CAPILLARY 0.8 mm IN DIAMETER.

Alcohol, %	Pressure of atomising gas, atm				Rel. viscosity (20 °C)
	0.75	0.84	1.05	1.40	
0	1.00	1.00	1.00	1.00	1.00
5	0.82	0.86	1.09	1.13	—
10	0.83	0.85	1.10	1.28	1.53
20	1.00	1.10	1.30	1.61	2.17
30	1.18	1.23	1.47	1.96	2.70
40	—	1.27	1.69	2.24	2.90
50	1.30	1.30	1.75	2.32	2.86
60	—	1.31	1.83	2.32	2.66
70	—	1.18	1.68	2.20	2.36
80	1.08	1.00	1.55	2.03	2.00
90	—	0.77	1.35	1.76	1.60
100	0.61	0.61	0.97	1.29	1.18

TABLE II.—TIME REQUIRED FOR ATOMISATION OF 5.00 ml OF SOLUTION, REFERRED TO AQUEOUS SOLUTIONS AS UNITS AT VARIOUS ALCOHOL CONCENTRATIONS, USING INDIRECT ATOMISATION WITH A CAPILLARY 0.4 mm IN DIAMETER.

Alcohol, %	Pressure of atomising gas, atm									Rel. viscosity (20 °C)
	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50	
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
5	1.02	1.09	1.09	1.06	1.09	1.09	1.08	1.12	1.10	—
10	1.66	1.21	1.16	1.14	1.13	1.13	1.14	1.21	1.17	1.53
20	1.73	1.49	1.40	1.29	—	—	—	1.36	1.31	2.17
30	2.20	1.90	1.50	1.43	1.40	1.50	1.38	1.50	1.42	2.70
40	2.73	2.25	1.64	1.58	1.50	1.49	1.48	1.59	1.53	2.90
50	2.75	2.30	1.72	1.64	1.56	1.50	—	1.66	1.55	2.86
60	3.00	2.35	1.74	1.66	1.59	1.54	1.49	1.66	1.52	2.66
70	2.76	2.20	1.72	1.61	1.52	1.49	1.49	1.59	1.51	2.36
80	2.77	2.08	1.52	1.52	1.44	1.40	1.39	1.56	1.40	2.00
90	1.81	1.53	1.31	1.38	1.36	1.38	1.33	1.44	1.36	1.60
100	1.33	1.48	1.21	1.23	1.24	1.26	1.22	1.31	1.24	1.18

## RESULTS

Relative atomising times are shown in Table I for the concentric atomiser, while those for the non-concentric atomiser are shown in Table II. Because capillaries of 0.5 and 0.6 mm resulted in similar-type results with the data for Tables I and II, these are not shown separately.

In connection with these investigations, to make complete the experiments, we determined also the emission at various temperatures (direct atomiser) and various gas pressures (indirect atomiser). Our results are shown in Figs. 1 and 2.

## DISCUSSION

According to the data of Table I the time of atomisation (for 0.33 ml of liquid) shows a minimum at low alcohol concentrations and low gas pressures. Because the viscosity of the solutions shows a maximum with increasing alcohol concentrations, and at low alcohol concentrations the viscosity increases, the minimum in atomising time indicates that apart from the viscosity of the solution the surface tension also has an effect on the atomising time. The fact that the relationship between the time of atomisation and alcohol concentration has a much lower run than the viscosity

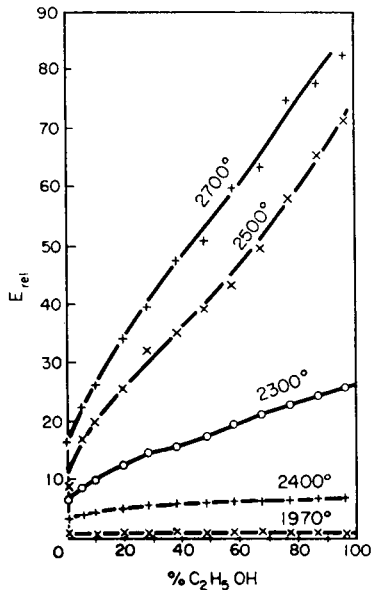


FIG. 1.—Relative emission (sodium emission) as a function of alcohol concentration at various temperatures measured in a Beckman photometer (direct concentric atomiser)

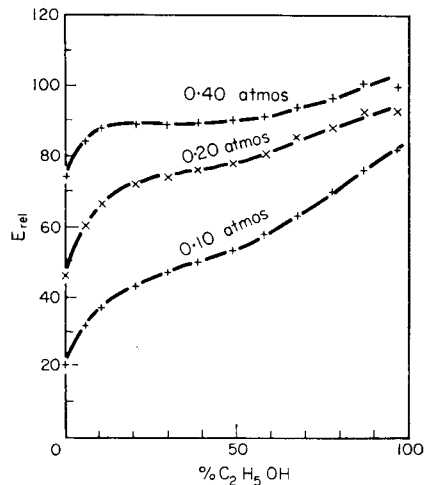


FIG. 2.—Relative emission (sodium emission) as a function of alcohol concentration at various pressures measured in a Beckman photometer (indirect non-concentric atomiser).

function, also supports this view. At the same time, it can be seen from the table that the minima of atomising time curves diminish at a special rate of atomisation. It could also be established that if capillaries of various diameters were used, the minimum diminished always at that atomising rate where 30 msec were needed for lifting of the liquid column with the diameter of the capillary.

The pressure in the Hagen-Poiseuille law, therefore, as indicated by the results, must include up to a special flow rate, also surfacial pressure from the surfacial tension of the liquid.

Results of the investigations carried out with the Zeiss-atomiser do not show minima in the atomising time with increase of alcohol concentration. This fact and the formerly mentioned one have the same cause. In the case of the Zeiss atomiser the direction of liquid current is rectangular to that of the gas. Therefore the surface of the liquid, flowing out from the capillary, is deformed by the gas current to such an extent that the component of the surfacial pressure, in the direction of the liquid flowing into the capillary, becomes negligible. For the concentric atomiser, if low flow rates are

used, the flow of the liquid is laminar. If the pressure of outflowing liquid is increased, a turbulent gas current is formed, and therefore the surface of the liquid flowing out from the capillary and being in connection with the liquid in the capillary, becomes strongly deformed. The higher the surface of the liquid is deformed, the lower is the component of surfacial pressure in the direction of the capillary.

For the mathematical treatment of our results, we define the following function between surfacial pressure and flow rate of the liquid from the capillary:

$$\ln \frac{p_0 - p}{p_0} = -kt.$$

where  $p$  is the surfacial pressure at that atomisation rate where the liquid column is lifted during time  $t$  up to the height of the diameter of the capillary,  $p_0$  is the surfacial pressure of a drop with a radius similar to that of capillary, and  $k$  is the reciprocal of the 30 msec mentioned above.

From this equation  $p$  can be obtained from the following equation:

$$p = p_0 (1 - e^{-kt})$$

Putting this into the Hagen-Poiseuille equation:

$$V_e = \frac{(P_h - p_0 + p_0 e^{-kt}) \pi r^4}{8 l \eta}$$

where  $P_h$  is the hydrostatic pressure. Dividing this expression into separate terms, the following equation, which is suitable for calculations, is obtained:

$$V_e = \frac{a}{\eta} - \frac{b\sigma}{\eta} + \frac{b\sigma}{\eta} e^{-kt}.$$

Thus, the rate of atomisation is expressed by the characteristics of the solution.

If non-concentric atomisers are used, because of the small value of  $t$  the value of the exponential term is nearly equal to 1, and therefore the effect of surfacial tension has no role on the rate of atomisation. Our theoretical and experimental results, gained by this method, are shown in Table III for a concentric atomiser. It is seen that the semi-empirical equation yields the experimental results with a good approximation.

The liquid passed through the atomiser may arrive directly in the flame or may pass through a tube system after homogenisation. The emission, however, is not defined uniformly by the amount of substance passed into the flame. Previous work has established the extent of coagulation of aerosols at various alcohol concentrations, using indirect atomisers.<sup>5</sup> The effect of rate of atomisation on the flame emission has also been investigated in the case of direct atomisers.<sup>6</sup> The investigations of Baker and Vallee<sup>7</sup> resulted also in a function between rate of atomisation, excitation energy and flame photometric emission. Taking these into consideration the correlation between flame photometric emission, flame temperature and alcohol concentration, shown in Fig. 1, can be explained. As has previously been pointed out for direct atomisers using low rates of atomisation (in the case of water, 0.5 ml/min), the emission for a given volume of liquid passed into the flame per sec is directly proportional to the surfacial tension of the liquid.<sup>8</sup> This result indicates that the dispersion grade of the atomised liquid has changed together with the decrease of surfacial tension. Quantitative investigation of this question is in progress. Similar investigations were made by

Littaye<sup>9</sup> as well as by Nukiyama and Tanasawa.<sup>10</sup> The latter workers also developed a mathematical expression for the drop size.

From our experiments we can establish, that in burner atomisers used today, at practical gas pressures the amount of atomised liquid depends on the viscosity of the solution and hydrostatic pressure, apart from the characteristics of the capillary, but it is independent or depending only slightly on the surfacial tension of the solution. The

TABLE III.—CALCULATED AND MEASURED ATOMISING TIMES (SEC)  
(amount of atomised solution: 0.33 ml; radius of capillary: 0.4 mm).

Alcohol conc. vol. %	Pressure of atomising gas, atm							
	0.75		0.84		1.05		1.40	
	calc.	meas.	calc.	meas.	calc.	meas.	calc.	meas.
0	63.5	62.4	48.8	51.6	23.6	23.0	9.5	8.3
5	52.0	58.8	42.0	47.5	25.8	27.6	10.7	10.3
10	52.3	59.6	41.1	46.4	26.1	29.8	12.3	10.9
20	63.6	66.6	53.7	56.7	30.6	35.3	15.3	14.4
30	74.7	72.8	60.0	59.4	34.8	41.3	18.6	19.3
40	—	—	62.0	64.0	40.0	45.8	21.2	20.4
50	82.8	79.5	63.2	63.7	41.3	47.4	22.0	21.4
60	—	—	63.3	59.2	43.4	46.2	22.0	21.0
70	—	—	57.8	54.2	39.8	41.5	21.0	19.3
80	68.2	60.2	49.0	46.8	36.6	36.8	19.3	18.6
90	—	—	37.8	35.4	32.0	29.8	16.7	14.5
100	39.0	37.2	29.2	28.3	22.9	22.9	12.3	11.8

flame photometric results, are however, also influenced by the surfacial tension, because the grade of dispersity increases in the flame with decrease of surfacial tension, and thus the further reaction of the aerosol in the case of direct atomisers becomes faster in the high temperature area because of the increase of surface, and thus the amount of emitting substance increases in the optical area of the flame photometer (see Fig. 1). In the case of indirect atomisers, the surfacial tension of alcohol also yields an increase of dispersity grade, because the finely distributed aerosol coagulates to a smaller extent, and therefore though the rate of atomisation decreases, more substance is transferred into the flame at medium alcohol concentrations, than in the case of aqueous solutions (see Fig. 2).

**Zusammenfassung**—Es wurde nachgewiesen, dass bei konzentrischen Zerstäubern die Flächendruckkomponente nach dem Hagen-Poiseuilleschen Gesetz mit dem Turbulenzgrad des Gasstromes wechselt. Die durch die Kapillare fließende Flüssigkeitsmenge ist daher von der Viskosität der Lösung und wie früher schon dargelegt, auch mehr oder wenig von der Oberflächenspannung abhängig. Bei nichtkonzentrischen Zerstäubern hat die Oberflächenspannung auf den Wirkungsgrad des Zerstäubers keinen Einfluss. Für konzentrische Zerstäuber können die Resultate auch quantitativ behandelt werden.

**Résumé**—Les auteurs ont établi qu'en utilisant des pulvérisateurs concentriques, la composante de surface de la pression due à la loi de Hagen-Poiseuille varie selon le degré de turbulence du courant gazeux. La quantité de liquide passant par le capillaire dépend de la viscosité de la solution et, plus ou moins, ainsi qu'il est indiqué précédemment de la tension superficielle. Si le pulvérisateur n'est pas concentrique, la vitesse de pulvérisation est indépendante de la tension superficielle. Dans le cas des pulvérisateurs concentriques les résultats obtenus peuvent être expliqués de manière quantitative.

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# PHOTOMETRISCHE MOLYBDÄNBESTIMMUNG MIT PHENYLHYDRAZIN—I

## NEUE UNTERSUCHUNGEN ÜBER DEN PHENYLHYDRAZIN-MOLYBDÄNKOMPLEX

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(Eingegangen am 14 August 1962)

**Zusammenfassung**—Wir haben die Eigenschaften, Struktur und Bildungsbedingungen des Phenylhydrazin-Molybdänkomplex untersucht und bestimmten die Zusammensetzung des festen Komplexes. Wir haben ein Strukturmodell zusammengestellt und suchten eine Erklärung für den Reaktionsmechanismus.

### EINFÜHRUNG

Das Phenylhydrazin gibt mit Molybdationen in schwach saurer Lösung in Abhängigkeit von der Molybdatkonzentration einen roten Niederschlag bzw. eine resarotefärbung.<sup>1</sup> Diese Reaktion ist spezifisch für Molybdän und darum lässt sie sich zum tüpfelanalytischen Nachweis<sup>2</sup> bzw. zur photometrischen Bestimmung<sup>3</sup> anwenden.

Man findet nur wenig Angaben über die Bildung des Komplexes. Die Zusammensetzung der farbigen Verbindung und ihr Reaktionsmechanismus ist noch nicht näher geklärt. Nach Feigl<sup>2</sup> oxydiert das Molybdation das Phenylhydrazin wahrscheinlich zu Diazoniumsalz und dieses tritt mit dem überschüssigen Phenylhydrazin in Verbindung. Nach Okáč<sup>4</sup> bildet sich ein Azofarbstoff. In den Mitteilungen über photometrische Methoden<sup>5</sup> findet man keine näheren Angaben.

Unsere Untersuchungen bezweckten die Darstellung von wasserlöslichen und wasserunlöslichen farbigen Verbindungen, ferner das eingehende Studium ihrer Eigenschaften, Struktur und Bildungsbedingungen.

### EXPERIMENTELLER TEIL

#### *Apparaten und Reagenzien*

*Beckman DU Spectrophotometer*

*Phenylhydrazin-HCl Lösung:* 10 g in Wasser pro 100 ml. Frisch zubereitet.

*Molybdät-Lösung:* Aus  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{34} \cdot 4 \text{H}_2\text{O}$ , in Wasser, in verschiedenen Konzentration.

*Puffer-Lösung:* pH: 2,2, aus  $\text{Na}_2\text{HPO}_4 - \text{H}_3\text{PO}_4$ .

Alle Reagenzien sind in p.a. Qualität.

### I. EIGENSCHAFTEN DES WASSERLÖSLICHEN KOMPLEXES

Nach Unseren Erfahrungen, in der photometrischen Bestimmung unter einer Konzentration von 0,1 millimol Mo/liter bildet sich kein Niederschlag. Die Farbentönung und die Farbenintensität der klaren Lösung des Komplexes hängt von der Konzentration des Phenylhydrazins bzw. Molybdationen, von dem pH, von der Temperatur und von der Wartezeit ab. Das optimale pH in einer mit Azetat, oder Phosphatpuffer versetzten Lösung liegt zwischen 2,2-2,5. Das Absorptionsmaximum



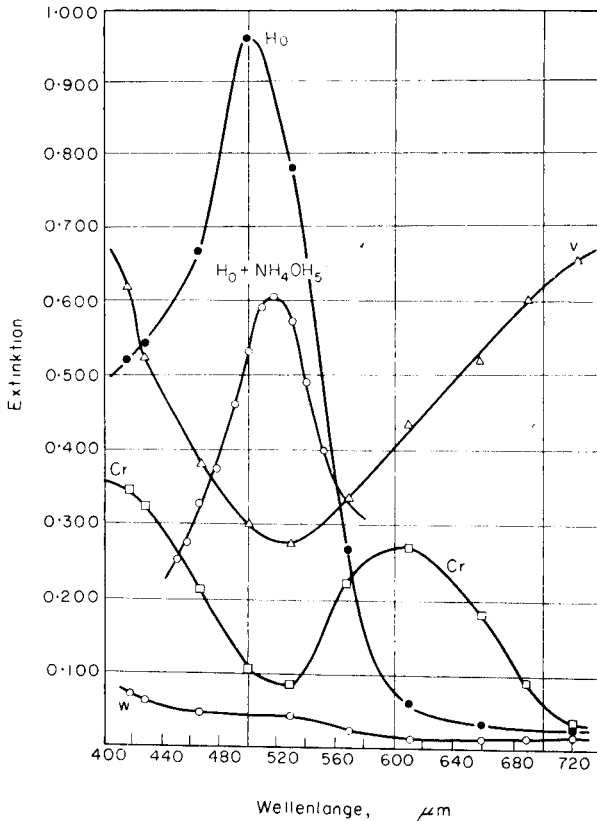


ABB. 1.—Die Absorptionskurven des Mo-Komplexes bei pH 2,2 und 8. Die Absorptionskurven von Cr(III), VO<sub>3</sub> und WO<sub>4</sub><sup>2-</sup>-Reaktionsprodukten. (2,9 mg Mo, 800 mg Cr<sub>2</sub>(SO<sub>3</sub>) 2,000 g Na<sub>2</sub>WO<sub>4</sub> und 2,00 g NH<sub>4</sub>VO<sub>3</sub> in 250 ml, pH: 2,2.)

liegt bei 505 m $\mu$ . (Abb. 1.) Die Farbe der Lösung wird zwischen pH 6-9 violette und das Absorptionsmaximum verschiebt sich auf 520 m $\mu$ . Der Komplex ist in alkalischer Lösung unbeständig und verblasst bei pH 9 in einigen Minuten. (Tabelle I.)

TABELLE I.—DIE LÖSUNGS FARBE IN VERSCHIEDENEN GRUNDLÖSUNGEN

Grundlösung	pH	Lösungsfarbe	Grundlösung	pH	Lösungsfarbe
cc H <sub>2</sub> SO <sub>4</sub>		gelb	H <sub>3</sub> PO <sub>4</sub>	1	rosarot
cc HCl		gelb	Weinsäure	2	gelber Niederschlag
HCl 1 n	0	orange			
HCl 0,1 n	1	orangerot			
HCl 0,01 n	2	blassrot	Ameisensäure	2	rosarot
HCl 0,001 n	3	blassorange	Oxalsäure	2	blassrosa
			ges. Borsäure	6,5	blassrosa
Phosphatpuffer	2,5	rosarot	NaHCO <sub>3</sub>	7	blassviolett
Essigsäure	3	rosarot			
Azetatpuffer	4	blass rosa	Phosphatpuffer		
Azetatpuffer	5,5	blass orange	mit Hydrazin	2,5	rosarot
			mit Hydrochinon	2,5	rosa
NH <sub>4</sub> Cl-NH <sub>4</sub> OH	8	violettrot	mit Ca(H <sub>2</sub> PO <sub>2</sub> ) <sub>2</sub>	2,5	violettrot
Na <sub>2</sub> CO <sub>3</sub>	9	farblos	mit SnCl <sub>2</sub>	2,5	weisser Ndsch.

Man gibt in verschiedenen Grundlösungen zu 5 ml (2,9 mg) Mo-Lösung 10 ml 10 %-ige Phenylhydrazin-HCl -Lösung, wärmt in 95°C bis 5 Min. und füllt zu 250 ml.

Die Farbenintensität und die Bildungsgeschwindigkeit des Komplexes häng von der Temperatur ab. Nach längeren Zeit werden die Lösungen auch bei niedriger Temperatur rot und ihre Extinktion erreicht den gleichen Granzwert. (Abb. 2.)

Die Farbenintensität und die Eigenschaften werden von der Konzentration des Molybdations bzw Phenylhydrazins und vom Verhältnis der Konzentrationen stark beeinflusst. (Tabelle II.)

Bei einen pH-Wert von 2,5 ist neben dem farbigen Komplex auch freies Phenylhydrazin zugegen, da die Lösung mit Formaldehyd einen Niederschlag gibt. Die Farbe wird durch Pb(II), Hg(II), Zn(II), Cd(II), Mn(II), Fe(II), Fe(III), Ni(II), Co(II), Al(III), Mg(II), Cu(II) in Phosphat-Puffer nicht gestört. Die blassgrüne Lösung des Cr(III)-Reaktionsprodukt zeigt bei 505 m $\mu$  nur eine geringe Absorption. Viel Vanadat enthaltende Lösung gibt beim längeren Kochen ein violetter Niederschlag.<sup>6</sup> Viel Wolframat stört nicht, es tritt nur eine blassblaue Färbung auf. (Abb. 1.) Stark oxidierende Anionen z.B. MnO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, ClO<sub>4</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, BrO<sub>3</sub><sup>-</sup>, JO<sub>3</sub><sup>-</sup> geben mit Phenylhydrazin einen gelben Produkt. Aus SeO<sub>4</sub><sup>2-</sup>, TeO<sub>4</sub><sup>2-</sup> oder Pd(II)-Lösung fällt mit Phenylhydrazin elementares Se, Te oder Pd. Oxalsäure, Ameisensäure und

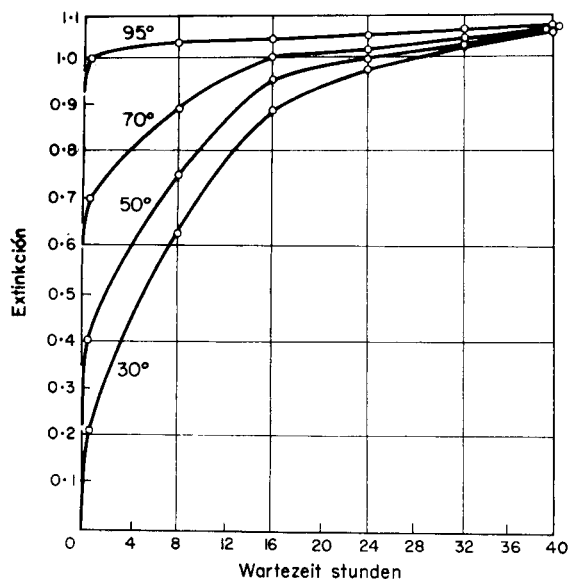


ABB. 2.—Die Abhängigkeit der Farbenintensität von der Temperatur und der Wartezeit (2,9 mg Mo in 250 ml, pH: 2,2.)

Borsäure stören durch Bildung Anionenkomplexen (Oxalato-Molybdat, Formiato-Molybdat). Der Komplex lässt sich mit Amylalkohol ausschütteln, Benzol, Butylazetat und Chloroform lösen ihn nicht. Der Komplex zerstört sich in Gegenwart von Oxidationsmitteln und entfärbt sich. In Gegenwart von Hydrazin, Hydroxilamin und Hypophosphit ändert sich die rote Farbe nicht.

Die Geschwindigkeit der Reaktion kann mit vorheriger Oxydation des Phenylhydrazins wesentlich beschleunigt werden. Die Kochzeit von 2-3 Minuten vermindert sich auf 30 Sekunden, falls die Phenylhydrazin mit einer 0,1 n KBrO<sub>3</sub> oder KJO<sub>3</sub> Lösung oxydiert wird.

TABELLE 2.—DIE FARBIGE PRODUKTEN DES MOLYBDÄNS UND PHENYLHYDRAZIN BEI VERSCHIEDENEN MOL-VERHÄLTNISSEN

Mo, mg	Phenylhydrazin-HCl, mg	Phenylhydrazin pro 1 atom Mo, mol	Lösungsfarbe	Extinction
0,30	1300	2880	rosaret	1,050
0,30	900	1990	rosarot	1,020
0,30	700	1580	rosarot	1,000
0,30	450	995	rosarot	1,000
0,30	350	790	rosarot	0,940
0,30	225	497	rosarot	0,750
0,30	90	199	blassrosa	0,240
0,30	45	99,5	blassrosa	0,060
0,30	22,5	49,7	farblos	—
0,30	9	20	farblos	—
0,30	4,5	10	farblos	—
2,30	22,5	0,65	farblos	—
2,30	9	0,25	farblos	—
2,30	4,5	0,13	farblos	—
12	100	5,53	farblos	—
30	1300	28,8	violettrote Niederschlag	—
42	1300	20,5	violettrote Niederschlag	—
42	120	1,9	blaue Lösung	—
42	22,5	0,54	dunkelblaue Lösung	—
42	9	0,22	blaue Lösung	—
42	4,55	0,11	blassblaue Lösung	—
500	1300	1,7	violettrote Niederschlag	—

In Phosphatpuffer pH 2,5. Volumen: 50 ml.

## II. DIE EIGENSCHAFTEN DES WASSERÜNLÖSLICHEN KOMPLEXES

Bei der Untersuchung der photometrischen Bestimmung haben wir oft die Abscheidung eines feinverteilter, violetttrötkicher Niederschlags beobachtet. Die Farbenintensität vermindert sich, die Extinction wächst aber infolge der Trübung. In pufferhaltiger Lösung bei pH 2,2-2,5 bildet 3 mg Mo noch einen löslichen Komplex und selbst durch Erwärmen entsteht kein Niederschlag. (Tabelle III)

TABELLE 3

pH	Molybdänkonzentration in 100 ml Volumen		
	unten 2 mg	2-4 mg	über 4 mg
0-2	rote Färbung kein Niederschlag	rote Färbung Kein Niederschlag	Rote Färbung roter Niederschlag
3-4	schwache Rotfärbung trübe Lösung	rote Färbung, wenig violettrötkicher Nieder- schlag	rote Färbung, veil roter Niederschlag
5-7	Keine Reaktion	farblose Lösung, Benzolbildung (wenig)	violetter Niederschlag farblose Lösung
8-10	Keine Reaktion	sofortige Benzol- bildung	viel Benzol

Den wasserunlöslichen Komplex haben wir auch in grösseren Menge hergestellt aus Ammoniumheptamolybdat.

5,000 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$  haben wir in 100 ml Wasser gelöst und dann zu je 20 ml dieser Lösung haben wir 1,3 g Phenylhydrazin-HCl, gelöst in je 100 ml Lösung von verschiedenen pH, zugeben. Schliesslich wurde die Lösung auf  $95^\circ\text{C}$  erwärmt.

Bei pH: 0: Es bildete sich eine dunkel-weichselfarbige Lösung. In Phosphatpufferlösung, pH: 2,2: bildete sich ein violetteroter Niederschlag. In Wasser, pH: 6. Schon kalt scheidete sich viel violetteroter Niederschlag aus. Der Niederschlag filtriert und mit Wasser gewaschen wurde. Aus dem Filtrat wurde mit Phenylhydrazin keine weitere Abscheidung beobachtet. Der Schmelzpunkt des Produktes liegt über  $270^\circ\text{C}$ . Das getrocknete, violettrote Pulver löst sich in Wasser nicht. In konzentrierten Säuren löst es sich unter Zersetzung mit gelber Farbe. Mit wachsendem pH vermindert sich die Löslichkeit. Die Farbe wird orangerot, dann rot. In alkalischen Lösung über pH 7,5 ändert sich der Farbton. es wird violetter und die Löslichkeit wächst auch, beim Stehen entfärbt er sich schnell.

Der Komplex löst sich nur wenig in einwertigen Alkoholen. Er ist wenig löslich in Phenolen, in hydroaromatischen Alkoholen, in Azeton und hydroaromatischen Ketonen. In wässriger Lösung organischer Säuren löst er sich nicht. Er ist unlöslich in Kohlenwasserstoffen und in den Halogenderivaten dieser. Am besten löst er sich in Pyridin.

Der violettrote Komplex gekocht mit Oxydationsmitteln ( $\text{H}_2\text{O}_2$ ,  $\text{NaNO}_2$ ) bei pH 2,2, verlor seinen violetten Farbton, er wurde weichselfarbig. Das feste Produkt enthält wahrscheinlich auch Molybdänblau, wodurch der violette Farbton verursacht wird. Das Mo-Blau wird oxydiert und nur die rote Komponente bleibt zurück.

In Gegenwart von Hydrochinon oder 2-Naphtol bildet sich kein roter Komplex. Mit der Bindung der Aminogruppen des Phenylhydrazins lässt sich das Auftreten der Farbenreaktion.

#### *Analyse und Konstitution des wasserunlöslichen Komplexes*

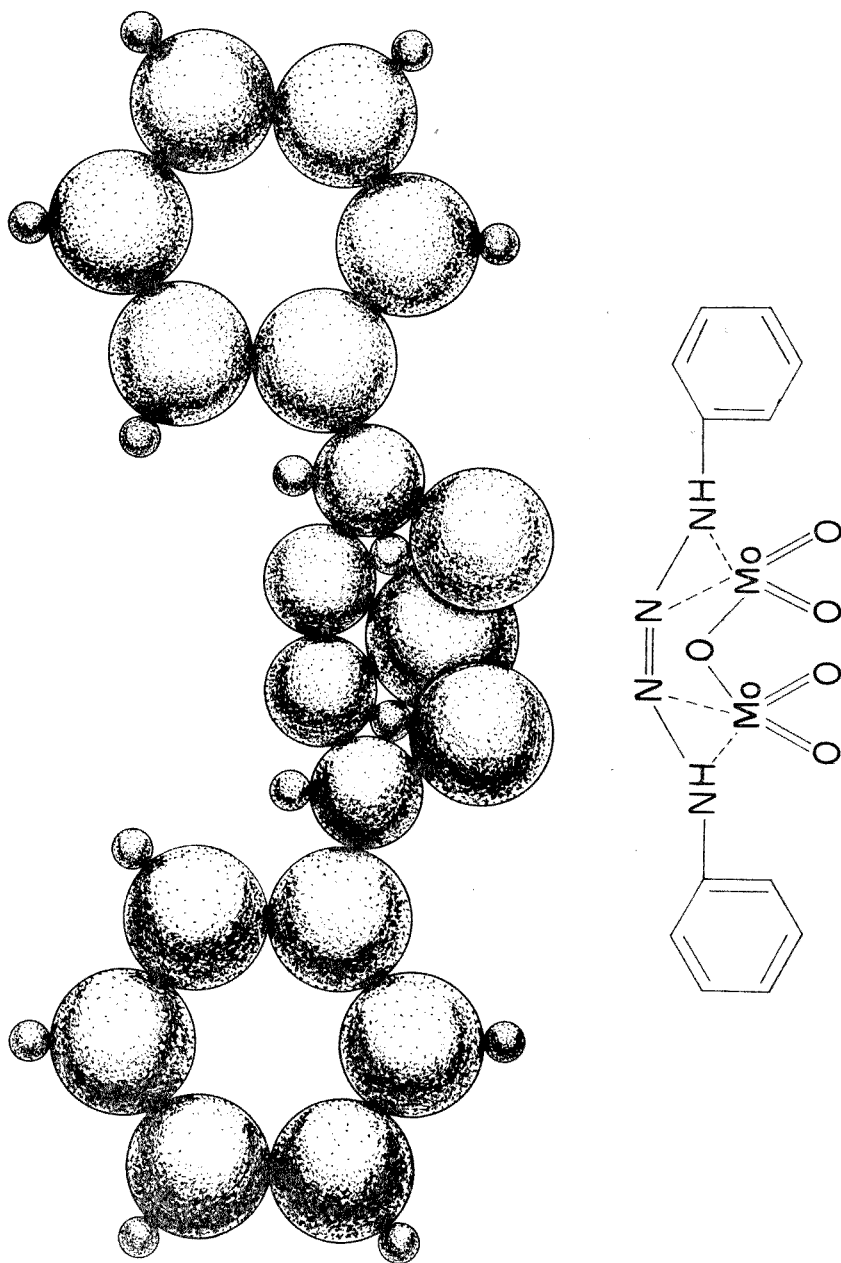
Den C-Gehalt des getrockneten violettrote Pulver haben wir nach Verbrennung in Sauerstoffstrom durch Messung des  $\text{CO}_2$ -Volumens, den Imino-N-Gehalt nach Kjeldahl, den Mo-Gehalt nach Zerstörung der organischen Bestandteile mit O-Oxychinolin und den Cl-Gehalt nach alkalischen Zerstörung mit  $\text{AgNO}_3$  bestimmt (Tabelle 4.)

TABELLE 4.—DIE BERECHNETE UND GEFUNDENE ZUSAMMENSETZUNG DES KOMPLEXES

Zusammensetzung	C, %	Imino-N, %	Gesamt-N, %	Mo, %	Cl, %
Berechnet	29,77	5,77	11,54	39,6	—
Gefunden	29,72	5,67	11,34	44,7	—

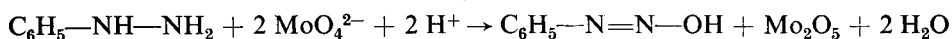
Das Molekül enthält 2 Phenyl-, 2 Imino- und eine Azo-Gruppe, und  $\text{Mo}_2\text{O}_5$ . Die räumliche Anordnung des Moleküls zeigt Abb. 3. Zwischen vier N-Atomen ein  $\text{Mo}_2\text{O}_5$ -Molekül Platz haben kann. Die Sauerstoffatome liegen unter den Stickstoffatomen. Die Zusammensetzung des Komplexes: Diphenyl-tetrazen-Mo(V)-oxyd. Das feste Produkt neben den roten Diphenyl-tetrazen-Komplexe auch wenig kolloidales Mo-Blau ( $\text{Mo}_2\text{O}_5$ ) enthält.

Die Konstitution und Zusammensetzung des wasserlöslichen Komplexes stimmt mit der Formel. Die chemischen Eigenschaften sind gleich. Das Molekulargewicht des löslichen Produktes ist noch nicht festgestellt, wahrscheinlich es bildet eine kolloide Lösung feiner Dispersität.

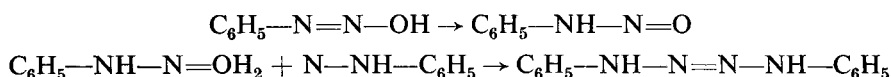


*Bildungsweise des Komplexes*

Das Molybdation ist ein schwache Oxydationsmittel und oxydiert das Phenylhydrazin in saueren Lösung bei pH 2-3 zu Diazosäure:



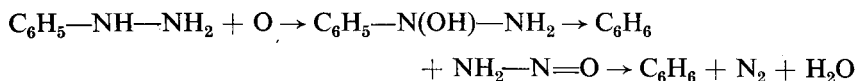
Diazosäure kann in zwei Modifikationen (in Syn- und Anti-Form) existieren. Nach der Bildungswahrscheinlichkeit, bzw im Gleichgewichtsfalle beträgt das Konzentrationsverhältnis der Syn- und Anti-Form 1:1000. Durch Umlagerung der Diazosäure entsteht Aminoxim und dieses kondensiert sich mit dem überschüssigem Phenylhydrazin zu Diphenyl-tetrazen.



Die vier Stickstoffatome der Diphenyltetrazen sind mit koordinativen Bindung an das durch Reduktion des Molybdations entstandenes  $\text{Mo}_2\text{O}_5$  gebunden. (Abb. 3.) Das Doppelbindung enthaltende Diphenyltetrazen hat auch zwei Modifikationen. Der farbige Komplex besteht aus Syn-diphenyltetrazen-Mo(V)-oxid. Das Antidiphenyltetrazen gibt aus stereochemischen Gründen keinen Komplex mit  $\text{Mo}_2\text{O}_5$ .

Die Geschwindigkeit der Phenylhydrazin-Molybdat-Reaktion, sowie die Umlagerungsgeschwindigkeit der Diazosäure zu Aminoxim wird vom pH stark beeinflusst. Die Entwicklungszeit der Farbenreaktion und die Kondensationsgeschwindigkeit wird von der Temperatur beeinflusst. Der hohe Bedarf an Phenylhydrazin wird durch die gleichzeitige Bildung und Verhältniss der analytischen aktiven Syn-Form und der inaktiven Anti-Form begründet. Die Farbe des Komplexes hängt vom pH ab. In der orange bzw gelben Lösung, unter pH 1,5 ist wahrscheinlich nur Diazosäure zugegen.

Die Kondensation wird auch vom pH beeinflusst. In stark saurerer Lösung die Diazosäure lagert sich nicht um und kondensiert nicht mit Phenylhydrazin. Die Umlagerung der Diazosäure und die Kondensation erfolgt nur bei pH 2-3. Über pH 3 vermindert sich die Geschwindigkeit der Reaktion Phenylhydrazin-Molybdat, und es wird weder  $\text{Mo}_2\text{O}_5$ , noch Diazosäure gebildet. In alkalischen Lösung tritt keine Farbenreaktion auf, da das Phenylhydrazin durch den Sauerstoff der Luft zu Benzol oxydiert wird. In Gegenwart von Oxydationsmitteln erfolgt die Zersetzung noch schneller:



In Gegenwart von Reduktionsmitteln bildet sich kein roter Komplex, da keine Diazosäure entsteht. Die vorherige Oxydation des Phenylhydrazins in gepufferten Lösung führt zu einer Vergrößerung der Diazosäurekonzentration, wodurch die Entwicklungszeit der Farbenreaktion verkürzt wird. Der rote Komplex verliert in ammonia-kalischer Lösung seine Farbe, da das Diphenyltetrazen im alkalischer Lösung sich zersetzt.

**Summary**—The properties, structure and conditions for the formation of the phenylhydrazine complex of molybdenum have been investigated, and also the composition of the solid complex. A structural model and an explanation of the reaction mechanism have been proposed.

**Résumé**—On présente une étude des propriétés, de la structure, et des conditions de formation du complexe obtenu par action du molybdène sur la phénylhydrazine, et de la composition du complexe solide. On propose d'un modèle de structure et un mécanisme de réaction.

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## DERIVATOGRAPHIC DETERMINATION OF THE CALCITE CONTENT OF BAUXITES

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(Received 14 August 1962)

**Summary**—A derivatographic method has been developed for the determination of the calcite content of bauxites. The amount of calcite, calculated from the thermogravimetric curve, is in many cases higher than the true value. This positive error arises from the fact that a number of bauxite minerals only decompose completely above 650°, and therefore they overlap the thermal decomposition of calcite. A new graphic method is recommended for the estimation of this error.

CALCITE is an undesirable constituent of bauxites because it transforms the sodium hydroxide used for dissolution into sodium carbonate, the regeneration of which is an expensive and a tedious task. In most cases carbon dioxide is bound in bauxites in the form of calcite, and only rarely in that of dolomite or other minerals. In practice, total carbon dioxide content is determined in bauxites. Using this method the sample must be treated with concentrated sulphuric acid, and the amount of carbon dioxide removed is weighed indirectly.

Earlier investigations on bauxites<sup>1-6</sup> established that, according to the experimental conditions, carbonate minerals decompose more or less independently of the other bauxite minerals. The accuracy of the determination of carbonate derivatographically has now been examined.

### EXPERIMENTAL

The principle of derivatography has been described in earlier papers.<sup>3,6</sup> The present measurements were carried out with a 676 type GyEM derivatograph, which measures simultaneously the weight change of the sample (TG), the rate of weight change (DTG), the temperature and the enthalpy change caused by thermal reactions (DTA). The measurements were made with a 17-mm tall sample holder, 11 mm in diameter. The weight of samples was about 1 g, and a 10°/min heating rate was applied.

The change in the thermal decomposition of pure calcite, if strongly diluted with other minerals in bauxites, was first examined (Fig. 1). For this purpose curves for pure calcite, and also for samples containing 90 or 99% of aluminium oxide in addition to calcite were recorded. Although most of the bauxite minerals do not influence the identification of calcite, the later parts of their thermal decomposition curves overlap the curves for calcite decomposition, and therefore influence the accuracy of determination of smaller amounts of calcite. To determine the error of the method a bauxite was selected as a standard which (Figs. 2-3, curve 1) did not show the presence of calcium carbonate in its derivatogram. To this we added various known amounts of calcite, and after thorough homogenisation they were investigated with the derivatograph (Table I, Figs. 2, 3, curves 2, 4, 6, 8). The same measurements were also carried out also in a carbon dioxide atmosphere (Table I, Figs. 2, 3, curves 3, 5, 7, 9). Bauxites which contained smaller or larger amounts of calcite, determined previously gravimetrically (Table I, experiments 10-18) were also examined. The origin of these bauxites and their mineral compositions are shown in Table II.

The error of determination can be estimated graphically. The principle of the method is shown in Fig. 3, on which the DTG and TG curves of the original bauxite and those of experiments 6 and 7 are drawn. Fig. 3 illustrates the origin of errors ( $h_1$  and  $h_2$ ) and its elimination.



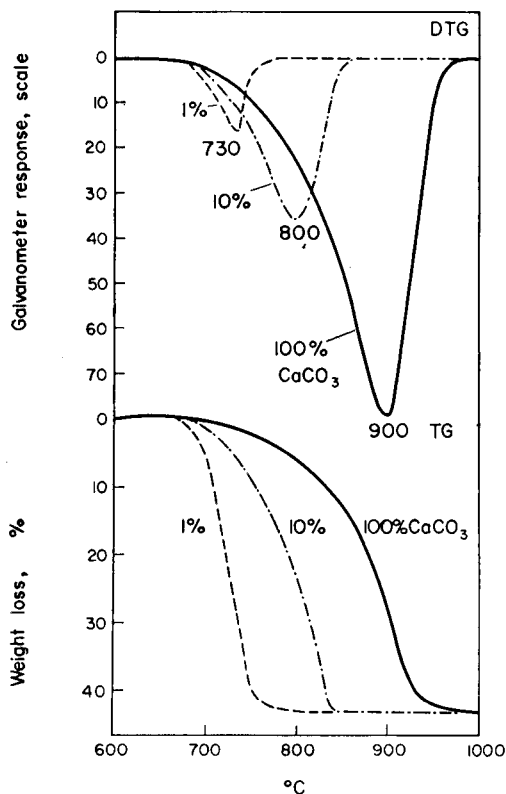


FIG. 1.—Decomposition of calcite diluted with other minerals present in bauxite.

### RESULTS

From the point of view of the derivatographic identification of calcite, it is important that pure calcite decomposes at much higher temperatures (Fig. 1) than if it is diluted with other compounds, like aluminium oxide. This phenomenon can be explained by the fact that at higher dilutions carbon dioxide cannot be built up inside the sample to the same extent as in the case of pure calcites, and therefore the decomposition of calcite is suppressed only slightly.<sup>1,2</sup>

The experimental results (Table I, Fig. 2, curves 2, 3) indicate that the presence of about 0.5% of calcium carbonate can be identified with certainty in bauxites, on the basis of a maximum of 740°. On the derivatogram of the investigated bauxite the characteristic DTG maximum was missing although 0.3% of carbon dioxide could be found in it gravimetrically. This indicates that the carbon dioxide was not present in the form of calcite or dolomite, but as some other metal carbonate. Probably this is the cause of the occasional differences between derivatographic and gravimetric results (Table I, bauxites 17 and 18).

The identification or determination of calcite is strongly interfered with by an occasional pyrite or alunite content of the bauxites,<sup>7</sup> because their thermal decomposition or the decomposition of their products, like iron<sup>II</sup> and iron<sup>III</sup> sulphates, and aluminium sulphate, also take place between 600° and 800°. The peak for calcite can be easily identified, however, if the test is repeated, under similar circumstances,

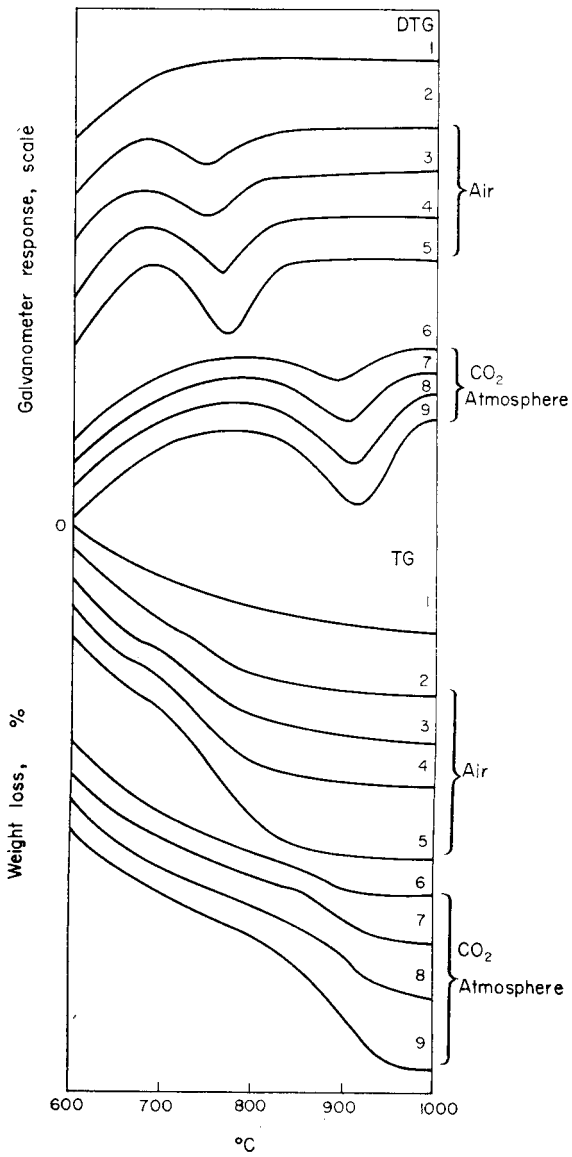


FIG. 2.—Decomposition of bauxite in air and carbon dioxide.

TABLE I.—DERIVATOGRAPHIC RESULTS

Number	Added or determined $\text{CaCO}_3$ , %	Corrected $\text{CaCO}_3$ , %	Uncorrected $\text{CaCO}_3$ , %	Correction $\text{CaCO}_3$ , %	Correction, % of original $\text{CaCO}_3$	Deviation from true value, %	Relative error, %	Standard deviation
2	0.73	0.84	2.27	1.43	195	+0.11	+15.6	
3	0.73	0.82	1.01	0.19	26	+0.09	+12.5	
4	0.96	0.93	1.96	1.03	107	-0.03	-2.4	
5	0.96	0.84	1.37	0.53	55	-0.12	-11.9	
6	1.66	1.71	2.73	1.02	61	+0.05	+2.7	
7	1.66	1.71	2.04	0.33	20	+0.05	+2.7	
8	1.92	1.98	2.75	0.77	40	+0.06	+3.1	
9	1.92	1.96	2.23	0.27	14	+0.04	+2.1	0.335
10	0.82	0.96	1.90	0.94	114	+0.14	+16.6	
11	1.18	1.14	2.14	1.00	88	-0.04	-3.8	
12	1.18	1.25	2.41	1.16	93	+0.07	+5.8	
13	1.30	1.48	2.72	1.24	95	+0.18	+1.40	
14	1.32	1.61	2.15	0.54	41	+0.29	+22.4	
15	2.80	2.98	3.18	0.20	7	+0.18	+6.5	
16	4.71	4.82	5.05	0.23	5	+0.11	+2.4	
17	10.70	9.10	9.31	0.21	2	-1.60	-14.8	
18	12.30	11.50	11.8	0.30	2	-0.80	-6.6	

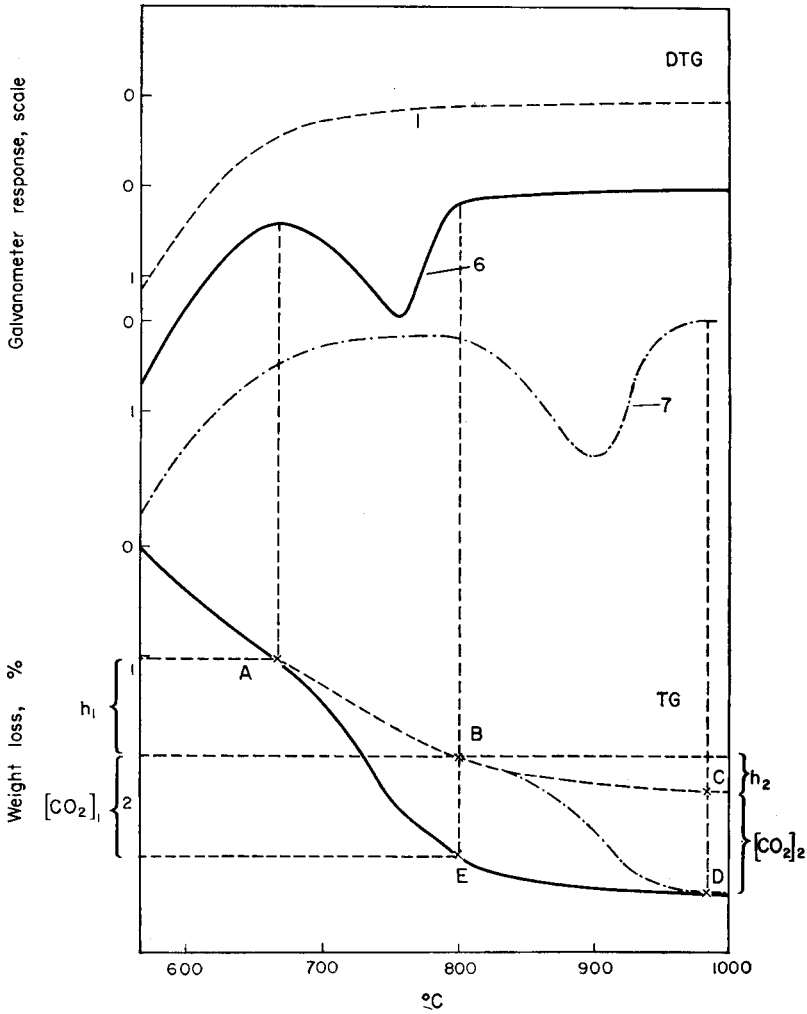


FIG. 3.—Method of determining error.

TABLE II.—NATURE OF BAUXITES USED

Number	Origin	Hydrargyllite, %	Boehmite, %	Caolinite, %
1.	Iszkaszentgyörgy	40.1	16.6	2.0
10.	Szöc	49.9	27.2	—
11.	Szöc	46.6	27.9	—
12.	Nyirád	46.6	24.2	+
13.	Iszkaszentgyörgy	40.3	28.9	+
14.	Halimba	0.41	55.8	10.6
15.	Szöc	47.6	17.8	—
16.	Halimba	2.1	65.0	—
17.	Halimba	2.6	17.6	57.1
18.	Halimba	6.0	11.5	45.0

but in a carbon dioxide atmosphere. In this case the thermal decomposition of smaller amounts of calcite also takes place in the neighborhood of 900° (Figs. 2, 3, curves 3, 5, 7, 9). The carbon dioxide atmosphere has no effect on those decomposition reactions which do not produce carbon dioxide, or where the oxygen of air takes no part. The lack of oxygen is advantageous in the case of pyrites, because in such circumstances iron<sup>II</sup> and iron<sup>III</sup> sulphates do not form, there is therefore no weight loss from decomposition of pyrite between 700° and 1000°,<sup>7</sup> and consequently only the interference of alunite can be expected.

It was found that the decompositions of diaspore, boehmite, caolinite and even of hydrargyllite<sup>5</sup> are not complete at 650°, and above this temperature some 0.1% weight loss can be experienced in the sample. This weight loss is in addition to the weight loss from calcium carbonate decomposition, and therefore the amount of calcium carbonate determined by this method will be higher than the true value. The error is greater for smaller amounts of calcium carbonate (Table I number 9). The error decreases if the measurement is carried out in a carbon dioxide atmosphere (Table I, number 9, Fig. 3,  $h_1 - h_2$ ). The error can be estimated, and thus eliminated, by the following graphical method:

Bauxite 1 changed its weight between 600° and 1000° according to curve 1. If 1.66% of calcium carbonate was mixed with it, the shape of the TG curve varied in air and carbon dioxide atmosphere according to curves 6 and 7, respectively. If the sample had not contained calcite, its weight would change according to the AB curve instead of the AE one. The weight loss,  $h_1$ , therefore gives the error which must be subtracted from the weight loss shown by curve 6 to yield the true value of carbon dioxide, represented as  $[\text{CO}_2]_1$  in Fig. 3. Fig. 3 also indicates that the error becomes much smaller ( $h_2$ ), if the measurement is made in a carbon dioxide atmosphere. In the case of an unknown bauxite sample only the resultant curve can be obtained (curves 6 or 7), but with a little practice the corresponding base-curve (curve 1) can be easily obtained. The resultant curve must be extrapolated between the points A and B, which can be deduced from the former shape of the curve when it is considered that the weight-loss decreases with increasing temperature. The extrapolation can be made on the basis of the shape of the resultant curve before point A and after point B. If measurements are made in a carbon dioxide atmosphere, the smaller error can be eliminated similarly.

**Zusammenfassung**—Eine derivatographische Methode zur Bestimmung von Calcit in Bauxit wurde ausgearbeitet. Der aufgrund der thermogravimetrischen Kurve erhaltene Calcitgehalt ist in vielen Fällen höher, als der tatsächliche Gehalt. Dieser Fehler wird auf die Tatsache zurückgeführt, dass manche Bauxite erst oberhalb von 650°C vollkommen zersetzt werden und so eine Überschneidung mit dem thermalen Zersetzungsbereich des Calcits zustandekommt. Eine graphische Methode zur Abschätzung dieses Fehlers wird empfohlen.

**Résumé**—Une méthode de dosage de la calcite dans les bauxites a été mise au point par thermogravimétrie dérivée. La teneur en calcite, calculée à partir de la courbe thermogravimétrique est, dans de nombreux cas, plus élevée que la valeur vraie. Cette erreur par excès est due au fait qu'un certain nombre de minerais de bauxite sont complètement décomposés au-dessus de 650°C et leur décomposition vient se superposer à celle de la calcite. Une nouvelle méthode graphique est recommandée pour l'estimation de cette erreur.

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## APPLICATION OF THE FLASK METHOD TO THE ANALYSIS OF HIGHLY HALOGENATED ORGANIC MATERIALS

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(Received 14 August 1962)

**Summary**—The Mikl-Pech-Schöniger flask method has been used in the analysis of highly halogenated substances. Combustion is encouraged with powdered sugar, and the combustion products are absorbed in ammonia solution. In this way the time of shaking can be reduced. The halide ions can be titrated with silver nitrate in the presence of Variamine Blue redox indicator. If the excess of ammonia is removed after combustion, titration of the halogen can be carried out better in the salt free solution.

The Mikl-Pech-Schöniger flask method is one of the most frequently used rapid micro methods applied recently to the analysis of many of the elementary components of organic substances.<sup>1</sup>

Papers dealing with the method present data mainly for materials which contain about 20-50% of halogen. Bennewitz,<sup>2</sup> however, mentions that his modified method, applicable to liquids, is not adequate if the substance contains 70-80% of bromine or chlorine. Results obtained for trichloroethylene, tetrachloroethylene or ethylene bromide showed large deviations and as a rule less than half the theoretical value was attained. Bennewitz suggests that this error is caused by inadequate combustion.

The present authors found equally low results if strongly chlorinated solid substances were examined. In the belief that the low results arise not only from incomplete combustion, but also from incomplete absorption, experiments were made to eliminate both sources of error.

Combustion can be made more complete either by reduction of the sample size, or by dilution of the sample. Because the first method also reduces the accuracy, the second one was examined. As a diluent ordinary powdered sugar seemed to be suitable, being a substance of high carbon content. The sample and about a threefold amount of powdered sugar were weighed on an L-shaped filter paper, the sugar being weighed first and spread out, and the sample weighed on this. A weighing vessel with a handle was used. Because of the larger amount of organic substance, a 500-ml flask was used for the combustion.

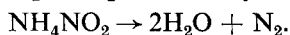
If the combustion was carried out without sugar, the characteristic smell of the substance being analysed could be noted, and the results were lower than expected, even if the absorption was effected by a more efficient method.

Lower results were also obtained if, after combustion, the combustion products were shaken with an alkaline hydrogen peroxide solution for 10-12 min; this is usually sufficient if the substance to be analysed contains small or medium amounts of halogen. If the time of shaking was increased, results became higher, and after a 30 to 35-min shaking time results were generally correct.

It was thought that the unusually long shaking time could be reduced if, instead of the usual alkaline hydrogen peroxide, another absorbing solution was employed. For this ammonia solution appeared to be suitable; ammonia gas should react with hydrogen halides or halogens formed in the combustion more completely than the droplets of alkaline hydrogen peroxide. Shaking would therefore be needed only for the collection of the ammonium halide droplets.

This reasoning proved to be correct; after shaking for 1-2 min the mist disappears, and after 4-6 min correct results are obtained. The lack of hydrogen peroxide does not cause any error if chlorine- or bromine-containing substances are combusted: the solution does not contain hypohalite or halate ions, and argentometric titration of halide ions<sup>3</sup> gives accurate results.

At the high temperature of combustion nitrogen oxides may be formed from ammonia; these would react with the excess of ammonia forming ammonium nitrite and nitrate. Ammonium nitrite, which could cause errors in the indicator reaction if Variamine Blue is used, decomposes spontaneously, however, especially if heated:



Nitrate ions do not interfere.

If iodine-containing substances are heated, hypiodite, iodate and iodine are formed, and the absorbing solution turns yellow. If, however, about 1 g of hydrazine sulphate is added to the absorbing solution before or after combustion, complete reduction to iodide occurs in the case of all three products. Excess of hydrazine sulphate does not interfere with the indicator, and therefore any excess need not be decomposed before titration.

If the halide ions are determined by argentometric titration in the presence of Variamine Blue redox indicator, as previously described,<sup>3</sup> the use of ammonia has the further advantage that in the almost salt-free solution it is easy to adjust to the required pH value.

## EXPERIMENTAL

### *Apparatus and reagents*

500-ml combustion flask.

Oxygen source.

Ammonia solution: 1:1.

Nitric acid: 1:1.

Nitric acid: 1M.

Hydrazine sulphate solution: Halide-free, 10%. If necessary, hydrazine sulphate can be purified by recrystallisation.

Buffer solution: (pH 3.6, according to Walpole): Mix 15 ml of 0.2M sodium acetate solution with 185 ml of 0.2M acetic acid solution.

Silver nitrate standard solution: 0.01N

Variamine Blue acetate (or sulphate) solution: 1%: Either Variamine Blue base can be dissolved in the corresponding acid, or, if only Variamine Blue hydrochloride is available, the following procedure can be followed: To Variamine Blue hydrochloride solution add sodium hydroxide, to precipitate the base. Shake the latter with benzene, and dissolve from the organic layer with 20% acetic acid solution. The solution is stable for about 1 week.

Dimethyl yellow indicator solution: 1%.

### *Powdered sugar*

The reagents must be tested for halogens in a blank experiment.

### *Procedure*

On the middle of an L-shaped filter paper, commonly used for such combustions, pour 20-30 mg of powdered sugar, spread it out somewhat, and weigh 8-10 mg of sample on it, using a weighing vessel with a handle. Fold the filter paper, and place in the platinum basket of the combustion flask.

Liquid samples must be weighed according to Bennewitz<sup>2</sup> by sucking into a glass capillary 1 cm

TABLE I

Compound analysed	Halogen calculated or measured, %	Halogen measured by present method, %	Mean, %	Difference, %
Octachlorocyclopentene	82.53	82.03	82.12	-0.41
		82.22		
		82.61		
		82.07		
		81.66		
Hexachlorocyclopentadiene	77.99	78.16	77.80	-0.19
		78.32		
		77.56		
		77.72		
		77.24		
Hexachlorocyclohexane	73.15	72.68	73.17	+0.02
		73.04		
		73.66		
		73.32		
		73.17		
Tetrachlorophthalic acid	46.67	46.51	46.09	-0.58
		46.04		
		45.93		
		46.00		
		45.97		
<i>p</i> -Chloroaniline	27.79	28.61	28.28	+0.49
		27.72		
		28.52		
Tribromophenol	72.25	72.02	71.83	-0.42
		71.80		
		71.10		
		72.16		
		72.06		
<i>p</i> -Bromophenol	46.19	45.73	46.02	-0.17
		45.98		
		46.30		
		45.59		
		46.52		
<i>p</i> -Bromotoluene	46.72	46.98	46.35	-0.37
		45.96		
		45.80		
		46.42		
		46.60		
<i>p</i> -Bromoaniline	46.45	46.68	46.16	-0.29
		46.90		
		45.97		
		45.84		
		45.41		
Iodoform	96.69	97.12	96.98	+0.29
		97.20		
		96.60		
		97.02		
		96.96		
<i>p</i> -Nitroiodobenzene	50.96	49.94	50.22	-0.74
		50.36		
		49.78		
		50.26		
		50.77		
<i>p</i> -Iodoaniline	57.94	57.62	58.38	+0.44
		58.10		
		58.88		
		58.72		
		58.60		



long and of 1 mm internal diameter. Place the capillary on the L-shaped filter paper so that its open end lies in the sugar. Fold the filter paper, and place it in the platinum basket of the combustion flask.

Into the combustion flask pour 20 ml of distilled water and 2 ml of 1:1 ammonia solution. If iodine-containing substances are to be analysed, also add 10 ml of 10% hydrazine sulphate solution.

Fill the flask with oxygen gas, moisten the ground-glass joint, light the ignition strip, and insert the stopper immediately in the flask. After combustion has ended, pour water on the neck of the flask, and shake the flask vigorously for 5-6 min. After opening the flask, rinse the stopper and the walls with small amounts of water, and neutralize the solution with 1:1 nitric acid solution to the dimethyl red indicator end-point. If the indicator turns red, add some drops of ammonia and neutralise accurately with nitric acid once more. Add 5 ml of buffer solution and 5-6 drops of Variamine Blue redox indicator, and titrate, stirring constantly, with 0.01N silver nitrate standard solution until the pale-blue suspension turns violet.

If an iodine-containing substance is combusted, and thus iodine ions are being titrated, the silver iodide precipitate adsorbs a part of the indicator on its surface and this part turns violet. Therefore the end-point can only be detected properly if the precipitate is allowed to settle and the supernatant solution is inspected near the end-point of the titration.

1 ml of 0.01N silver nitrate standard solution  $\equiv$  0.3546 mg of Cl, 0.7992 mg of Br or 1.2691 mg of I.

The results of some determinations for high and medium halogen contents are shown in Table I.

The halogen contents of non-standard pure samples were analysed by the modified Grote-Krekeler method.<sup>4,5</sup> Of these, hexachlorocyclopentadiene is a liquid with a low surface tension.

Absorption in ammonia can also be recommended for the analysis of substances of low and medium halogen content, because not only can the time of shaking be reduced, but also the relatively salt-free solution resulting from the removal of the excess of ammonia is favourable for any method of halide determination.

*Acknowledgement*—The authors wish to thank Prof. L. Erdey, Head of the Institute, for his interest and help in this work.

**Zusammenfassung**—Die Mikl-Pech-Schöniger Kolbenverbrennung wurde zur Analyse hochhalogener Substanzen herangezogen. Die Verbrennung wird durch Zuckerpulver erleichtert und die Verbrennungsprodukte werden in wässrigem Ammoniak absorbiert. Derart kann die Dauer des Schüttelns gekürzt werden. Die Titration der Halogenidionen wird mit Silbernitrat in Gegenwart von Variaminblau als Indikator bewerkstelligt. Wenn der Überschuss von Ammoniak nach der Verbrennung entfernt wird, kann die Titration in der an Ionen armen Lösung sehr leicht und genau durchgeführt werden.

**Résumé**—La méthode de Mikl-Pech-Schöniger a été utilisée pour l'analyse des substances fortement halogénées. La combustion est facilitée par l'addition de sucre en poudre et les produits de combustion sont absorbés dans une solution ammoniacale. De cette façon, la durée de l'agitation peut être réduite. Le titrage des halogènes peut être effectué par le nitrate d'argent en présence de bleu de variamine comme indicateur d'oxydo-réduction. Il est avantageux d'éliminer l'excès d'ammoniaque après la combustion.

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## NEW METHODS FOR THE DETERMINATION OF *p*-AMINOSALICYLIC ACID

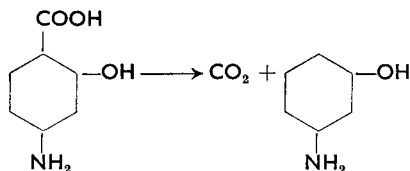
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(Received 14 August 1962)

**Summary**—In an acidic aqueous solution, *p*-aminosalicylic acid decarboxylates on boiling. The amount of carbon dioxide formed can be measured by using the simple distillation method earlier suggested by the authors. Decarboxylation also yields *m*-aminophenol and on brominating this product, tribromoresorcinol and ammonia are obtained. The quantity of ammonia formed can be measured by distillation, while the bromination reaction makes it possible to carry out a bromatometric measurement.

SINCE the discovery of the anti-tuberculosis effect of *p*-aminosalicylic acid (PAS), a number of authors have evolved methods for the determination of this compound. These determinations are based partly on acidimetric measurements in non-aqueous solutions,<sup>1-3</sup> and partly on photometric<sup>4-6</sup> or oxidimetric<sup>7-10</sup> measurements.

The methods of determination evolved by us are based, in turn, on the spontaneous decarboxylation of PAS:



In an acidic aqueous solution decarboxylation takes place quickly and quantitatively by boiling. On applying the simple distillation procedure described previously,<sup>11,12</sup> it is possible to carry out the rapid and accurate determination of PAS through the carbon dioxide formed.

On decarboxylating PAS, *m*-aminophenol forms. The determination of this latter compound presents a new possibility for the measurement of PAS. Namely, *m*-aminophenol can be brominated. However, the bromination yields a homogeneous product only when it is carried out under strictly prescribed conditions. According to our investigations, a mixed precipitate appears when bromine water is added in small portions to an acid solution of *m*-aminophenol. This precipitate is partly white and partly brownish-black. However, an entirely homogeneous precipitate is obtained on following the Koppeschaar method suggested for the determination of phenol.

Investigation of the composition of the brominated product gave surprising results. According to the authors of communications dealing with the determination of PAS based on direct bromination, tribromo-aminophenol is supposed to form.

In contrast to that, our investigations proved that no amino groups are present in the product formed on the bromination of the acid aqueous solution.

These investigations were carried out as follows. The solution of an exactly known amount of PAS was acidified with sulphuric acid and decarboxylated by boiling. On cooling the solution, it was brominated according to Koppeschaar. However, subsequent to bromination, the solution was acidified with sulphuric acid. Excess bromine was then reduced by sodium sulphite added dropwise "quasi titrated". The solution with the formed precipitate did not contain any contaminations of brownish-black colour. Subsequently, the brominated product was shaken four times with 20-ml portions of chloroform. On evaporating the chloroform extracts on a water bath, a portion of the residue was subjected to an alkaline flux and the other portion destroyed with concentrated sulphuric acid. In the alkaline flux the halogen content and in the sulphuric acid solution the eventually formed ammonia were determined. According to the determination of halogen, the product was a tribromo derivative. After the destruction by sulphuric acid, in turn, it was not possible to detect even traces of any ammonia. On measuring the content of ammonia in the aqueous phase after the extraction with chloroform, the amount of ammonia proved to be equivalent to that of the PAS taken initially. This indicates that on brominating *m*-aminophenol in an aqueous solution, the amino group splits quantitatively to form ammonia.

Accordingly, the deamination of *m*-aminophenol by bromination offers also a possibility for the determination of PAS through ammonia. In our investigations it was found that ammonia splits not only on brominating *m*-aminophenol but also on brominating PAS. However, in the latter case the quantity of liberated ammonia amounts only to about 80% of the amino group.

On isolating the product obtained in the bromination of *m*-aminophenol, it proved to be a tribromo derivative. In our opinion this bromination product is actually tribromoresorcinol which may be considered as the product of the hydrolysis of tribromo-aminophenol. It is known that on measuring resorcinol according to Koppeschaar on a 0.1-*N* scale, the titrated solution recovers its blue tint after standing for a while because of the liberation of iodine. We encountered the same experience in the case of *m*-aminophenol. However, on carrying out the bromatometric determination on a 0.05-*N* scale and allowing the solution to stand for a longer period after addition of potassium iodide, the blue colour reappears only 2–3 min after observation of the end-point.

The determination of PAS by the afore-described three measurements (of carbon dioxide, of ammonia and of the bromatometric measurement) also makes possible calculation of the quantity of decomposition products (*m*-aminophenol or eventually phenol). Therefore, for the purpose of a qualitative evaluation, we are of the opinion that it is necessary to carry out all three measurements.

## EXPERIMENTAL

### *Determination of p-Aminosalicylic Acid through the Carbon Dioxide Formed on Decarboxylation*

#### *Reagents*

0.1*N* Barium hydroxide solution (containing 5% of barium chloride) and 0.01*N* barium hydroxide solution (containing 5% of barium chloride and 30% of ethanol): These standard solutions are stored in automatic burettes equipped with soda-lime tubes. The solutions are covered by a layer of pentane.

*0.1N and 0.01N Hydrochloric acid solutions*

20% Sulphuric acid solution

1% Solution of thymol blue in ethanol

Pumice (diameter of 1.5–2.0 mm)

Pentane

*Procedure*

Weigh 0.7–1.0 g of sodium *p*-aminosalicylate dihydrate or a corresponding amount of *p*-aminosalicylic acid, wash into a 100-ml volumetric flask with distilled water (previously boiled and cooled) and make up to volume.

Fill the tube of the funnel with a stopcock of the distilling apparatus<sup>11</sup> in a bubble-free way (by sucking up boiled out and cooled distilled water from below). Transfer 40–50 ml of distilled water and 2–3 ml of sulphuric acid into the 100-ml flask of the apparatus, add 10–15 pieces of pumice, close the apparatus and start to boil. Steady boiling is attained by using electric heating, *i.e.*, a variable resistor inserted before the heating coil. When steam passes through the end of the condenser tube, continue boiling for a further 1–2 min in order to remove air and carbon dioxide from the system. Then, without interruption of boiling, attach a receiver flask with 15.00 ml of barium hydroxide solution to the apparatus, and introduce the solution to be tested into the apparatus through the funnel with stopcock, in the way already described.<sup>11</sup> During distillation, conventional cooling is applied.

After continuing distillation for 20–25 min, which period appears to be satisfactory for the complete decarboxylation of PAS and absorption of carbon dioxide, open the lower stopcock of the condenser. On lowering the level of the cooling water, the solution of barium hydroxide is removed from the condenser tube. Lower the receiver flask so that the end of the condenser tube remains just above the surface of liquid. Continue boiling for 1–2 min in order to rinse the inside of the condenser tube with the distilling water. Only suspend reheating after this operation.

After distillation, add 10 drops of thymol blue solution to the liquid in the receiver flask and titrate with 0.1N hydrochloric acid. During titration, vigorously stir the solution and add the hydrochloric acid solution dropwise. On approaching the end-point, stopper the flask periodically and shake the liquid. At the actual end-point the solution discloses a stable green tint. Subsequently, 15.00 ml of barium hydroxide is titrated in the presence of 5 ml of pentane as sealing liquid. The difference between the consumption of titrant in the two titrations is proportional to the quantity of carbon dioxide and *p*-aminosalicylic acid, respectively: 1 ml of 0.1N barium hydroxide  $\equiv$  7.656 mg of *p*-aminosalicylic acid or 10.558 mg of sodium *p*-aminosalicylate dihydrate.

On carrying out the determination on a 0.01-N scale, the operations are the same except that the conditions of titration must be prescribed more precisely. Namely, a solution of 50-ml volume is titrated. When the volume of barium hydroxide solution after distillation is below this value, it must be made up to 50 ml with boiled and cooled distilled water. For this reason, a 50-ml volume sign should be previously marked on the receiver flask. According to our experience in the case of measurements on a 0.01-N scale, a blank should also be carried out with the distillation method. During a single determination (distillation and titration) carbon dioxide corresponding to 0.1–0.2 ml of 0.01N barium hydroxide solution is introduced into the system. On operating on a 0.1-N scale, this quantity is negligible (being smaller than the drop error). Otherwise, the determination on a 0.1-N scale is carried out just as described previously in the case of operations on a 0.01-N scale.

The results of some determinations are summarised in Table I.

*Determination of p-Aminosalicylic Acid through the Formation of Ammonia**Reagents*

0.01N Hydrochloric acid

0.01N Sodium hydroxide solution

50% Sulphuric acid (ammonia free)

20% Sodium hydroxide solution

0.1N Potassium bromate solution

Potassium bromide (solid)

1.5M Sodium sulphite solution

Pumice

*Procedure*

Dissolve 0.30–0.35 g of sodium *p*-aminosalicylate dihydrate or a corresponding amount of *p*-aminosalicylic acid in a 50-ml beaker in about 20 ml of water. Neutralise the solution with sulphuric acid in the presence of 1–2 drops of methyl red indicator, then acidify with a further 1 ml of sulphuric acid. Add some pieces of pumice and boil for 15–20 min (periodically replacing the evaporating

TABLE I.—DETERMINATION OF *p*-AMINOSALICYLIC ACID THROUGH THE CARBON DIOXIDE FORMED ON DECARBOXYLATION

PAS-Na·2H <sub>2</sub> O Standard solution, g/100 ml	PAS-Na·2H <sub>2</sub> O Solution taken, ml	0·1N Ba(OH) <sub>2</sub> solution consumed, ml		PAS-Na·2H <sub>2</sub> O found		
		Single values	Mean	mg	%	
0·7987	10·06	7·55	7·55	79·70	99·2	
		7·55				
	5·01	3·73	3·74	39·48	98·7	
		3·73				
	2·00	1·48	1·49	15·73	98·5	
		1·49				
0·0914	10·06	0·01N Ba(OH) <sub>2</sub> solution consumed, ml		8·984	97·7	
		Single values				
		Mean				
		8·46				
		8·51				
		8·52				
	5·01	4·26		4·24	4·476	97·8
		4·24				
		4·23				
	2·01	1·71		1·71	1·805	98·3
		1·70				
		1·74				

water), then cool, rinse into a 100-ml volumetric flask and make up to volume with distilled water.

Transfer a 10·00-ml aliquot of the prepared solution by pipette into the 100-ml flask of the distillation apparatus, treat with 20 ml of potassium bromate solution and add 0·5 g of potassium bromide. When the potassium bromide is completely dissolved, acidify the solution with 3 ml of sulphuric acid, stir and allow to stand 20 min. After adding 4–5 ml of sodium sulphite solution and then a few pieces of pumice, boil the solution 10–15 min on an asbestos plate. When the sulphur dioxide has been removed, assemble the distillation apparatus. A 100-ml Erlenmeyer flask with 20·00 ml of 0·01N hydrochloric acid serves as receiver (the condenser outlet must reach to the bottom of the receiver). Subsequently, make the solution alkaline in the presence of a few drops of phenolphthalein by adding sodium hydroxide through the funnel equipped with stopcock, then start distillation by slow heating. When air has been removed from the system (vigorous cooling is to be applied till the termination of distillation), allow the solution to boil strongly. On distilling 10–15 ml of water (this requires about 20 min), stop the distillation and titrate the liquid in the receiver with 0·01N sodium hydroxide solution in the presence of 2 drops of methyl red indicator: 1 ml of 0·01N hydrochloric acid  $\equiv$  2·111 mg of sodium *p*-aminosalicylate dihydrate or 1·531 mg of *p*-aminosalicylic acid, respectively.

The results of our measurements are presented in Table II.

*Determination of p-Aminosalicylic Acid by the Bromatometric Measurement of  
m-Aminophenol formed during Decarboxylation*

**Reagents**

- 0·1N Potassium bromate solution
- Potassium bromide (solid)
- 0·05N Sodium thiosulphate solution
- 50% Sulphuric acid

TABLE II.—DETERMINATION OF *p*-AMINOSALICYLIC ACID THROUGH THE FORMATION OF AMMONIA

PAS-Na·2H <sub>2</sub> O Standard solution, g/100 ml	PAS-Na·2H <sub>2</sub> O Solution taken, ml	0·01N HCl consumed, ml		PAS-Na·2H <sub>2</sub> O found	
		Single	Mean	mg	%
0·3121	10·06	14·78	14·78	31·20	99·39
		14·79			
		14·76			
	5·01	7·38	7·36	15·54	99·39
		7·36			
		7·36			
2·00	2·95	2·94	15·50	99·45	
	2·93				
	2·94				

Potassium iodide (solid)

1% Starch solution: Decomposed and preserved by 0·1% of salicylic acid.

#### Procedure

Weigh 0·16–0·20 g of sodium *p*-aminosalicylate dihydrate or a corresponding amount of *p*-aminosalicylic acid and boil in a medium acidified with sulphuric acid as prescribed previously for the determination of ammonia. Rinse the solution into a 100-ml volumetric flask and make up to volume with distilled water.

Pipette a 10·00-ml portion of the prepared solution into a 100-ml Erlenmeyer flask fitted with a ground-glass stopper, then add 10·00 ml of 0·1N potassium bromate solution and 0·5 g of potassium bromide. Acidify with 3 ml of sulphuric acid, stopper the flask and gently shake the solution. Allow to stand 20 min, add about 1 g of potassium iodide, quickly restopper the flask and shake the solution again. Allow to stand 15 min, then titrate with 0·05N sodium thiosulphate solution using starch as indicator.

Carry out a blank test under similar conditions with 10·00 ml of 0·1N potassium bromate solution. The difference between the titrant consumption in the two titrations is proportional to the quantity of *p*-aminosalicylic acid present:

1 ml of 0·05N sodium thiosulphate solution  $\equiv$  1·760 mg of sodium *p*-aminosalicylate dihydrate or 1·276 mg of *p*-aminosalicylic acid, respectively.

The results of our measurements are presented in Table III.

TABLE III.—DETERMINATION OF *p*-AMINOSALICYLIC ACID BY THE BROMATOMETRIC MEASUREMENT OF *m*-AMINOPHENOL FORMED ON DECARBOXYLATION

PAS-Na·2H <sub>2</sub> O Standard solution, g/100 ml	PAS-Na·2H <sub>2</sub> O Solution taken, ml	0·05N KBrO <sub>3</sub> solution consumed, ml		PAS-Na·2H <sub>2</sub> O found	
		Single	Mean	mg	%
0·1868	10·06	10·45	10·45	18·39	97·8
		10·45			
	5·01	5·26	5·25	9·25	98·7
		5·24			
	2·00	2·10	2·10	3·69	98·9
		2·10			

In our investigations, recrystallised sodium *p*-aminosalicylate dihydrate was used. On the basis of analysis by the Kjeldahl method, it proved to be of 99·41% purity, calculated from its nitrogen content.

**Zusammenfassung**—*p*-Aminosalizylsäure decarboxyliert beim Kochen in wässriger Säure. Mittels einer früher beschriebenen Apparaturen ist es leicht möglich die gebildete Kohlensäure aufzufangen und zu messen. Die Decarboxylierung liefert *m*-Aminophenol als Zersetzungsprodukt. Durch Bromierung dieses Produktes wird Tribromresorzin und Ammoniak erhalten. Die Bromierung erlaubt eine bromatometrische Bestimmung. Das gebildete Ammoniak macht nach erfolgter Destillation eine azidimetrische Bestimmung der Paraaminosalicylsäure möglich.

**Résumé**—En solution aqueuse acide, l'acide *p*-amino salicylique perd son groupement carboxylique par ébullition. Il est possible de doser la quantité de gaz carbonique dégagée en utilisant une méthode de distillation très simple suggérée par les auteurs. La décarboxylation conduit au *m*-aminophénol. Par action du brome sur ce produit on obtient du tribromorésorcinol et de l'ammoniaque. Il est possible de doser la quantité d'ammoniaque formée par distillation, lors de l'action du brome rend possible un dosage bromatométrique.

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# ÜBER DIE BESTIMMUNG VON *p*-AMINOENZOESÄURE- *N,N*-DIÄTHYLLEUCINOLESTER-METHANSULFONAT UND SEINER ZERFALLPRODUKTE MIT TETRABUTYLAMMONIUMMETOXYD

## ANWENDUNG EINER MULTIPLIKATIONSZAHL BEI DER ANALYTISCHEN BERECHNUNG VON GEMISCHEN

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(Eingegangen am 14 August 1962)

**Zusammenfassung**—Durch Anwendung einer graphisch darstellbaren Multiplikationszahl, die auch mathematisch unterstützt werden kann, wurden auf Wege der Gemischnberechnung die gegebenenfalls vorhandenen Verunreinigungen des *p*-Aminobenzoessäure-*N,N*-diäthylleucino-lester-methansulfonat durch *p*-Aminobenzoessäure bzw. PAB und *N,N*-Diäthylleucinol-methansulfonat prozentuell berechnet. Der Methansulfosäure- und Carboxylgehalt der Verbindungen wurde in einem Dimethylformamid-Medium mit 0,05 *N* Tetrabutylammonium-metoxyd, die tertiären Stickstoffatome hingegen—nach Extraktion mittels Chloroforms—in einem  $\text{CHCl}_3\text{-(CH}_3\text{CO)}_2\text{O}$ -Medium mit 0,05 *N* Perchlorsäure bestimmt.

EINE, zur Bestimmung von binären Gemischen brauchbare Methode besteht in der gleichzeitigen Titration der funktionellen Gruppe mit identischem Charakter, die in einer, oder in beiden Komponenten enthalten ist. Aus der jeweiligen variierenden Einwägung lässt sich der theoretische Wert der Titration für jene beiden Grenzfälle berechnen, in denen die Hauptkomponente (*A*), bzw. die verunreinigende Komponente (*B*) rein anwesend sind. Der Versuchswert fällt zwischen diese beiden Grenzwerte und aus seiner Lage kann die prozentuelle Zusammensetzung des Gemisches errechnet werden.

Handelt es sich um Serienbestimmung, so ist diese Methode zu langwierig, sie kann jedoch durch Anwendung einer *Multiplikationszahl* vereinfacht werden, die von der Einwägung unabhängig ist, und lediglich eine Funktion der Äquivalenzgewichte der Komponente (*A* und *B*) darstellt.

Abb. 1 veranschaulicht den Zusammenhang des Quotienten— $E_A/E_B$ —der Äquivalenzgewichte  $E_A$  und  $E_B$  mit dem Titrationsergebnis und mit den Prozenten der Komponente *B*. Im Falle äquimolarer, binärer Gemische können die derart erhaltenen Punkt *a* und *b* mit einer Geraden verbunden werden, welche die Achse *y* bzw. *x* in einem Verhältniss von 4:1 schneidet. Der Prozentwert der Verunreinigenden Komponente *B* in äquimolaren, oder in binären Gemischen mit beliebigen Komponentverhältniss (*c,e* und *d,f*) wird gefunden, wenn man entlang der Tangent welche die Linie *Y-X* schneidet, jene prozentuelle Menge der Verunreinigung bestimmt, die den



Titrationen entspricht. Die Tangente ist, bezüglich jedes Äquivalenzgewichtsquotienten jeweils eine andere.

Der Schnittpunkt der Tangente auf Linie  $Y-X$  kann bestimmt werden, wenn man unter Berücksichtigung der theoretisch verbrauchten Milliliter des äquimolaren binären Gemisches, das prozentuelle Ergebnis der Titration, weiterhin die prozentuelle Menge der Komponente  $B$  im Gemisch berechnet. Die beiden schneiden irgendwo die Linie  $Y-X$  und dieser Schnittpunkt wird mit "100%" verbunden. Die derart erhaltene Tangente ist auf jedes Verhältniss eines binären Gemisches von gegebenen  $E_A/E_B$ -Wert anwendbar.

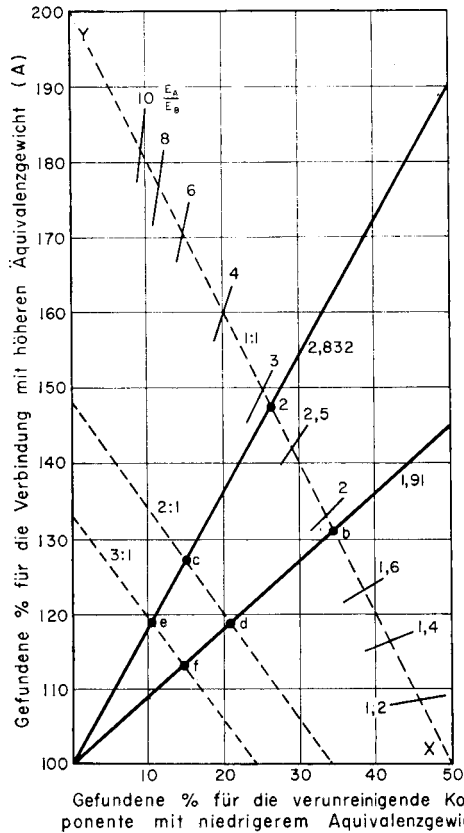


ABB. I.—Graphische Darstellung des Zusammenhanges zwischen den, mit Titration ermittelten %, dem Äquivalenzgewichtsquotienten ( $E_A/E_B$ ) der Komponente des binären Gemisches und den % der verunreinigenden Komponente ( $S_B\%$ )

Z.B. PAN-Äqu.-gewicht/PAB-Äqu.-gewicht = 2,832

PAN-Äqu.-gewicht/PAB + LEUM-Äqu.-gewicht = 1,91.

Verhältniss des Äquivalenzgewichtes: 1:1, 2:1, 3:1

Abb. 2 veranschaulicht den Zusammenhang zwischen den auf Abb. 1 dargestellten  $E_A/E_B$ -Werten und den Prozenten der Titration im Falle eines äquimolaren Verhältnisses: die Projektion der auf der Kurve liegenden Schnittpunkte auf Abb. 1 ergibt die Lage der Tangente, welche die Linie schneidet.

Obiges Verfahren lässt sich auch mathematisch unterstützen, wodurch eine einfache Formel erhalten wird:

$$S_B\% = 100 \left( \frac{t \cdot f \cdot E_A}{M \cdot J} - 1 \right) \cdot \frac{1}{\frac{E_A}{E_B} - 1}, \text{ d.h. } S_B\% = T \cdot F$$

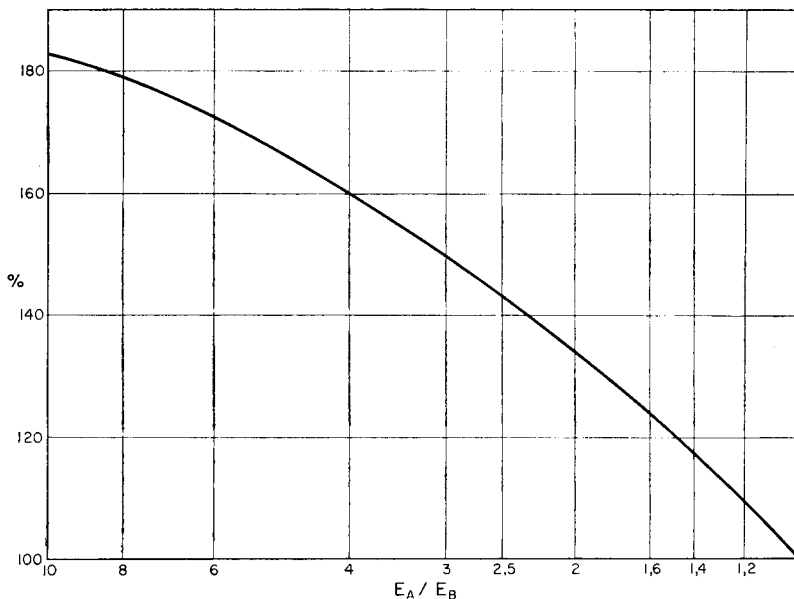


ABB. II

Es bedeuten:  $t$  die bei der Titration des Gemisches verbrauchten ml;  $f$  den Faktor der Lösung;  $M$  die Gesamtmenge des eingewogenen Gemisches in mg;  $J$  die mit dem milliäquivalenten  $A$  proportionale Messflüssigkeit;  $S_B$  die in  $B$  enthaltene, verunreinigende Komponente in %;  $T$  die Titrationsdistanz (d.h. die prozentuelle Abweichung von "100%") und schliesslich  $F$  die *Multiplikationszahl*.

Die  $B$ -Komponente äquimolarer oder binärer Gemische mit anderem Molverhältniss wird erhalten, wenn man die über "100%" erhaltene Prozente mit der  $F$ -Multiplikationszahl multipliziert.  $F$  ist in der Funktion des Äquivalenzgewichtsquotienten jeweils verschieden, muss jedoch bei einem gegebenen Verbindungspaar nur einmal errechnet werden. So beträgt z.B. im Falle von *p*-Aminobenzoesäure-*N,N*-diäthylleucinolester-methansulfonat (PAN) und der verunreinigenden *p*-Aminobenzoesäure die Multiplikationszahl—eine 0,05 N Messlösung vorausgesetzt—0,54534.\*

Die im Titel angeführte Verbindung kann mit *p*-Aminobenzoesäure (PAB) verunreinigt sein (binäres Gemisch), sie kann aber im Laufe einer Hydrolyse zerfallen, wobei neben der PAB äquimolare Mengen *N,N*-Diäthylleucinol-methansulfonat (LEUM) entstehen (ternäres Gemisch).

\* Bei Errechnung der Multiplikationszahl ist wegen  $-1$  zweckdienlich, eine fünfstelligen Logarithmus zu verwenden.

TABELLE I.—BESTIMMUNG VON GEREINIGTEN PAN MITTELS TBAM-MESSLÖSUNG

Eingewogen, mg	99,7	119,6	139,6	159,5	199,4
Gefunden, %	99,9	99,9	99,2	99,4	99,6

1 ml 0,05 N TBAM entspricht 19,42 mg PAN. Mittelwert und wahrscheinliche Fehlergrenze:  $99,6 \pm 0,2\%$ .

TABELLE II.—TITRATION VON GEREINIGTEN PAN UND BEIGEFÜGTER PAB

Gemisch, eingewogen, mg	99,7	119,6	139,5	159,5	199,4	199,4
PAB% theoretisch	1,42	1,71	1,95	1,08	1,42	0,87
PAB% gefunden	0,98	1,80	1,53	1,09	1,15	0,87

Bei der Gemischberechnung benützte Multiplikationszahl: 0,54534. Messfehler im Falle von 1–2% PAB:  $90 \pm 13$  rel. –%.

TABELLE III.—BESTIMMUNG VON HANDELSÜBLICHEN PAN (A), PAB (B), BZW. EINER VERUNREINIGUNG VON ÄQUIMOLAREM PAB UND LEUM (B + C) MITTELS TBAM-MESSLÖSUNG

PAN, eingewogen, mg	186,4	196,7	190,6	$\frac{E_A}{E_B}$	$\frac{E_A}{(E_B + E_C)}$	F
					$\frac{2}{2}$	
PAN, gefunden %	109,6	109,6	109,5			
B gefunden %	5,24	5,18	5,18	2,832		0,54534
(B + C)% gefunden	10,5	10,4	10,4		1,91	1,0965

Die Zusammensetzung der Mischung ist demnach: 89,5% PAN + 6,9% LEUM + 3,5% PAB. PAN-Molgewicht 388,5 ( $E_A = 192,4$ ); LEUM-Molgewicht 269,3 ( $E_B = 134,6$ ); PAB-Molgewicht 137,1 ( $E_C = 68,5$ ).

TABELLE IV.—TITRATION VON PAN MITTELS 0,05 N PERCHLORSÄURE

PAN gereinigt, eingewogen, mg	178,8	193,0	199,1	200,4	Mittelwert:
gefunden, %	101,4	99,0	99,6	98,3	$99,6 \pm 0,95\%$
PAN des Handels, eingewogen, mg	196,7	197,3	199,8	200,6	Mittelwert:
gefunden, %	100,1	98,8	98,4	99,2	$99,1 \pm 0,5\%$

Zwecks Bestimmung des Verhältnisses der Verunreinigungen führten wir folgende Versuche durch: 1. Gereinigtes PAN wurde in 20 ml neutralen Dimethylformamid (DMF) gelöst und in Anwesenheit von Thymolbalu mit 0,05 N benzolisch-methanolischem Tetrabutylammoniummetoxyd (TBAM) titriert. 2. Gereinigtes PAN verunreinigten wir mit 1–2% PAB und titrierten wie unter 1. 3. Handelsübliches PAN titrierten wir mit TBAM-Messlösung. 4. Nach einer Alkalisierung mit Kaliumhydrogencarbonat wurde mit Chloroform ausgeschüttelt und die Basen mit 0,05 N Perchlorsäure titriert (Tab. I–IV). Beim 2. bzw. 3. Versuch verwendeten wir folgende Multiplikationszahlen: 0,54534 bzw. 0,54534 und 1,0965.

Wird eine Hydrolyse der Titelverbindung angenommen, so sind im ternären Gemisch zwei Zeretzungsprodukte (PAB + LEUM) in äquimolarer Menge vorhanden. Die beiden Komponenten können gemeinsam als eine Verbindung betrachtet werden, die über zwei funktionelle Gruppen verfügt: über eine Methansulfosäure und eine Carboxylgruppe. Auf Grund des gemeinsamen Äquivalenzgewichtes der beiden Gruppen beträgt daher die Multiplikationszahl 1,0965.

Um entscheiden zu können, ob die untersuchte Handelsprobe 5,20% PAB enthält (Tab. III), oder aber ob neben diesem auch äquimolares LEUM zugegen ist, wurde 5 ml wässrige Lösung der Probe

mit 1 g  $\text{KHCO}_3$  alkalisch gemacht, fünfmal mit je 5 ml  $\text{CHCl}_3$  extrahiert, den vereinigten Chloroformanteilen 5 ml Essigsäureanhydrid zugesetzt und nach 20 Min. in Gegenwart von Kristallviolett, mit 0,05 *N* Perchlorsäure titriert. Die PAB wird in das Kaliumsalz umgewandelt, die in der organischen Phase befindlichen Aminogruppen der Basen von PAN und LEUM werden acetyliert und nur der in den Molekülen befindliche tertiäre Stickstoff wird titriert. Der Farbumschlag des Indikators ist sehr scharf.

Hätte die Probe des Handelsproduktes 5,20% PAB enthalten, so würde das Titrationsergebnis 95% ergeben haben. Die erhaltenen Werte lagen jedoch bei 99%, da wir die Base der Titelverbindung und das, ein geringeres Molgewicht besitzende *N,N*-Diäthylleucinol gemeinsam bestimmt hatten. Die Titration mit Perchlorsäure entschied demnach, dass beim Titrieren mit TBAM die richtige Multiplikationszahl 1,0965 ist, nicht aber 0,54534.

Nach der Titration mit TBAM und dem Ausschütteln mit  $\text{CHCl}_3$ , scheint die perchlorsäure Methode—gemeinsam angewendet—zur PAN-Bestimmung geeignet zu sein. Wird die TBAM-Methode und die Gemischberechnung herangezogen, so erhält man die Verunreinigungsprozente der Probe. Mit der Perchlorsäure Methode kann entschieden werden, ob es sich um ein binäres oder Tertiäres Gemisch handelt, weiterhin, welche von den beiden Multiplikationszahlen anzuwenden ist.

**Summary**—The impurities in *p*-aminobenzoic acid-*N,N*-diethylleucinol methane sulphonate [*p*-aminobenzoic acid (PAB) and *N,N*-diethylleucinol methane sulphonate] have been evaluated using a multiplication factor through a graphical procedure. The contents of methane sulphonic acid and of carboxylic groups have been determined in dimethylformamide medium with 0.05*N* tetrabutylammonium methoxide; the tertiary nitrogen atoms are titrated (after extraction with chloroform) in  $\text{CHCl}_3$ - $(\text{CH}_3\text{CO})_2\text{O}$  medium with 0.05*N* perchloric acid.

**Résumé**—Les impuretés se trouvant dans l'acide *p*-aminobenzoyl-*N,N*-diethylleucinol-méthane-sulfonique (acide *p*-aminobenzoiïque, PAB, et *N,N*-diethylleucinol-méthane sulfonique) ont pu être évaluées à partir de procédés graphiques en utilisant un facteur de multiplication.

La teneur en acide méthane sulfonique et en groupements carboxyliques a été déterminée dans la diméthylformamide par le méthylate de tétrabutylammonium à 0,25 *N*; les atomes d'azote tertiaire sont dosés (après extraction au chloroforme) par l'acide perchlorique à 0,05 *N* en milieu  $\text{CHCl}_3$ - $(\text{CH}_3\text{CO})_2\text{O}$ .

## ANALYTICAL CONTROL METHODS FOR POLYVITAMIN PREPARATIONS

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(Received 14 August 1962)

**Summary**—Analytical control methods for determining the vitamin contents of polyvitamin preparations are studied. With the proposed methods it is possible to determine in a sample vitamins A, B<sub>2</sub>, B<sub>6</sub> and E spectrophotometrically, vitamin K polarographically, and nicotinamide in terms of ammonia after selective hydrolysis. The new methods make the separation of vitamins unnecessary before analysis of polyvitamin preparations.

THERE is already a very extensive literature<sup>1</sup> on the analysis of vitamins. Relatively few authors have, however, dealt with the analytical control of preparations containing several vitamins and also even some drugs.<sup>2-6</sup> Almost all authors studying this theme attempted to solve the problem by separating the components and subsequently determining the various separated vitamins.<sup>7-10</sup> Because these preparations contain only minute amounts of a number of vitamins and because the majority of vitamins are rather labile compounds, quantitative separation is a difficult task involving many errors.

Thus, an attempt has been made to evolve an analytical route which makes possible the direct determination of some of the main components of polyvitamin preparations in the presence of other vitamins and accessories, or their determination after only a partial separation. In solving this problem reliance had to be placed mainly on instrumental methods of analysis, particularly on spectrophotometry and polarography.

### I—SPECTROPHOTOMETRY

The absorption spectra of the vitamins in question were established in the visible and ultraviolet regions. In addition to absorption maxima and minima, the wavelengths were also determined where light absorption of the single vitamins begins in their conventional concentration in drugs (Table I).

Spectrophotometric measurements were carried out in the case of vitamins B<sub>1</sub>, B<sub>2</sub>, B<sub>6</sub>, C, K and nicotinamide in aqueous solution, but in the case of vitamins A, E and D in chloroform solution. In the latter case, chloroform was deliberately chosen in place of other solvents suggested in literature because oily vitamin preparations are all soluble in chloroform and the vitamin content can mostly be determined directly in the chloroform solution by spectrophotometry.

As the data of Table I show, among the water-soluble vitamins, vitamin B<sub>2</sub> can be determined by spectrophotometry in the presence of all other vitamins on the basis of the maximum at 448 m $\mu$  (or at 373 m $\mu$ ). Among the fat-soluble vitamins, there is a similar possibility for the determination of vitamin A in chloroform solution, using the

TABLE I.—POINTS OF ANALYTICAL IMPORTANCE IN THE VISIBLE AND ULTRAVIOLET ABSORPTION SPECTRA OF VITAMINS

No.	Vitamin	Site of absorption maxima, $m\mu$	Site of absorption minima, $m\mu$	Light absorption begins at		Notes
				Concentration, $mg/100\ ml$	Wave-length, $m\mu$	
1	B <sub>1</sub>	263, 238	253	3	305	
2	B <sub>2</sub>	448, 373, 267	402, 305, 240			Does not depend on pH
3	B <sub>6</sub>	325, 291	310, 262	2	355	Strong dependence on pH; measurement in an aqueous solution of pH 5
4	C	262		100 100	315 290	Titrated with iodine
5	K	307, 265	290	5	365	Depends on pH; measurement in an aqueous solution of pH 5
6	Nicotinamide	272	240	1	315	
7	A	333 328		3	390	In chloroform solution In isopropanol solution
8	E	288		10	300	In chloroform solution

The absorption curves of the vitamins listed under 1–6 were established in solutions in distilled water.

maximum at 333  $m\mu$ . Further, the absorption maximum of vitamin B<sub>6</sub> at 325  $m\mu$  in aqueous solution and of vitamin E appearing at 288  $m\mu$  in chloroform solution may serve as a basis of spectrophotometric measurements. In the case of these maxima, it is still possible to eliminate the interference of other vitamins which show similar absorptions at the given wavelengths (in the case of vitamin B<sub>6</sub>: vitamins B<sub>2</sub> and K; in the case of vitamin E: vitamin A).

When carrying out measurements in aqueous solution, the effect of pH on absorption must be taken into account. The absorption spectrum of vitamin B<sub>2</sub> proved to be independent of pH in the range 2 to 7. Thus, in the knowledge of the absorption of the aqueous extract of the polyvitamin preparation measured at 488  $m\mu$  (the site of the maximum of vitamin B<sub>2</sub>), the actual content of vitamin B<sub>2</sub> can be calculated by simple multiplication (*cf.* Table II, No. 1). A further multiplication (*cf.* Table II, No. 2) yields the absorption of vitamin B<sub>2</sub> at 325  $m\mu$ , at the wavelength of the maximum of vitamin B<sub>6</sub>. In this way, it is relatively easy to eliminate the interference of vitamin B<sub>2</sub> in the determination of vitamin B<sub>6</sub>.

The determination of *vitamin B<sub>6</sub>* is, however, by far not so simple a task, because of the dependence of its absorption spectrum on pH (Fig. 1). Namely, polyvitamin preparations also generally contain substances of various pH which sometimes have buffering effects. At the site of absorption maxima, absorption values are affected not only by the pH but also by the concentration of solute (Fig. 2). Thus, even on applying an adequate buffer solution, it is not possible to obtain identical absorption values at the wavelength of maxima when investigating various preparations of identical content of vitamin B<sub>6</sub>. At the wavelength of the isosbestic point (304 mμ), measurement is impossible because vitamins B<sub>1</sub>, B<sub>2</sub>, C and K show similarly absorptions. This is why it was not possible to determine the content of vitamin B<sub>6</sub> in polyvitamin preparations by spectrophotometry.

The problem could be solved spectrophotometrically, however, by applying the

TABLE II.—MULTIPLICATION FACTORS APPLIED IN VITAMIN ANALYSIS

No.	Vitamin	Wavelength of measurement, mμ	Multiplication factor (f) Vitamin content = E . f (mg/100 ml)	Multiplication factor (F)		Solvent
				E <sub>x</sub> . F = E <sub>y</sub>	F y	
1	B <sub>2</sub>	448	3.1			water
2	B <sub>2</sub>	448		0.23	325	water
3	A	333	1900 (int. units/100 ml)			chloroform
4	A	333	0.654			chloroform
5	A	333		0.352	288	chloroform
6	E	288	21.8			chloroform

E is the value of absorption measured, x is the wavelength of measurement (mμ), and y is the wavelength (mμ) to which absorption values are calculated.

*additive method of evaluation* already well known in organic polarography. In this case, the pH of the aqueous extract of the polyvitamin preparation containing vitamin B<sub>6</sub> is adjusted to about pH 5–7, e.g. with sodium acetate buffer. Subsequent to measuring the absorption (at the site of the maximum: 325 mμ), a standard solution of known content of vitamin B<sub>6</sub> is added to the extract and the absorption is again measured. From these two measurements, taking into account the dilution as well, it is possible to calculate the content of vitamin B<sub>6</sub>.

It appears from Fig. 3 that the absorption spectrum of *vitamin K* also depends on pH. At the site of the maximum absorption of vitamin B<sub>6</sub>, the absorption curve of vitamin K discloses an abrupt section. Thus, when vitamin B<sub>6</sub> is to be determined in the presence of vitamin K (and when an adequate correction value is applied in the knowledge of the content of vitamin K from another measurement), even differences in adjustment of the slit width of the spectrophotometer may lead to appreciable errors of measurement.

Once again the problem can be solved by using the additive method of evaluation. Namely, the content of vitamin K is determined in another sample by polarography. On measuring at the site of the maximum absorption of vitamin B<sub>6</sub>, an aliquot of the test solution is mixed with a standard solution of known vitamin K content, and the measurement is repeated without any changes in adjustment of the spectrophotometer. From these two measurements, taking into account the dilution as well, it is possible to

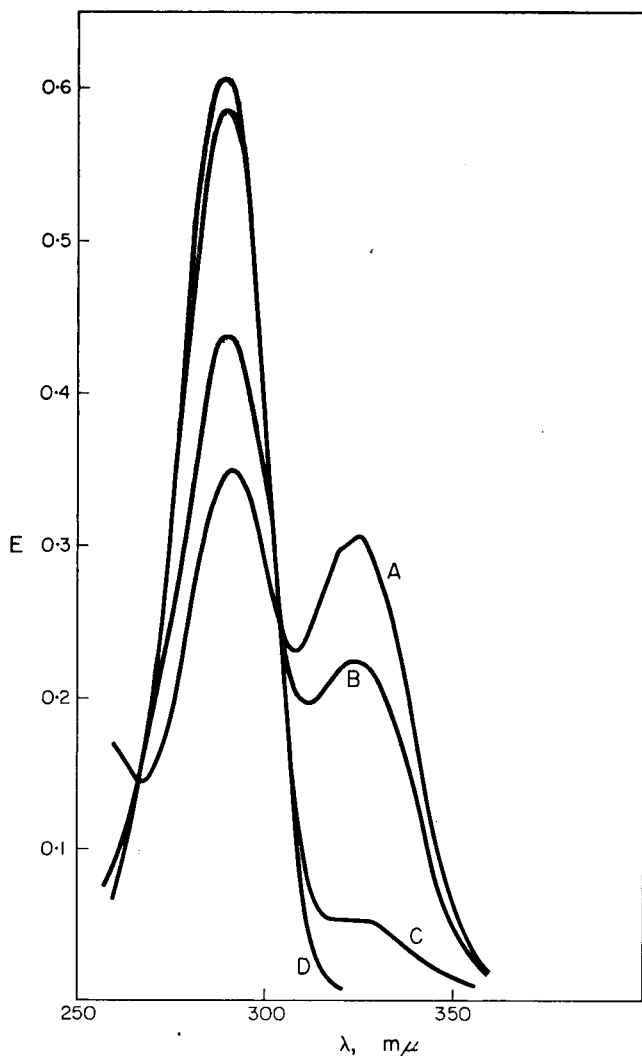


FIG. 1.—Absorption spectra of vitamin B<sub>6</sub>:

- (A). pH 5.0,
- (B). pH 4.6,
- (C). pH 3.6,
- (D). pH 2.1.

calculate at the site of the maximum of vitamin B<sub>6</sub> the absorption from the content of vitamin K present in the test solution.

By this method it is possible to determine the content of vitamin B<sub>6</sub> in polyvitamin preparations with an error of  $\pm 5\%$ , even in the presence of appreciable quantities of vitamin B<sub>2</sub> and of not more than a ten-fold amount of vitamin K (Table III). The other mentioned vitamins do not interfere with the measurement.

The prerequisite of the application of the additive method of evaluation is the validity of the Lambert-Beer law under the given conditions in the given concentration range. As it appears from the aforementioned considerations, alterations in pH or



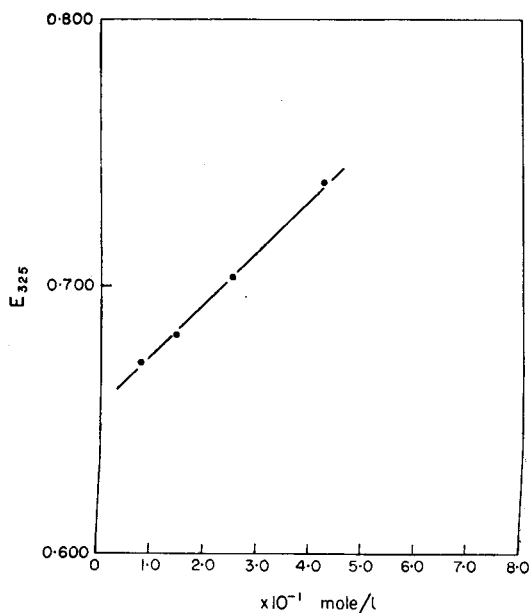
FIG. 2.—Dependence of absorption of vitamin B<sub>6</sub> on ionic strength of solution.

TABLE III

Amount of vitamin B <sub>6</sub>				Other vitamins present,	
Weighed, mg	Found, mg	$\Delta$ mg	$\Delta$ %	mg	
0.325	0.326	+0.001	+0.3	K	2.0
	0.340	+0.015	+4.6	B <sub>2</sub>	1.0
	0.322	-0.003	-0.9		
0.425	0.435	+0.010	+2.4	K	2.0
	0.425	$\pm 0.0$	$\pm 0.0$	B <sub>2</sub>	1.0
	0.430	+0.005	+1.2	B <sub>1</sub>	1.0
				C	50.0
				Nicotinamide	5.0

even in the ionic strength may be responsible for changes in absorption values. Thus, the concentration of the standard solution used for quantitative evaluation must be 10–20 times higher than that of the unknown solution in order to reduce the extent of dilution of this latter solution by the addition of the standard solution of known vitamin content.

The determination by spectrophotometry of the *fat-soluble vitamins* in chloroform solution is a simpler task. Namely, the vitamin content (Table II, Nos. 3 and 4) can be calculated from the absorption measured at the site of maximum of vitamin A (acetic ester) at 333  $m\mu$ , by one single multiplication. No other vitamin, even sunflower oil (*ol. Helianthi*) used for oily preparations, interferes with the determination.

The determination of vitamin E on the basis of the absorption measured at the maximum at 288  $m\mu$ , in turn, is greatly affected by the presence of vitamin A and

sunflower oil. However, this error can be easily corrected. By one single multiplication, the absorption of vitamin A at 288  $m\mu$  can be calculated from the absorption of vitamin A measured at 333  $m\mu$  (Table II, No. 5). Because the oily vitamin preparations contain relatively small amounts of vitamins and the absorption of sunflower oil is still low at 288  $m\mu$ , only an insignificant error is committed by considering the total weighed sample as sunflower oil for correction of the absorption of sunflower oil. In this way, only one multiplication is required to obtain the absorption of sunflower oil at 288  $m\mu$  (namely, the sunflower oil content mg/100 ml multiplied by 0.00237 =  $E_{288}$ ).

By using this method, it is possible to determine by direct spectrophotometry the

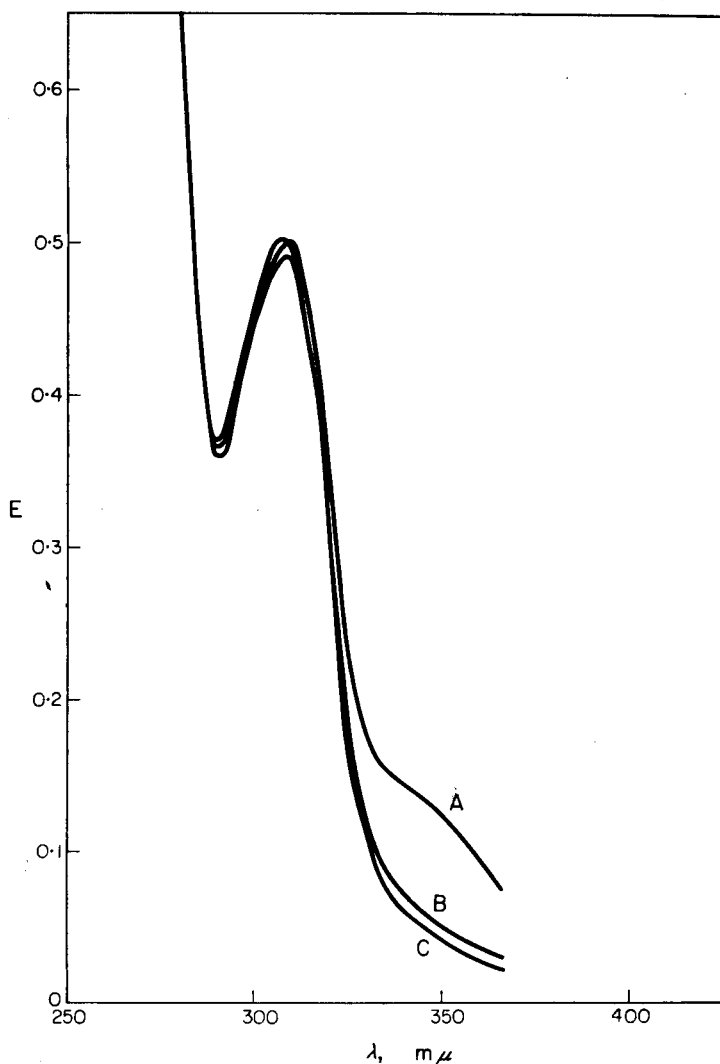


FIG. 3.—Absorption spectra of vitamin K:

- (A). pH 7.1,
- (B). pH 4.7,
- (C). pH 2.0.

vitamin content of oily preparations containing vitamins A and E, subsequent to dissolving the samples in chloroform. Thus, the cumbersome alkaline saponification and the separation by extraction<sup>11</sup> can be eliminated. At the same time, the error of determination increases only slightly, in that vitamin A can be determined with an error of  $\pm 2\%$  and vitamin E with an error of  $\pm 8\%$  (Table IV).

## II—POLAROGRAPHY

It appears from Table I that the presence of several vitamins interferes with the spectrophotometric measurement (site of maximum:  $307\text{ m}\mu$ ) of vitamin K (menaquinone sodium hydrogen sulphite). Vitamin K, in turn, interferes with the spectrophotometric determination of vitamin B<sub>6</sub>. Accordingly, determination of the content of vitamin K is a prerequisite of the measurement of vitamin B<sub>6</sub>.

A great number of polarographic methods have been evolved for the determination of compounds with vitamin K activity (with respect to the fact that these are quinones or hydroquinones). To the author's regret, the method suggested for the measurement of menaquinone sodium hydrogen sulphite,<sup>12</sup> which is very widespread because of its solubility in water, can only be used after separation of the vitamin. Thus, it was felt necessary to make a thorough investigation of this problem. The effect of pH and of the accompanying vitamins on the reduction wave of vitamin K have been established and the results will be published elsewhere in detail.<sup>13</sup> It was found in these investigations that, because of the presence of accompanying substances, the polarograms suffer a deformation to such an extent that evaluation on the basis of calibration curves becomes quite impossible. In this case the additive method of evaluation also proved to be suitable, in that vitamin K could be directly determined in the aqueous extract of a polyvitamin preparation containing ten various vitamins. The error of determinations with this method is about  $\pm 5\%$ .

## III—SELECTIVE HYDROLYSIS

Nicotinamide represents an important component of polyvitamin preparations. According to the data in the literature,<sup>1</sup> it is impossible to determine nicotinamide in the presence of other vitamins without a previous separation. Even the presence of minute amounts of other vitamins interferes with the described spectrophotometric, photometric and polarographic methods.

This problem was solved by selective hydrolysis and subsequent determination of the ammonia formed. By boiling nicotinamide with  $1M$  sulphuric acid for 1 hr under reflux,<sup>14</sup> it hydrolyses quantitatively to nicotinic acid and an equivalent amount of ammonia. On making alkaline, the ammonia content of the solution can be distilled and measured in the conventional way (1 ml of  $0.01M$  sulphuric acid  $\equiv 2.442$  mg of nicotinamide).

Under such conditions, no ammonia or any product of alkaline reaction distillable from an alkaline medium is split off from other vitamins and accompanying substances. The sole source of error in this method is that vitamin B<sub>1</sub> decomposes on boiling with alkali to an alkylamine of alkaline reaction, and thus the results of measurements will not be accurate. With respect to this fact, the solution is made alkaline after termination of the acid hydrolysis (and prior to distilling ammonia) with a borate buffer at most to pH 9.

In some preparations, vigorous foaming may take place in the distillation of ammonia because of the presence of accompanying substances of capillary activity.

Foam formation can be prevented in such cases by adding a few drops of octyl alcohol. In a polyvitamin preparation containing 10 various vitamins, on weighing nicotinamide equivalent to 5–10 ml of 0.01M sulphuric acid, the error for the method was about  $\pm 5\%$  (Table V).

#### IV—APPLICATION AND ACCURACY OF THE METHODS

The prerequisite of the application of the aforementioned spectrophotometric methods is the absence of any substance in the preparation which may show an absorption at a wavelength over 320  $\mu$ , obviously with the exception of the vitamins to be determined. The presence of the conventional agents used for granulation and tablet preparation (sucrose, lactose, talcum, gelatin, cellulose-acetophthalate, *etc.*) does not interfere with the determination. However, the coloured coatings of the tablets must previously be carefully removed. In the case of drugs which also contain other active substances in addition to vitamins, the effect of these substances on the absorption spectra of vitamins must be established in a separate test.

The content of vitamins A and E of oily preparations which completely dissolve in chloroform can be determined immediately after their dissolution.

In the case of preparations which contain some vitamins soluble in water and others soluble in fats, these vitamin types must be separated from each other. Thus, the carefully homogenised sample is stirred with 0.01M hydrochloric acid, washed into a separating funnel, shaken several times, and the suspension repeatedly shaken with adequately prepared chloroform. The chloroform phase is washed with 0.01M hydrochloric acid. The obtained aqueous and chloroform phases, respectively, are filtered and analysed.

Separation of this type is superfluous when vitamin K is determined by polarography and when nicotinamide is determined by selective hydrolysis.

For the polarographic determination of vitamin K (menaquinone sodium hydrogen sulphite), the

TABLE IV

Vitamin				$\Delta$ mg for vitamin		$\Delta\%$ for vitamin	
A	E	A	E	A	E	A	E
Weighed, mg		Found, mg					
3.50	10.0	3.45	9.40	-0.05	-0.6	-1.4	-6.0
		3.48	9.7	-0.02	-0.3	-0.6	-3.0
		3.56	10.6	+0.06	+0.60	+1.7	+6.0
1.00	5.0	0.98	4.80	-0.02	-0.20	-2.0	-4.0
		0.99	4.87	-0.01	-0.13	-1.0	-2.6
		1.01	5.30	+0.01	+0.30	+1.0	+6.0

1 mg of vitamin A = 2905 int. units

TABLE V

Nicotinamide				Other vitamins present, mg	
Weighed, mg	Found, mg	$\Delta$ mg	$\Delta\%$		
10.0	9.52	-0.48	-4.8	B <sub>1</sub>	1.0
	9.89	-0.11	-1.1	B <sub>2</sub>	1.0
	10.3	+0.3	+3.0	C	50.0
				K	2.0
20.0	20.4	+0.4	+2.0		
	20.9	+0.9	+4.5		
	19.8	-0.2	-1.0		

TABLE VI—ANALYSIS OF SOME POLYVITAMIN PREPARATIONS

Vitamins	B <sub>2</sub>		B <sub>6</sub>		K		Nicotinamide		A		E		Other vitamins present, mg
	Single measurements, mg	Mean values, mg	Single measurements, mg	Mean values, mg	Single measurements, mg	Mean values, mg	Single measurements, mg	Mean values, mg	Single measurements, mg	Mean values, mg	Single measurements, mg	Mean values, mg	
Labelled content	1.50	0.66	2.41	31.2	31.2	2.04	A	1					
	1.63	0.60	2.51	29.5	29.5	2.12	C	50					
	1.48	0.63	2.37	32.0	32.0	2.04	B <sub>12</sub>	1					
	1.53	0.62	2.42	32.1	31.2	2.06	B <sub>1</sub>	1					
	1.5	0.6	2.5	30	30	2.07		2.0					
Labelled content	1.02	3.64	50.2	B <sub>1</sub>	5								
	1.00	3.39	49.6										
	0.99	3.62	49.2										
	1.00	3.70	50.6	49.9	50								
Labelled content	1.0	3.59	50										
	1.0	4.0											
Labelled content	Int. Units												
		8010	15.8	D <sub>2</sub>	0.1								
		8070	14.7										
		7910	14.2										
Labelled content		7940	7980	15.4	15.0								
			8000	15									
Labelled content	0.51	0.26	8.09	5050	B <sub>1</sub>	0.75							
	0.52	0.23	8.01	5100	C	50							
	0.50	0.25	7.89	5020									
	0.49	0.26	8.00	4980	5040								
Labelled content	0.50	0.25	8.0	5000									

vitamin is extracted from the carefully pulverised or homogenised sample with a few ml of 0.5M potassium chloride solution. (Namely, measurement is conducted in a supporting solution of 0.5M potassium chloride.)

For the determination of nicotinamide, the pulverised and homogenised sample, respectively, can be subjected to acid hydrolysis without any particular preparation, then the amount of the ammonia formed is measured by conventional methods.

In order to establish the error of the presented methods, mixtures were prepared from doses of vitamins weighed with an analytical accuracy. These vitamins were previously controlled according to U.S.P. XV and Pharm. Hung. V and analysed according to the Merck prescriptions.<sup>1</sup> The analytical results obtained are presented in Tables III–V. Subsequently, the methods were also tested with some commercial polyvitamin preparations. Some of the results obtained are presented in Table VI.

It appears from Tables III–VI that, under the prevailing conditions, the accuracy of the suggested methods is quite satisfactory. On comparing the results with literature data, one finds that the error of the methods hardly exceeds the error involved when only one single vitamin type is determined in the same range of concentration.

#### V—INSTRUMENTS AND REAGENTS

For the spectrophotometric measurements, a Beckman DU quartz spectrophotometer and 1-cm quartz cuvettes were used. A hydrogen lamp served as the light source. The polarographic measurements were carried out with a Radiometer PO3 polarograph.

The reagents were of analytical purity. Chloroform was purified further,<sup>11</sup> and the distilled chloroform was preserved by adding 2% by volume of pentane.

**Zusammenfassung**—Analytische Kontrollmethoden zur Bestimmung des Vitamingehaltes in Multivitaminpräparaten wurde untersucht. Mittels der vorgeschlagenen Methode ist es möglich den Gehalt an Vitamin A, B<sub>2</sub>, B<sub>6</sub> und E spektrophotometrisch den an K polarographisch und den an Nikotinsäureamid auf Grund des durch Hydrolyse gebildeten Ammoniaks zu bestimmen. Die Methode macht die Trennung der Vitamine vor ihrer Bestimmung unnötig.

**Résumé**—L'auteur a étudié le contrôle analytique des préparations constituées d'un mélange de vitamines. Par les méthodes décrites il est possible de déterminer la teneur en vitamines A, B<sub>2</sub>, B<sub>6</sub> et E d'un échantillon par spectrophotométrie, la vitamine K par polarographie et la nicotinamide sous la forme d'ammoniaque après une hydrolyse sélective. Ces nouvelles méthodes rendent inutiles la séparation des vitamines avant analyse.

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## ARGON IONISATION DETECTOR IN GAS-LIQUID CHROMATOGRAPHY OF ORGANO-SILICON COMPOUNDS

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(Received 14 August 1962)

**Summary**—The feasibility and limits of applying gas-liquid chromatography to the qualitative and quantitative analysis of organosilicon compounds in a gas chromatograph equipped with an argon ionisation detector is demonstrated. Results obtained with methylchlorosilanes indicate that the instrument is unsuitable for the analysis of these compounds. However, the results permit some conclusions on the dissociation processes occurring in the ionisation space to be drawn. Relative retention data of some organosilicon compounds are established in a column containing Apiezon-M and silicone elastomer. The quantitative analysis of these compounds is feasible with the instrument. Reproducible pyrolysis chromatograms of high molecular linear and cross-linked siloxane polymers, obtained with a special pyrolysis chamber mounted on top of the column, are shown.

MUCH progress has been made in the last few decades in the chemistry of organosilicon compounds. A great number of novel reactions and compounds have been described. Because of this rapid development, reaction mechanisms, structural problems in the case of polymers as well as the effect of polymerisation conditions on reproducibility, often remained unexplained. In order to clear up these problems, sensitive analytical methods and in some cases analysis of trace components are required.

Gas chromatography was found to be a feasible analytical method for the analysis of various organosilicon compounds.<sup>1-5</sup> In the course of our work various types of organosilicon compound were investigated in a gas chromatographic apparatus equipped with an argon ionisation detector of high sensitivity.\* Informative experiments were undertaken on the basis of these findings on the application of this instrument for the analysis of organosilicon high polymers.

### METHYLCHLOROSILANES

Organic chlorosilanes form the principal monomer basis of siloxane polymers. Investigations were carried out to determine whether the Pye-Argon chromatograph is suitable for the analysis of methylchlorosilanes. The following compounds may be present in the raw product of their synthesis:  $\text{SiCl}_4$  (in the following referred to as Q),  $(\text{CH}_3)_3\text{SiCl}$  (M),  $(\text{CH}_3)_2\text{SiCl}_2$  (D),  $\text{CH}_3\text{SiCl}_3$  (T),  $\text{SiHCl}_3$  and  $\text{CH}_3\text{SiHCl}_2$ .

The experiments to be described were carried out using a specially purified Argon gas† as carrier gas. The glass column belonging to the apparatus was packed with "Celite for gas chromatography 80-120 mesh"‡, containing 10% of dioctyl phthalate

\* Argon Chromatograph, W. G. Pye & Co. Ltd., Cambridge, England.

† "F Argon" (Egyesült Izzólámpa és Villamossági RT).

‡ British Drug Houses Ltd., Poole, Dorset, England.

as stationary phase. The temperature regulator of the equipment was not used, and column temperature thus varied between 20 and 25°. On account of the high hydrolysis rate of the introduced samples, the mixture was sealed in glass capillaries, according to the method of Joklik,<sup>6</sup> and the capillaries were broken while constantly flushing the breaking device with argon. Less than 1 mg of silane could be weighed this way. Measurements were carried out at a flow rate of 30-40 ml of argon/min.

Some characteristic chromatograms are shown in Fig. 1.

As revealed by the chromatograms, the sensitivity of the instrument to the individual chlorosilanes varies within a wide range, and is low even in the case of the most readily detectable (M). The chromatograms were selected with the aim of illustrating this fact. Besides the comparison of the chromatograms in Fig. 1, this becomes also

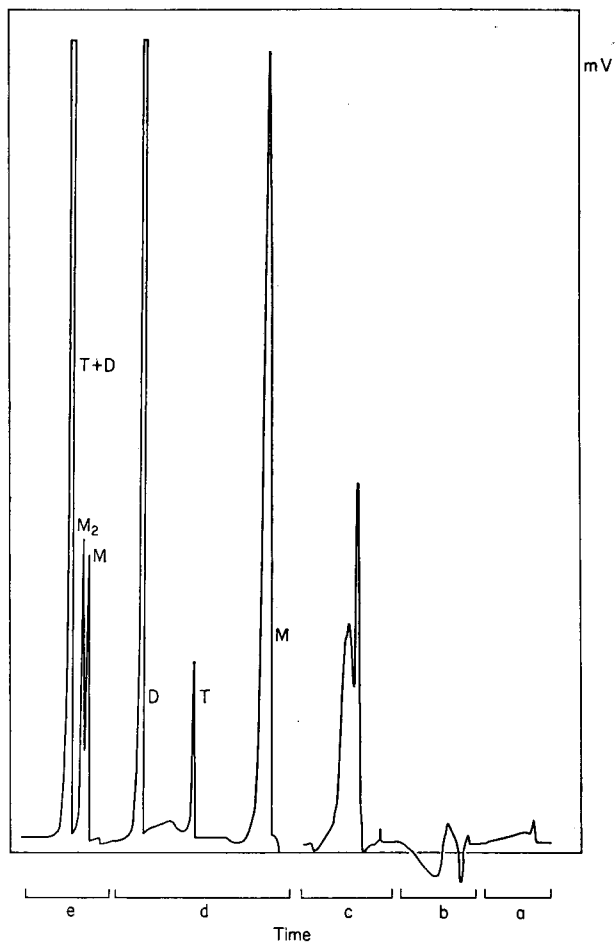


FIG. 1.—Gas chromatograms of methylchlorosilanes obtained on a column packed with Celite containing 10% dioctyl phthalate:

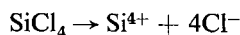
- (a) Q; sample of less than 1 mg; detector voltage: 1000 V;
- (b) Q; sample of a few mg; detector voltage: 1000 V;
- (c) Q; sample of less than 1 mg; detector voltage: 2000 V;
- (d) M, T, D; samples of less than 1 mg; detector voltage: 1250 V;
- (e) Equimolecular Q-M-T-D mixture of about 1 mg; detector voltage: 1500 V.



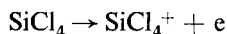
evident from the occurrence of a hexamethyldisiloxane ( $M_2$ ) peak of the same height as the peak for  $M$  in  $Q$ - $M$ - $T$ - $D$  mixtures. This peak is to be attributed to a contamination—formed by hydrolysis—of the  $M$  component of the mixture. Its presence in the pure monomer is not detectable by a detector working on the principle of thermal conductivity. The total insensitivity of the detector to  $Q$  is especially evident from the figure.

The following explanation is suggested to account for the observed phenomenon. As indicated by Lovelock,<sup>7</sup> some chloro compounds have a very high affinity for free electrons, ion-recombination therefore occurs in their presence with the electrons produced by the ionisation of argon, which reduces the sensibility of their detection.

No complete dissociation takes place as a consequence of collisions between  $\text{SiCl}_4$  molecules and excited Ar atoms, the dissociation energy of the process:

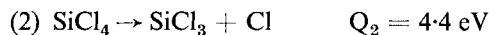
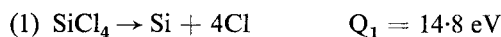


being 97 eV and the excitation potential value of Ar 11.6 eV. The process



also appears improbable on account of the symmetry and the stable electron configuration of the  $\text{SiCl}_4$  molecule.

Moreover, considering the following data:<sup>8</sup>

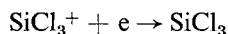


it is reasonable to suppose that collision with the excited Ar atoms proceeds according to the scheme:

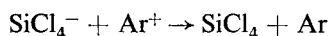


It is easy to understand that the energy requirement of process (2) is higher than  $\frac{1}{4}$  of the energy required for total dissociation. Just the opposite is valid for the ionisation process, and thus a process involving the splitting of one  $\text{Cl}^-$  and proceeding at an ionisation potential less than  $97/4 = 24$  eV, appears to be most likely.

In view, however, of the electron capturing disposition of chlorine compounds, which may also lead to negative molecule-ion formation (in our case  $\text{SiCl}_4 + e \rightarrow \text{SiCl}_4^-$  is also possible), the recombination process



lowering the sensitivity, should also be taken into account. Considering further the possibility of  $\text{SiCl}_4^-$  molecule-ion formation, and the fact that the rate of ion recombination between positive and negative molecule ions is by  $10^5$  to  $10^8$  orders of magnitudes higher than that of electron and positive ion recombination, the possibility of the process



has to be definitely reckoned with. This latter causes a decrease in the standing ionisation current from the carrier gas and, when occurring alone, results in a negative deviation on the chromatogram. As easily understood, this phenomenon is met on the shown diagrams in the case of substantial samples and low detector potentials.

The gradually increasing sensitivity to methylchlorosilanes of lower functionality and the simultaneous insensitivity relative to the  $M_2$  peak, for example, are easily explained on the basis of the above considerations.

A further study did not seem to be justified in view of this problem, because the high sensitivity of the apparatus cannot be utilised in the analysis of the compounds in question.

#### LOW MOLECULAR WEIGHT POLYMERS AND METHYLETHOXYSILANES

Investigations were carried out on the utilisability of the Pye-Argon chromatograph for the analysis of other organic silicon compounds. Thus, linear and cyclic polymers of low molecular weight and methylethoxysilanes were assayed. Ten % Apiezon M and a devolatilised linear siloxane polymer (the Hungarian product HV-Au-120, mol.wt. 59000) were used as stationary liquids on the same support material and column as above. Samples were introduced with the 0.025-0.1  $\mu$ l pipette, furnished with the apparatus, using the following operating conditions: cell voltage: 1000 V; argon flow rate: 20-25 ml/min. Results obtained are summarised in Table I.

TABLE I

Column temperature, °C: Stationary liquid:	Relative retention time			
	75° APM	100° APM	100° Silicone	150° Silicone
	Low molecular siloxane polymers $t_{RX}/t_{RD_4}$			
$M_2^*$	0.12	0.14		
$D_3$	0.29	0.30	0.30	0.29
$M_2D$	0.45	0.50		
$D_4$	1.00	1.00	1.00	1.00
$M_2D_2$	1.71			
	Methylethoxysilanes $t_{RX}/t_{RT}$			
$M_{ethox}$		0.20		
$D_{ethox}$		0.45		
$T_{ethox}$		1.00		
$Q_{ethox}$		1.90		

\*  $D_3$  = hexamethylcyclotrisiloxane,  $D_4$  = octamethylcyclotetrasiloxane,  $M_2D$  = octamethyl-trisiloxane,  $M_2D_2$  = decamethyltetrasiloxane. Similarly, as in the case of methylchlorosiloxanes, the symbols of methylethoxysilanes indicate functionality, the functional group in this case being "ethoxy" instead of "chloride".

The following data are given in addition to Table I:

$D_4$ specific retention volume <sup>9</sup>	$V_g = 147$ ml 100° (APM 10%)
$D_4$ specific retention volume	$V_g = 300$ ml 75° (APM 10%)
$CH_3Si(OC_2H_5)_3$ retention volume	$V_g = 78$ ml 100° (APM 10%)

The quantitative analytical results obtainable with the help of this measuring device were, according to our experiments both in the case of cyclical polymers and methylethoxysilanes, of a well reproducible character. Peak-areas were determined by planimetric methods.

The quality of the material had some influence on the sensitivity of the detector even in the case of the investigated compounds; the use of standard curves was, therefore, essential for quantitative purposes.

## MICROPYROLYTIC-GAS CHROMATOGRAPHIC TECHNIQUE

The rapid development and the widespread use of gas chromatography as an analytical tool arises from the fact that it can be applied nowadays practically to all mixtures, the components of which can be vaporised up to 350° without decomposition. In addition, the gas chromatographic analysis of pyrolysis products of high molecular substances offers the possibility of identifying natural and synthetic resins of low volatility as well as the determination of their purity and structure.<sup>10</sup> According to the method, the sample is subjected to flash pyrolysis in a pyrolysis-chamber, located at the top of the column. Volatile pyrolysis products are swept into the column by the carrier gas stream for qualitative and possibly quantitative analysis.

It is very likely that useful results are to be expected from the application of this method to siloxane polymers, and primarily so in the identification and in the control of the reproducibility of cross-linked polymers (resins). Experiments carried out so far are considered as preliminary experiments.

The pyrolysis-chamber, fitted on the chromatographic column as illustrated in Fig. 2\*, may be dismantled at plane grinding A assembled with a clamping spring.

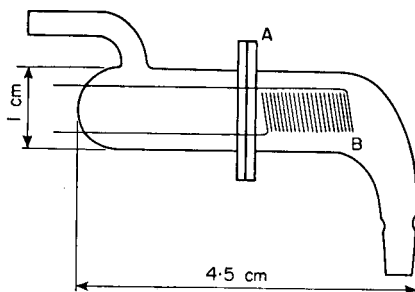


FIG. 2.—Pyrolysis chamber.

The platinum wire coil B can be heated to about 600-700° by an accumulator battery. The sample, generally dissolved in an appropriate solvent, may be dripped directly on the coil or alternatively it may be slid into the coil in a small, thin walled silica tube. The bulk of the solvent is removed by gently heating the coil prior to the fitting of the chamber on the column. The residual traces of the solvent are removed from the sample after the assembling of head and column by similar heating in an argon stream. The complete removal of the solvent is indicated by the detector. The coil was heated generally for 2 sec. Before introduction of the next sample, the coil was heated for a substantial period in an argon stream to remove traces of the preceding sample.

Operating conditions in the case of linear polymers were as follows: column and solid support were the same as mentioned earlier, containing 10% Apiezon-M; detector voltage: 1000 V; column temperature: 100°; argon flow rate: 20 to 30 ml/min. The wire coil was heated for varying periods with a current of 3.1 A. The sample was applied in these experiments in a solvent-free state on the coil.

When comparing the pyrolysis chromatograms of the three linear methylsiloxane polymers (mol. wt. 217,000, 425,400 and 775,200, respectively), results completely similar to that shown in Fig. 3 were obtained.

\* The authors wish to express their thanks to Mr. Oszkár Nagy for the preparation of the chamber.

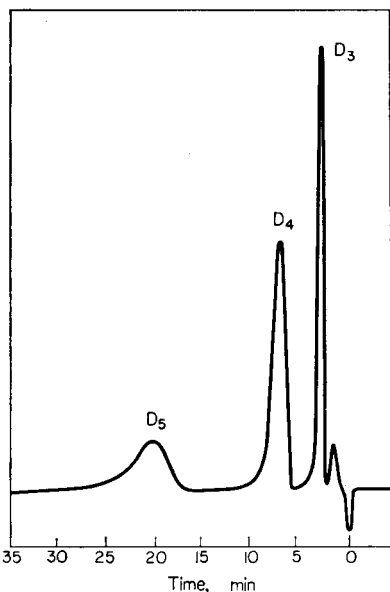


FIG. 3.—Pyrolysis chromatogram of a linear siloxane polymer.

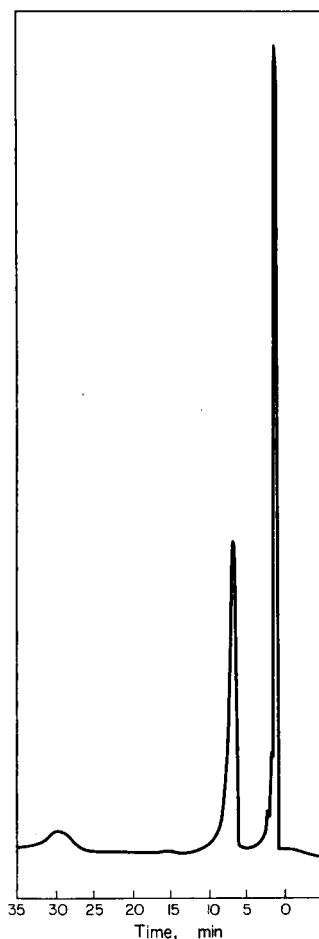


FIG. 4.—Pyrolysis chromatogram of a cross-linked siloxane polymer.

In conformity with data in the literature, no splitting of C—H and C—Si bonds was observed.<sup>11</sup> The characteristic peaks occurring on the chromatogram correspond, on the basis of the retention volumes determined earlier, to D<sub>3</sub>, D<sub>4</sub> and D<sub>5</sub>. Independently of the quantity and the molecular weight of the sample, D<sub>4</sub> is represented by about 45% in the pyrolysis products. With the decrease in height of the D<sub>4</sub> peak, which is to be considered according to previous findings as a measure of the quantity of the sample, the quantity of D<sub>3</sub> is increased at the expense of D<sub>5</sub>. The quantity of the sample may be substantially reduced. The method will most probably furnish this way more characteristic relations of another type concerning the relative quantities and possibly also the qualities of the pyrolysis products.

The investigations of cross-linked siloxane polymers were carried out in solutions. Our aim was to determine those conditions that lead to qualitative reproducibility of pyrolysis chromatograms. The chromatogram of the resin shown in Fig. 4 is readily reproduced under the applied conditions. These were as follows: column and solid support as before, containing 10% linear siloxane polymer as stationary phase;

detector voltage: 1750 V; argon flow rate: 30 ml/min; column temperature: 50°; the same coil as in the pyrolysis of the linear polymers, heated with a current of 3.1 A for 2 sec. The pyrolysis chromatograms of the 20% solution of cross-linked methylsiloxane polymers in butyl acetate is qualitatively identical with that shown in Fig. 4, independently of the  $\text{CH}_3/\text{Si}$  ratio of the sample.

The identification of the peaks occurring on the chromatogram has not yet been attempted, because it was thought expedient first to obtain more characteristic chromatograms of higher resolution by varying the stationary phases and the conditions of pyrolysis.

**Zusammenfassung**—Eignung und Begrenzung der Anwendung von Gas-Flüssigkeit-Chromatographie zur qualitativen und quantitativen Bestimmung von organischen Siliziumverbindungen in einem mit einem Argondetektor ausgerüsteten Gaschromatographen werden untersucht. Ergebnisse mit Methylchlorosilanen zeigen, dass das Instrument für diese Art von Analysen ungeeignet ist. Die Ergebnisse gestatten jedoch einige Rückschlüsse auf die im Ionisationsraum statthabenden Dissoziationsvorgänge. Relative Retentionszeiten für einige Verbindungen werden für eine Apiezon M-Siliconelastomer enthaltende Säule mitgeteilt. Quantitative Bestimmungen sind möglich. Reproduzierbare Pyrolysechromatogramme von hochmolekularen, linearen und polymerisierten Siloxanen werden mittels einer speziellen vor die Säule geschalteten Pyrolysekammer erhalten.

**Résumé**—Possibilités et limites de l'application de la chromatographie gaz-liquide à l'analyse qualitative et au dosage des composés organosiliciens dans un chromatographe muni d'un détecteur à argon. Les résultats obtenus avec le méthylchlorosilane montrent que l'appareil ne convient pas à l'analyse de ces composés.

Cependant on peut établir quelques conclusions relatives aux procédés de dissociation dans l'espace d'ionisation. Les constantes de rétention de quelques composés organosiliciens dans une colonne garnie d'Apiezon-M et d'élastomère siliconé ont été établies. Le dosage est alors possible. Quelques chromatogrammes reproductibles de pyrolyse de siloxanes à haut poids moléculaire et à liaisons transversales ont pu être effectués par addition d'une chambre de pyrolyse spéciale montée au sommet de la colonne.

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## A GENERAL PAPER CHROMATOGRAPHIC METHOD FOR ORIENTATIVE QUALITATIVE ANALYSIS

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(Received 14 August 1962)

**Summary**—One drop of a solution of the unknown substance in hydrochloric acid is run by the ascending method on paper with ethanol-hydrochloric acid-water as solvent for about 20 hr at room temperature. Subsequently, the strip is sprayed with a 0.2% solution of morin in ethanol. The chromatogram is viewed after drying in this "acid" state and again after treatment with ammonia vapours, both in reflected and in transmitted sunlight and ultraviolet light. From the appearance, shade of colour, fluorescence and location of the spots visible under different circumstances, conclusions can be drawn as to the composition of the sample.

PAPER chromatography, since its adaptation for inorganic analysis, has been used primarily for the simultaneous identification of elements in their mixtures, for the selective isolation of some elements from such mixtures, and for the separation of higher and lower valency forms of the same element.<sup>1,7</sup>

Research work has already been carried out<sup>2,3,4</sup> with the aim of developing a paper chromatographic method for the separation, within a group, of ions belonging to the same analytical group. Retention factors for 24 cations in several different solvents were reported by Pollard and coworkers,<sup>5</sup> who differentiated between detection reagents for individual elements and those suitable for groups of elements.

In the vast literature on paper chromatography,<sup>1,6</sup> several procedures have been published for the separation and the determination of 2 or 3 elements. No method has, however, so far been developed, which permits determination of the composition of an unknown multicomponent mixture on the basis of a chromatogram prepared by using a single solvent and a single detection reagent. Ethanol-hydrochloric acid-water was found to be a suitable solvent for the paper chromatographic analysis of multicomponent mixtures. On a paper strip, run with ethanol-hydrochloric acid-water, the individual elements travelled different distances.

Morin was found to be a very satisfactory reagent for producing visible spots, because it forms fluorescent spots with some of the elements and dark spots with others. Fluorescence viewed under ultraviolet light and the different shades of dark colours viewed in sunlight may also be influenced by treatment with ammonia vapours. Thus, for example, the green fluorescence of minute quantities of indium and beryllium may be detected only after treatment with ammonia. The black spot of manganese appears also only under similar conditions.

### EXPERIMENTAL

#### Reagents

Ethanol (96%)

Concentrated hydrochloric acid (sp. gr. 1.19)

Morin (3,5,7,2',4'-pentahydroxyflavone)

Salts of analytical grade quality

### Procedure

A solution in hydrochloric acid, concentrated as far as possible and boiled with a few drops of hydrogen peroxide, is used for the analysis. Obviously, this solution cannot contain elements of the hydrogen chloride group, tungsten and earth acids. Iron, chromium, manganese and cerium will now be present as  $\text{Fe}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Mn}^{\text{II}}$  and  $\text{Ce}^{\text{III}}$ . A few  $\mu\text{l}$  of the solution or sufficient portions to give a total of 10–20  $\mu\text{g}$  of the metals, are applied to the starting line of a Schleicher-Schüll No. 2043/A paper strip, about 30 cm long. After drying the strip in a current of air, the chromatogram is run with a solvent mixture of 75% by volume of ethanol, 20% by volume of conc. hydrochloric acid and 5% by volume of water, by the ascending method at room temperature overnight. Subsequently, the strip is removed from the solvent when the front has travelled a distance of 20–22 cm from the starting line. The distance of the solvent front is marked on the paper, the strip dried under an infrared lamp and sprayed with a 0.2% solution of morin in 96% ethanol. The paper is viewed before and after spraying, in sunlight and then under an ultraviolet lamp. Any spots observed are marked. The paper is then introduced into the vapour space over concentrated ammonia solution, when the morin acquires a vivid yellow colour. When the paper is viewed again, any dark, light or fluorescent spots, appearing under ultraviolet light, are marked on the other side of the paper. The location of possible coloured spots (Co, Fe, Ti, Mo) is observed also in sunlight before and after spraying. From the colouration, fluorescence, formation of dark spots and the shade of these spots and their  $R_f$  values, observed on these five occasions, the presence of single ions can be ascertained. The absence of certain elements can also be established, or rather the limiting quantity up to which they may be present.

### DISCUSSION

Table I contains for 42 elements the smallest quantity which may be definitely detected under the defined conditions; also the character of the spots and the  $R_f$  values at which they appear when chromatographed by the described method. It should be mentioned, however, that the limits of detection contained in the table have a strict validity only if no other cations are present in the sample solution.

In the analysis of mixtures, the limits of detection shown in the table may be increased by 1 to 2 orders of magnitude in unfavourable cases.

It can be seen that the simultaneous presence of Zr, rare earth metals, Ni, Mn, Al, Ti, U, In, Be, Mo, Sb, Sn, Fe and Ga may easily be detected. The presence of Th can be stated definitely only if the mixture does not contain Zr. The rare earth metals cannot be separated either from one another or from the fluorescent yttrium, which migrates only by an  $R_f$  value of 0.01 to 0.02 farther than the rare earth metals. Similarly, neither can Sc-Al, Ni-Cr<sup>III</sup>, Cu-U, Bi-Pd and Sn-Zn be separated. Ni-Mn-Al, Cr<sup>III</sup>-Al, Ni-Al-Co, Sb-Pd, Sb-Sn, Sb-Bi, Li-Rh, Au-Pd-Zn and Cd-Ga are separable. Co and V cannot be identified when Ti is present in substantial quantities. The method is unsuitable for the identification of Na, K, Rb, Cs, Mg and Ca if numerous other metal ions are also present. To provide for an infallible identification of ions having an  $R_f$  value higher than 0.8 and migrating close to the front of the solvent, it is advisable to use a paper strip which has been run previously in the same solvent. In this way, metal ion contaminants of the paper, primarily iron, are washed out. The chromatogram proper is run only to a distance such that its front should not reach the height of the previous iron-contaminated front, which has been developed in the washing of the paper. The solvent travels at a somewhat higher rate on such paper, as compared to unwashed paper.

The developed, still moist chromatogram is expediently viewed before and after spraying in both reflected and transmitted sunlight. The strip sprayed with morin is viewed appropriately also under ultraviolet light, both by reflection and by transmission.

If the sample to be tested is insoluble in hydrochloric acid, it must be fused with alkali. It is advisable to apply spots of both the aqueous extract neutralised with hydrochloric acid and of the solution in hydrochloric acid of the precipitate formed.

TABLE I—SMALLEST QUANTITY OF ELEMENTS DETECTABLE BY THE PRESCRIBED METHOD, IN THE ORDER OF INCREASING  $R_f$  VALUES (REACTION WITH MORIN).

$R_f$	Element	Smallest detectable quantity, $\mu g$	Sprayed with 0.2% morin solution in ethanol			
			Sunlight	UV light	After $NH_3$ vapour treatment	
					Sunlight	UV light
0.00	Ba	—	—	—	—	—
	Zr	1.5	Y	G fl	Y i	G fl p
	Sr	10	—	p K	—	p G fl
	Th	0.3	Y G	G fl	Y	G fl p
	K	2	—	—	—	d
	Ce	0.2	—	—	B Y	d
	La	0.4	—	p G fl	Y Gy	d
	Na	—	—	—	—	Gy B
	Y	—	Y	fl	Y Gy	G fl
	0.10	Ca	1	—	K	—
	Cs	—	—	—	Y	d
0.20						
	Cr <sup>III</sup>	2	high quant.: Y	p d	Y	d
	Rb	—	—	?	—	l fl?
	Ni	0.07	high quant.: Y	low quant.: —	—	d
	Mg	0.4	—	G	—	G fl
0.30	Mn	0.2	—	—	high quant.: Y	i d
	Sc	—	Y	G fl	Y	G fl
	Al	0.02	Y	G fl	Y	G fl
	Co	0.1	K	d	K	d p
0.40	V	0.4	Y	d	B	d i
	Ti	0.04	R	B d	R	B d
	Rh	—	—	—	—	d
	Li	0.7	—	1	—	G fl



TABLE I—(contd.)

R <sub>f</sub>	Element	Smallest detectable quantity, $\mu\text{g}$	Sprayed with 0.2% morin solution in ethanol			
			Sunlight	UV light	After NH <sub>3</sub> vapour treatment	
					Sunlight	UV light
0.50	U Cu	3 0.2	high quant.: B Y	low quant.: — B d	p B B	B d d
0.60	In  Be Se	0.3  0.2	high quant.: Y  —	high quant.: p G fl  low quant.: —  —	high quant.: Y  —	G fl  G fl  —
0.70	Mo	0.15	B	d B	B	B d p
0.80	Te Bi Pt Pd		— — — B	— — d d	— Y — Y	— G y d d p
0.90	Sb Sn Hg <sup>II</sup> Au Zn Fe <sup>III</sup>  Cd Ga	0.5 4   1 1  2 0.06	Y Y — W — Gy G  — l	G fl G fl — l — d  — G fl	Y Y — W — B  — l	G fl p G fl — l G fl d  l fl G fl
1.00	Tl <sup>III</sup>		—	—	—	—

d = dark

l = light

p = pale and/or fading

i = intense or becoming more intense

fl = fluorescent

G = green or greenish

Y = yellow or yellowish

R = red or reddish

B = brown or brownish

Gy = grey or greyish

K = blue or bluish

W = white

Depending on the amount of sodium chloride, sodium appears as a darkish spot, extending up to  $R_f = 0.25$ , which can be identified only tentatively under ultraviolet light. The centre of smaller sodium chloride spots is located at  $R_f = 0.09$ . The presence of sodium does not interfere in the detection of other definitely identifiable ions in the same  $R_f$  range. When carrying out the test, the possible presence of constituents, such as germanium, which may volatilise when boiling with hydrochloric acid or when drying the paper strip, must naturally be taken into consideration.

The described procedure, though simple and using a readily available solvent and a single detecting reagent, has a high resolution. It has the further advantage that the chromatogram may be developed overnight, and thus gives rapid results.

**Zusammenfassung**—Ein Tropfen Lösung der unbekanntes Substanz in Salzsäure wird an Schleicher-Schüll Papier Nr. 2043/A mit Äthanol-konz. HCl-Wasser (75:20:5) für etwa 20 Stunden bei Zimmertemperatur absteigend chromatographiert. Anschliesse wird mit einer 0.2% igen Lösung von Morin in Äthanol behandelt und das Chromatogramm nach Trocknen im "sauren Zustand" und nach Räuchern mit Amminakdämpfen im reflektierten und durchscheinenden Sonnen- und U.V.-Licht betrachtet. Aussehen, Farbe, Fluoreszenz und Lage der Flecken unter den verschiedenen Bedingungen erlaubt Rückschluss auf die Zusammensetzung der Probe.

**Résumé**—Une goutte de la solution inconnue dans l'acide chlorhydrique est traitée par chromatographie ascendante sur du papier Schleicher-Schüll No. 2043/A avec un mélange d'éthanol, d'acide chlorhydrique concentré et d'eau dans les proportions 75:20:5 pendant 20 heures environ à la température ordinaire. On pulvérise sur la bande de papier, après développement, une solution à 0,2% de morin dans l'éthanol. Le chromatogramme, après séchage, et après un traitement par les vapeurs d'ammoniac est observé par réflexion et par transmission à la lumière du soleil et d'une lampe à rayons ultra-violets. D'après l'aspect, la teinte, la fluorescence et la position des spots visibles dans différents cas il est possible de tirer des conclusions sur la composition de l'échantillon.

#### REFERENCES

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- <sup>2</sup> F. H. Burstall, G. R. Davies, R. P. Linstead and R. A. Wells, *J. Chem. Soc.*, 1950, 516.
- <sup>3</sup> W. J. Frierson and M. J. Ammons, *J. Chem. Educ.*, 1950, 27, 37.
- <sup>4</sup> J. G. Surak and D. P. Schluetr, *ibid.*, 1952, 29, 144; J. G. Surak, N. Leffler and R. Martinovich, *ibid.*, 1953, 30, 20.
- <sup>5</sup> F. H. Pollard, J. F. W. McOmie and I. I. M. Elbeih, *J. Chem. Soc.*, 1951, 466, 470.
- <sup>6</sup> I. I. M. Elbeih and M. A. Abou-Elnaga, *Chemist-Analyst*, 1958, 47, 59.
- <sup>7</sup> A. Schneer and M. Ördögh, *J. Chromatography*, 1960, 4, 319.

## INORGANIC CHROMATOGRAPHIC INVESTIGATIONS IN A GLACIAL ACETIC ACID MEDIUM

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Museum körút 4/b, Hungary

(Received 14 August 1962)

**Summary**—The solubility of several salts in glacial acetic acid is determined. It has been found that on an alumina column, the glacial acetic acid sequence of chromatography, in order of increasing elution, is:  $\text{Pb}^{\text{II}}$ – $\text{Cd}^{\text{II}}$ – $\text{Cu}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Hg}^{\text{II}}$ – $\text{Ca}^{\text{II}}$ – $\text{Fe}^{\text{III}}$ ,  $\text{Zn}^{\text{II}}$ . Subsequent to chromatography, the iodometric determination of iron in the presence of copper has been carried out with a negative error not exceeding 3.5%.

SYSTEMATIC investigations of inorganic chromatography were first carried out by Schwab and coworkers,<sup>1</sup> who attempted to separate ions using alumina, on the basis of the methods of organic chromatography. This attempt was successful. Although partly by a mechanism other than that expected, ion exchange and hydrolysis also occurred in addition to adsorption. Subsequently, inorganic column chromatography developed in three different directions: (1) use of new adsorbents,<sup>2</sup> (2) chromatography of complexes (both inorganic and chelate complexes), and (3) investigations carried out in non-aqueous media.<sup>3</sup>

In order to elucidate the processes which take place on alumina during chromatography, and to carry out some separations on a micro scale, it appeared practical to follow method 3. The first solvent examined by us was glacial acetic acid, an easily purifiable liquid of not too high vapour pressure at room temperature.

Literature data in respect of the solubilities of inorganic substances in glacial acetic acid are rather scarce. Therefore, the solubilities of some salts required in our investigations were determined first. Glacial acetic acid was purified partly by freezing out and partly by distillation. Saturation was carried out by shaking for 30–60 min in an ultrathermostat. Subsequently, the salt content was determined by a chemical method on a sample withdrawn from the saturated solution and diluted to an adequate extent. Our results are presented in Table I.

In the light of this knowledge of the solubilities, chromatographic investigations were carried out.

Alumina of grade Brockmann III served as an adsorbent. A column of 1-cm diameter and of 15-cm length was prepared from a suspension of alumina in glacial acetic acid. The location of the single ions was established by transferring pairs of ions to the top of the column, eluting with glacial acetic acid, and detecting the ions in the eluate. The methods used for detection are summarised in Table II.

The sequence of the binding of ions established in our present investigations is given in Table III. This sequence differs essentially from that observed by Schwab<sup>1</sup> and Sacconi<sup>4</sup> in an aqueous medium, and by Lister<sup>3</sup> in a dioxane medium. Not only the sequence of bivalent metals proved to be different, but also iron was bound only weakly, quite in contrast to earlier experiences. This is obviously caused by the fact

TABLE I—SOLUBILITY OF SOME SALTS IN GLACIAL ACETIC ACID

Salt	Method of determination	Solubility, g/litre		
		25°C	30°C	35°C
AgNO <sub>3</sub>	Volhard	2.40	2.29	1.98
CH <sub>3</sub> COOAg	Volhard	2.80	1.23	1.27
Pb(NO <sub>3</sub> ) <sub>2</sub>	Complexometry	4.90		
(CH <sub>3</sub> COO) <sub>2</sub> Pb	Complexometry	788	713	678
Hg <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	Volhard	1.72	2.26	2.45
HgCl <sub>2</sub>	Volhard	1.99	0.72	0.39
(CH <sub>3</sub> COO) <sub>2</sub> Hg	Volhard	183	178	177
Cu(NO <sub>3</sub> ) <sub>2</sub>	Iodometry	71.9	83.5	104
(CH <sub>3</sub> COO) <sub>2</sub> Cu	Iodometry	2.10	3.09	6.73
(CH <sub>3</sub> COO) <sub>2</sub> Cd	Complexometry	165	212	235
CoCl <sub>2</sub>	Complexometry	1.80	1.52	1.03
ZnCl <sub>2</sub>	Complexometry	209	262	282
FeCl <sub>3</sub>	Permanganometry	185	189	192
CoCl <sub>2</sub>	Complexometry	135	146	176
Co(NO <sub>3</sub> ) <sub>2</sub>	Complexometry	83.9	117	147
BaCl <sub>2</sub>	Gravimetry	0.24	0.29	0.41

TABLE II

Ion	Method of detection
Fe <sup>III</sup>	KSCN
Cu <sup>II</sup>	K <sub>4</sub> [Fe(CN) <sub>6</sub> ]
Co <sup>II</sup>	KSCN
	KNO <sub>2</sub>
Cd <sup>II</sup>	H <sub>2</sub> S
Ca <sup>II</sup>	(NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
Pb <sup>II</sup>	H <sub>2</sub> S
Zn <sup>II</sup>	Radioactive zinc
Hg <sup>II</sup>	Diphenylcarbazide

TABLE III—SEQUENCE OF IONS IN A GLACIAL ACETIC ACID MEDIUM IN ORDER OF INCREASING ELUTION

Pb <sup>II</sup>
Cd <sup>II</sup>
Cu <sup>II</sup> Co <sup>II</sup> Hg <sup>II</sup>
Ca <sup>II</sup>
Fe <sup>III</sup> Zn <sup>II</sup>

that, while in an aqueous medium the trivalent and multivalent metals are bound mainly by hydrolytic processes,<sup>5</sup> in our experiments in a non-aqueous medium an acetato-complex was formed. Because this complex is unable to precipitate in the glacial acid medium, it appears at the bottom of the column.

The quantitative determination of iron in the presence of copper was attempted by the above described method of separation. Measurements were carried out by iodometry and the results are presented in Table IV. As proved by the values presented, it

TABLE IV—DETERMINATION OF IRON IN THE PRESENCE OF COPPER

Fe <sup>III</sup> taken, g	Cu present, g	Fe <sup>III</sup> found, g	Deviation	
			mg	%
0.00928	0.02	0.00902	-0.26	-2.8
0.01857	0.02	0.01803	-0.54	-2.9
0.04298	0.02	0.04220	-0.78	-1.8
0.0860	0.02	0.0835	-2.5	-2.9
0.00928	0.40	0.00895	-0.35	-3.5
0.01857	0.40	0.01790	-0.67	-3.6
0.04298	0.40	0.04210	-0.88	-2.1
0.0860	0.40	0.0840	-2.0	-2.3

is possible to carry out the determination of iron, in general, within an error limit of 3.5%. The negative nature of the deviations is probably caused by adsorption.

**Zusammenfassung**—Die Löslichkeit verschiedener Salze in Eisessig wurde bestimmt. Es wurde gefunden, dass an einer Aluminiumoxydsäule in Eisessig die Folge der Chromatogramme folgende ist: Pb(II)-Cd(II)-Cu(II), Co(II), Hg(II)-Ca(II)-Fe(III), Zn(II). Anschliessend an die Chromatographie ergab die iodometrische Bestimmung von Eisen in Gegenwart von Kupfer einen negativen Fehler, der 3.5% nicht überschritt.

**Résumé**—Les auteurs ont déterminé la solubilité de plusieurs sels dans l'acide acétique anhydre. Ils ont montré que sur une colonne d'alumine l'ordre d'éluion par l'acide acétique anhydre est le suivant: Pb(II)-Cd(II)-Cu(II), Co(II), Hg(II)-Ca(II)-Fe(III), Zn(II). A la suite d'une chromatographie, le dosage iodométrique du fer en présence de cuivre a été effectué avec une erreur par défaut inférieure à 3,5%.

## REFERENCES

- <sup>1</sup> G. Schwab and K. Jockers, *Naturwissenschaften*, 1937, **25**, 44; *Z. für angew. Chemie*, 1937, **50**, 546.
- <sup>2</sup> K. M. Olshanova and K. V. Oshmutov, *Zh. anal. Khim.*, 1953, **8**, 211.
- <sup>3</sup> B. A. J. Lister, *Disc. Faraday Soc.* No. 7, 1949, 237.
- <sup>4</sup> L. Sacconi, *Gazetta Chimica Italiana*, 1948, **78**, 583.
- <sup>5</sup> V. V. Rachinskii and T. B. Gapon, *Khromatografiya v biologii Moskva*, 1953, 134.

## NOTICES

(Material for this section should be sent directly to the Associate Editor)

The International Centre for Authentic Chemical Substances, functioning under the authority of the World Health Organisation, is responsible for the collection, storage and international distribution of chemical reference substances. Recently the number of substances available from the Centre has been increased by the addition of a set of 13 substances intended for checking instruments and methods for determining melting points.

The set of *WHO Melting Point Reference Substances* is as follows:—azobenzene (69°), vanillin (83°), benzil (96°), acetanilide (116°), phenacetin (136°), benzanilide (165°), sulphanilamide (166°), salophen (192°), sulphapyridine (193°), dicyandiamide (210°), saccharin (229°), caffeine (237°), phenolphthalein (263°).

Also available from the Centre are the following *Authentic Chemical Substances* of pharmaceutical importance (size of package indicated):—chloramphenicol (0.3 g), digitoxoside (0.05 g), ergometrine maleate (0.02 g), melarsen (1.0 g), oestrone (0.03 g), progesterone (0.065 g), tubocurarine chloride (0.03 g), vitamin-A acetate (5 capsules each containing 0.25 g of a solution in cottonseed oil containing 0.0344 g of vitamin-A acetate/g of solution: this represents 100,000 I.U./g).

These substances are sent free of charge to national administrations or laboratories and institutes working on a non-profit basis. Commercial laboratories are charged U.S. \$10.00 (or equivalent in other currencies) for a set of WHO Melting Point Reference Substances and U.S. \$4.00 per package of the other substances.

Orders should be sent to WHO International Centre for Authentic Chemical Substances, Apotekens kontrollaboratorium, Box 30019, Stockholm 30, Sweden.

### AUSTRALIA

*Monday–Friday 20–24 January 1964: Thirty-Seventh Congress of Australian and New Zealand Association for Advancement of Science.* Canberra, Australia.

Section B of the Congress is devoted to Chemistry, and amongst other fields research papers are invited on *Analytical Chemistry*. Authors intending to read papers at the Congress are asked to submit titles not later than 1 June, 1963. Further information may be obtained from the Joint Secretaries, Section B, A.N.Z.A.A.S., Department of Chemistry, School of General Studies, Australian National University, P.O. BOX 197, Canberra City, Australia.

### HUNGARY

*May (end) 1963: Symposium on Analytical Use of Ion Exchange Resins: Association of Hungarian Chemists.* Tihany, Lake Balaton.

For details write to Dr. J. INCZÉDY, Institute for General Chemistry, Technical University, Budapest XI, Gellért tér 4, Hungary.

### UNITED KINGDOM

At the *Annual General Meeting* of the Midlands Section, Society for Analytical Chemistry, Thursday, 28 March, 1963, the following Officers of the Section were elected for the forthcoming year:—

*Chairman:* Mr. W. H. STEPHENSON

*Vice-Chairman:* Mr. W. T. ELWELL

*Secretary:* Mr. M. L. RICHARDSON, J. and E. Sturge Ltd., Lifford Lane, Kings Norton, Birmingham.

*Treasurer:* Mr. F. C. J. POULTON

*Asst. Secretary:* Mr. R. ADKINS

## Notices

### **British Standards Institution announces the following New British Standards:**

*B.S. 1428: Microchemical apparatus: Part L 1: 1963: Micro-extraction apparatus.* This specifies and includes fully dimensioned drawings for a liquid-solid extraction apparatus employing percolation and consisting of the following parts: (a) flask (pear-shaped or round), (b) extraction chamber, (c) drip junction, and (d) extraction thimble (in 2 sizes). An appropriate type of condenser and alternative sizes of thimble are also recommended. (Price 3s.)

*B.S. 1748: Methods for the analysis of copper alloys: Part 9: 1963: Determination of zinc.* This lists reagents required and describes recommended methods of sampling and test procedures for the determination of zinc contents from 0.01 to 10%. (Price 4s.)

The following Revised British Standards are announced:

*B.S. 903: Methods of testing vulcanised rubber: Part B 15: 1963: Determination of manganese.* This gives details of reagents and procedure (replaces Section 8.3 of B.S. 903: 1950). (Price 3s.)

*B.S. 1428: Microchemical apparatus: Part D 2: 1963: Washout pipettes.* This specifies 5 sizes of pipette from 0.1 to 3 ml in capacity. Full dimensions are given, but the only one listed as mandatory is the internal diameter of the capillary portion, the remainder being included for the guidance of manufacturers. The approved methods of determining capacity and delivery time of these pipettes are described in an appendix. (Price 4s.)

*B.S. 1428: Microchemical apparatus: Part D 4: 1963: Capillary pipettes.* This specifies 3 sizes (0.1, 0.2 and 0.5 ml) of graduated pipettes each calibrated for delivery and for content, 4 sizes (0.005 to 0.05 ml) of one-mark pipettes and 2 sizes (0.1 and 0.2 ml) of two-mark pipettes. It specifies construction, graduations, tolerances and inscriptions. Also it gives full dimensions, all of which are mandatory except for the overall lengths of the pipettes which are recommended for the guidance of the manufacturers. (Price 4s.6d.)

*B.S. 1752: 1963: Laboratory sintered or fritted filters.* This specifies quality, pore size and permeability requirements for filters made of materials such as glass, silica, ceramics, metals, platinum sponge and plastics. It defines 8 grades of filter by maximum pore size up to 500  $\mu$ , and includes a method for determining acceptable maximum pore size and uniformity of pore size for each grade. Also it assesses permeability in terms of liquid and gas flow, and gives theoretical information on the determination of pore diameter and permeability. This revised edition supersedes B.S. 1969. (Price 6s.)

The following Amendment Slip is announced:

*B.S. 1673: Methods of testing raw rubber and unvulcanised compounded rubber: Part 2: 1954: Methods of chemical analysis. Amendment No. 4: PD 4796.* (Price 2s.)

## UNITED STATES OF AMERICA

*Monday-Friday 10-14 June 1963: Annual Symposium on Molecular Structure and Spectroscopy.* Ohio State University, Columbus, Ohio.

The tentative programme is as follows:

*Monday—Discussion of Lasers*

*Tuesday—Theory of Molecules*

*Wednesday—Triple Commission on Spectroscopy*

*Thursday—Electronic Band Spectra*

*Friday—Solid State Spectroscopy*

Throughout the week the mornings will be devoted to invited papers and the afternoons to contributed papers. Further information may be obtained from H. H. NIELSEN, Department of Physics, Ohio State University, 174 West 18th Avenue, Columbus 10, Ohio, U.S.A.

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*Tuesday-Friday 18-21 June 1963: Fourth Biennial ISA International Gas Chromatography Symposium.* Michigan State University, East Lansing, Mich.

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*Wednesday-Friday 19-21 June 1963: Summer Symposium on Metal Complexes in Analytical Chemistry: American Chemical Society, Division of Analytical Chemistry.* University of Arizona, Tucson, Arizona.

The programme is as follows:

*Wednesday Morning, 19 June*

*Kinetic Factors in Chelometric Titrations with Visual End-Points.*  
*Photometric Titrations as a Means to Increase Selectivity of Chelometry.*  
*Polyelectrolyte-Metal Ligand Complexes.*  
*Gas Phase Chromatographic Separation of Metal Complexes.*

C. N. REILLEY

H. FLASCHKA  
 K. J. LIU and H. P. GREGOR

R. E. SIEVERS

*Wednesday Afternoon, 19 June*

*Application of EDTA to Analysis of Non-Ferrous Materials.*  
*Role of Chelating Agents in Ferrous Analysis.*  
*Inhibition of Metalloenzymes by Chelating Agents.*  
*Chelates in Radio and Nuclear Chemistry.*

G. J. ABEL, JR., L. W. ANDERSON  
 and K. C. BRAUN

J. HAGUE  
 B. L. VALLEE  
 H. L. FINSTON

*Thursday Morning, 20 June*

*Chemistry and Analytical Applications of the vic-Dioximes.*  
*Some New Organic Analytical Reagents for Metals.*  
*Complexes and Complexing Agents in Inorganic Analysis.*

C. V. BANKS  
 R. BELCHER

P. W. WEST

*Thursday Afternoon, 20 June*

*New Chelating Agents which are S- and P-Donors.*  
*Electrochemical Behaviour of Metal Chelates.*  
*Metal Chelates of 8-Mercaptoquinoline.*

G. SCHWARZENBACH  
 R. L. PECOK  
 A. CORSINI, Q. FERNANDO and  
 H. FREISER

*Friday Morning, 21 June*

*Extraction of Metal Ions with Chelating Acids.*  
*Some Variables in the Solvent Extraction of Metal Chelates.*  
*Chemical Principles in the Extraction of Elements with 1,1,1-Trifluoro-2,3-thenoylacetone.*

D. DYRSSEN

G. K. SCHWEITZER

O. MENIS

Further information may be obtained from Professor H. FREISER, University of Arizona, Tucson, Arizona, U.S.A.

*Sunday-Friday 23-28 June 1963: Symposium on X-Ray and Electron Probe Analysis at Annual Meeting of A.S.T.M. Chalfonte-Haddon Hall, Atlantic City, N.J.*

Amongst the **Gordon Research Conferences for 1963**, the following may be of interest to analytical chemists. Further information may be obtained from W. GEORGE PARKS, Director of Gordon Research Conferences, University of Rhode Island, Kingston, Rhode Island.

**Conference on Instrumentation**

*Monday-Friday 12-16 August 1963. Colby Junior College, New London, New Hampshire. The programme includes:*

*Computer-Controlled X-Ray Diffractometer.*  
*Applications of the Laser to Instrumentation.*  
*Instruments for Atomic Absorption Spectroscopy.*  
*Neutron Capture Gamma Ray Analysis.*

H. COLE  
 G. F. SMITH  
 J. B. WILLIS  
 R. GREENWOOD



### Conference on Ion Exchange

Monday–Friday 19–23 August 1963. Kimball Union Academy, Meriden, New Hampshire. The programme is as follows:

#### Monday, 19 August—Reactions

*Cation Exchange from Concentrated Electrolyte Solutions.*

*Uptake of Electrolytes: Site Sharing.*

*Thermal Effects in Ion Exchange Equilibria.*

R. M. DIAMOND, K. A. KRAUS  
and F. NELSON

R. E. MEEKER

G. E. BOYD

#### Tuesday, 20 August—Membranes

*Influence of Inhomogeneity on Permeability of Ion Exchange Membranes.*

*Ion Transport across Membranes.*

*Transport in Ion Exchange Membranes.*

*Ion Exchange Fuel Cells.*

E. GLUECKAUF

B. C. DUNCAN

P. MEARES

W. A. MCRÆ

#### Wednesday, 21 August—Applications

*Kinetic and Mechanistic Aspects of Benzene Alkylation.*

*Kinetics of Ion Exchange Catalysis.*

*Inorganic Materials for Disposal of Radioactive Wastes.*

*Bile Acid Sequestrants.*

V. J. FRILETTE and W. O. HAAG

F. HELFFERICH

B. L. BAKER

F. J. WOLF

#### Thursday, 22 August—Structures

*Experience with Scavenger Resins.*

*Selective Ion Exchange on Chelating Polymers.*

Business Meeting: Report of Nomenclature Committee.

*Ligand Exchange.*

G. J. DE JONG

E. A. TOMIC

H. F. WALTON

#### Friday, 23 August—Structures (continued)

*Inorganic Ion Exchangers.*

*Nature, Behaviour and Use of Molten Ion Exchangers.*

A. CLEARFIELD

E. C. FREILING

### Conference on Analytical Chemistry

Monday–Friday 26–30 August 1963: New Hampton School, New Hampton, New Hampshire. The programme is as follows:

#### Monday, 26 August

*Atomic Absorption Spectroscopy.*

*Practical Aspects of Gas Chromatography.*

J. W. ROBINSON

R. S. JUVET

#### Tuesday, 27 August

*Polarography in Non-Aqueous Solvents.*

*Polarography of Organic Compounds.*

*Organic Functional Group Analysis.*

W. B. SCHAAP

S. WAWZONEK

J. S. FRITZ

#### Wednesday, 28 August

*Nuclear Magnetic Resonance.*

*Electron Paramagnetic Resonance.*

*Attenuated Total Reflectance.*

E. G. BRAME, JR.

L. H. PIETTE

D. R. JOHNSON

#### Thursday, 29 August

*Complexes.*

*Open Session.*

H. A. FLASCHKA

#### Friday, 30 August

*Reaction Kinetics in Analysis.*

W. J. BLAEDEL

*Wednesday–Friday 16–18 October 1963: Tenth National Vacuum Symposium: American Vacuum Society.* Statler Hilton Hotel, Boston, Mass.

The Programme Committee solicits contributed papers on all phases of vacuum technology from those who have new and original work to report, and particularly on:

- (a) Production and measurement of high and ultrahigh vacuum.
- (b) Surface phenomena at low pressures including friction, lubrication, sorption and permeation processes.
- (c) Structure and properties of thin films as related to their conditions of formation by evaporation and spluttering at low pressures.
- (d) Vacuum techniques related to space simulation, freeze drying and other vacuum processes.

Abstracts of papers must be submitted, by 15 June, to G. H. BANCROFT, 398 Kilbourn Road, Rochester 18, New York.

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*Monday–Wednesday 21–23 October 1963: Eleventh Detroit Anachem Conference: Association of Analytical Chemists.* McGregor Memorial Conference Centre, Wayne State University, Detroit, Mich.

The Conference will feature symposia in many fields of analytical interest. The *Detroit Section of the Optical Society of America* is sponsoring symposia on *Optical and X-Ray Spectroscopy*. Contributed papers are welcomed, and abstracts should be sent to Mr. C. M. GAMBRILL or Dr. A. G. GASSMANN, Ethyl Corporation, 1600 West 8 Mile Road, Detroit 20, Mich.

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## ERRATA—VOLUME 10

*Page 81, reference 13:* this should read *C. B. Belcher, unpublished results.*

*Page 316, fourth line of first paragraph:* this should read . . . *Recently Doležal and Novák . . .*

*Page 319, reference 5:* this should read *J. Doležal and J. Novák, Chem. Listy, 1958, 52, 582.*

## PAPERS RECEIVED

---

- Analysis of mixtures of mono and dialkyl orthophosphates:** R. B. LEW, H. GARD and F. JAKOB. (22 February 1963).
- The air-oxidation of vanadium<sup>IV</sup> in alkaline solution:** G. A. DEAN and J. F. HERRINGSHAW. (2 March 1963).
- The determination of traces of cobalt in samples of platinum by neutron-activation analysis:** D. F. C. MORRIS and R. A. KILLICK. (5 March 1963).
- The determination of traces of iron in samples of platinum by neutron-activation analysis:** D. F. C. MORRIS and R. A. KILLICK. (5 March 1963).
- The direct polarography of aluminium:** I. TALESNICK and JOHN A. PAGE. (8 March 1963).
- Thermogravimetric analyses of some interaction products of 1,2,3-benzotriazole hydrochloride with certain negative cyano-complexes of the transition metals:** R. F. WILSON and G. HENRY JR. (9 March 1963).
- Determination of nickel in high-purity niobium, tantalum, molybdenum and tungsten metals by chloroform extraction of nickel<sup>II</sup> dimethylglyoximate:** ELSIE M. PENNER and W. R. INMAN. (11 March 1963).
- Sorption of ferroin on silica and its analytical use:** F. VYDRA and M. MARKOVA. (11 March 1963).
- Bisdiacetylmonoxime-ethylenediimine and bisdiacetyl-monoxime-*o*-phenylenediimine as new gravimetric reagents for nickel and palladium:** N. K. MATHUR and C. K. NARANG. (14 March 1963).
- Coprecipitation of microgram amounts of beryllium and thorium with organic reagents:** K. SUDHALATHA. (14 March 1963).
- The effect of isotope abundances on neutron absorptiometry technique:** R. S. BRAMAN. (15 March 1963).
- Application de certains acides hydroxamiques dans la chimie analytique. III. Analyse spectrophotométrique et application analytique de la réaction de vanadium<sup>V</sup> avec l'acide thiopène-2-hydroxamique (ATH):** JERZY MINCZEWSKI and ZOFIA SKORKO-TRYBULA. (19 March 1963).
- Determination of impurities in the pure rare earths by radioactivation analysis:** TOSHI KAWASHIMA. (21 March 1963).
- International comparison of analytical methods for nuclear materials—I: Accuracy and precision of some techniques in routine trace analysis:** G. B. COOK, M. B. A. CRESPI and J. MINCZEWSKI. (21 March 1963).
- Absorptiometric determination of niobium with 4-(2-pyridylazo)-resorcinol as reagent:** R. BELCHER, T. V. RAMAKRISHNA and T. S. WEST. (26 March 1963).

## SOLUBILITIES OF INORGANIC AND ORGANIC COMPOUNDS

### Volume I, Part I.

Edited by H. STEPHEN and T. STEPHEN

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