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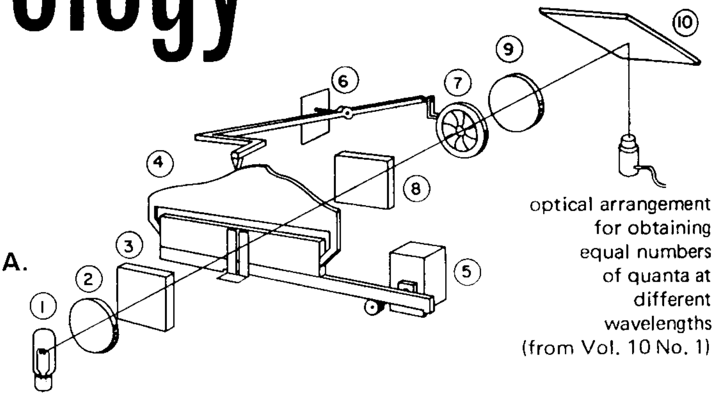

optical arrangement
for obtaining
equal numbers
of quanta at
different
wavelengths
(from Vol. 10 No. 1)

This is an established journal concerned with every aspect of photochemistry and photobiology. Its especial interests lie in the fields of the photochemistry of biological materials and related substances, the action of infrared, visible and ultraviolet light on biological systems, and particularly with the quantum aspects of these subjects.

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Talanta

An International Journal of Analytical Chemistry

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Aims and Scope

Established as a medium for the rapid publication of papers dealing with all aspects of analytical chemistry, *Talanta* is the natural vehicle for the international communication of progress in this field. As an international journal, its papers are expected to be of a very high standard and to make definite contributions to the subject: they must be new publications. Papers may be written in English, Frenc or German; all papers have abstracts in these three languages and also in Russian. Special importanc is attached to work dealing with the principles of analytical chemistry in which experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields or of hitherto widely scattered material are considered for publication, but should be critical. Original paper short communications and reviews are refereed in the normal manner. Preliminary communications ar refereed urgently and accorded priority in publication. Correspondence of interest to analytical chemis is welcomed by the Editor-in-Chief, at whose discretion it is published. A new feature is Annotations, which are critical commentaries on some aspect of analytical chemistry and deal with topics such as sources of error, or the scope and limitations of methods and techniques; these commentaries are refereed.

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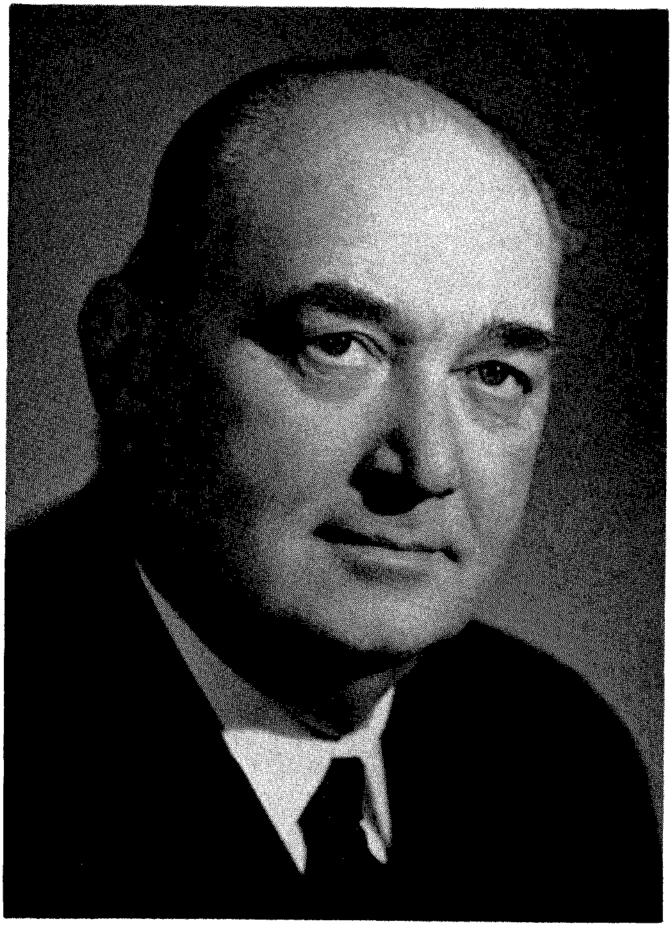

L. ERDEY

Talanta, 1970, Vol. 17, p. 1141. Pergamon Press. Printed in Northern Ireland

PROFESSOR L. ERDEY

A FEW DAYS after celebrating his sixtieth birthday, Professor Laszlo Erdey died after a heart attack on the 21st of February 1970.

L. Erdey was born on the 12th of February 1910, in the Hungarian town of Szeged. During his grammar school years he won the annual national contest for students in physics. He studied then at the P. Pazmdny (now L. Eötvös) University of Budapest and graduated in 1933 in chemistry, physics and mathematics. Working as a demonstrator and assistant lecturer he obtained his Ph.D. from the same University in 1938. In 1942 he joined the Municipal Chemical and Food Testing Institute of Budapest, and worked also as a part-time lecturer, later as a senior lecturer at the University. In 1949 he was appointed as Head of the Institute of General Chemistry at the Technical University of Budapest, became a full Professor in 1950 and held this post up to his death. He served as Dean of the Faculty of Chemical Engineering at the same University from 1950 to 1953. He was elected as a corresponding member of the Hungarian Academy of Sciences in 1951, and became a full member (Fellow) in 1955. He was a member of several Hungarian and International Chemical Societies. He was a member of the Analytical Committee of the International Union of Pure and Applied Chemistry and served on the Advisory Board of *Talanta* since the journal was started. He was also the Editor-in-Chief of the *Journal of Thermal Analysis* and Regional Editor of the *Journal of Radioanalytical Chemistry.*

He was twice awarded (1951 and 1958) the Kossuth Prize, which is the highest award in Hungary for cultural and professional activities. Among other Hungarian distinctions he was awarded the Golden Degree of the Work Order on his sixtieth birthday by the Hungarian authorities. He was also awarded the Hanus medal of the Czechoslovak Chemical Society.

With his research team in the Institute of General Chemistry at the Technical University of Budapest, which at one time had more than thirty graduate members, L. Erdey did research in almost all branches of analytical chemistry. First he dealt with ascorbinometric titrations, with redox and chemiluminescent indicators, gravimetric analysis and thermal analysis. He later worked also on electroanalytical methods including polarography, organic analysis, spectroscopy, gas chromatography, trace analysis and radiochemical analysis and published more than 500 papers; his textbook on *Quantitative Analysis* and *Volumetric Analysis* (now in their 10th Edition) are widely used by Hungarian-speaking chemists. His main work, *Gravimetric Analysis,* in three volumes, giving both a theoretical treatment of the subject and a critical survey of carefully selected and experimentally tested methods was published in Hungarian, German and English.

His death means a great loss to his friends, younger and older students and co-workers and to analytical chemistry in general.

GYULA SVEHLA

Talanta, 1970, Vol. 17, p. 1142. Pergamon Press. Printed in Northern Ireland

PROFESSOR LASZLO ERDEY

ONE of the penalties of later middle age is the gradual loss of one's friends. In time one learns to accept the inevitability with philosophy, but when a very special friend departs, particularly when it is unexpected, grief seems to have no bounds; the poignant memories flood in and there is not one road left to escape the torment of the spirit:

> "Give sorrow tears,
> The grief that does not speak,
> Whispers the o'erfraught heart."

But Laci Erdey would not have wanted us to mourn him for long and would rather that we remembered the many good times we all had together. I shall not speak of him as a scientist, nor of his massive contributions to his chosen field, for these are well known and, in any event, have been adequately covered in other obituaries. Instead I will pay tribute to Laci as a friend—the best of friends.

I first met Laci in Lisbon, at the 1956 IUPAC Congress. He was with that other great Hungarian chemist, the late Professor Schulek. At this time I also met, for the first time, R. Přibil and G. Schwarzenbach. All the forementioned, together with H. Flaschka, F. Feigl and C. L. Wilson took supper together. I sat next to Laci and this began our much too short friendship.

He was kind, charming, modest, humorous and highly cultivated. He loved his country beyond measure and took great pride in its achievements. He taught others to think in a like vein and to admire Hungarian contributions to science, medicine art, literature and music. It was always a pleasure to hear him talk on Hungarian wines. Nevertheless, Laci was no chauvinist; he loved Hungary, but in a framework of European culture of which it is part, and like myself felt at home in any country in Europe. Perhaps this represents the most rational way of thinking; to feel part of what one regards as a great unified structure, yet to cherish and maintain the individual character of each of its component parts.

Laci had had to take care of his health for some years after a bad heart attack in Moscow. Yet up to the moment of his death, he felt well and was full of ideas and plans for the future, never thinking that they would never be fulfilled. Perhaps the way of Laci's going is to be envied; though one's deepest sympathy goes out to his wife Anna, who bore the brunt and shock of sudden death.

The time for mourning is now past, let us think of the many and varied pleasures he brought to us. I shall never forget him.

Balatonfured R. BELCHER
31 *August* 1970

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DEVELOPMENT AND PUBLICATION OF NEW GRAVIMETRIC METHODS OF ANALYSIS

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Summary—A review is made of the factors affecting the accuracy of gravimetric methods, and which need to be investigated in the development of new methods. Recommendations are made for writing up such investigations for publication.

In the first paper of this series, Kirkbright[1] laid down a set of requirements for thorough investigation of any proposed new method of spectrophotometric determination and that paper was thought to be timely in view of the large number of reagents being developed for colorimetric analysis and the growing need for some agreement as to the minimum of investigation necessary and on the format for expressing results. Although gravimetric analysis has often been regarded as obsolescent, there are still as many papers published on it[2] as on radiochemical analysis, a field which is rapidly becoming prominent. This is mainly due to the need for elucidation of the theoretical fundamentals of gravimetric analysis (which had developed mainly empirically). Extensive research work is being done on the application of complexing agents to extend the possibilities for specific determination and separation of metal ions, and a certain reviviscence of the field has been brought about by the development of radiochemical analysis, especially activation analysis. Gravimetric methods have not lost their importance in spite of instrumentation and automation. It would be rather difficult to find an instrumental method which did not need the methods of classical chemical analysis to provide the composition of the standards used for calibrating the instrument. The fundamental operation in gravimetric analysis is the quantitative precipitation of the component to be determined, in a form which is free from contaminants and easy to separate from the mother liquor, *i.e.*, easy to filter off and wash. The precipitate must either itself be a stoichiometric compound that is easy to weigh, *i.e.*, involatile, non-hygroscopic, non-efflorescent, and inert to reaction with air, or easily convertible into such a compound by drying or ignition. However simple these requirements may seem, it is rather difficult to keep the error caused by dissolution losses, co- and post-precipitation *etc.* below 0·1%, which is in most cases required in practice. It is therefore the intention of this paper to lay down a standard set of requirements for development and publication of a gravimetric method, and to discuss the chemical background which makes these requirements necessary.

THE PRECIPITATION PROCESS

Nucleation and crystal growth

The kinetics and thermodynamics of precipitation are important not only in analysis but also in metallurgy, the chemistry of solids and very pure substances, the physics of semiconductors, *etc.* Although considerable effort has been expended on elucidating the fundamentals of the kinetics and thermodynamics of precipitation,[3,4] practically all of it has been devoted to the rather narrow field of precipitation of ionic compounds, although these form by far the minority of the compounds used in analytical practice, and even then, agreement has not finally been reached on such factors as the critical size of a nucleus for crystal growth. From the analyst's point of view, the important features are that contamination by adsorption or occlusion occurs to an extent that is largely governed by the surface area of the precipitate, so it is important to have a small number of crystal particles present, these being of relatively large size. Until the development of precipitation from homogeneous solution (PFHS) the basic rules for production of analytically suitable precipitates had not changed appreciably since von Weimarn.[5]

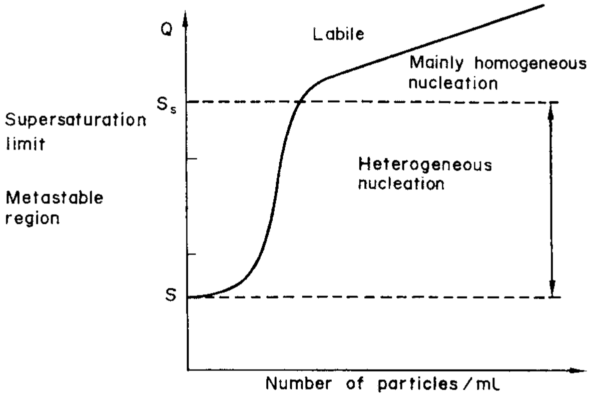

FIG. 1.—Number of particles precipitated, as a function of supersaturation. (Reprinted from *Chem. Anal. Warsaw*, 1968, **13**, 969, by permission.)

It is recognized that the number of precipitated particles and their size distribution are determined by the rate of nucleation and by the rate of growth of the nuclei (which can be defined as the rate of linear growth of a crystal plane). Nucleation occurs in supersaturated solution. The concentration interval between the equilibrium solubility (solubility of large particles) and the critical supersaturation was termed by Ostwald the metastable zone. At the critical supersaturation concentration crystal formation proceeds instantaneously and spontaneously. The metastable zone may greatly differ in width even for precipitates with the same solubility, and great difference may result in the morphology of precipitates, as shown in the case of barium sulphate and silver chloride. Nucleation can be homogeneous (*i.e.*, the nuclei are the same compound as the precipitate) in which case the nuclei are formed by agglomeration and dispersal of the constituents of the precipitate until, as a result of this statistical fluctuation between growth and decrease, a certain critical size is reached, and growth predominates; alternatively nucleation may occur at concentrations lower than the critical supersaturation concentration, and is then called heterogeneous and takes place on foreign surfaces such as those of impurities, vessel walls, or gas bubbles. A plot of number of particles per unit volume, as a function of supersaturation, gives a break-point at the critical supersaturation concentration, and at higher concentrations than this the number of particles produced rapidly increases, with a concomitant decrease in particle size (Fig. 1). A graphical representation gives a clear picture of the nature of nucleation.[6]

Kossel's theory of crystal growth[7] attempted to calculate the energy released when an ion, atom or molecule entered at different points of the lattice. Volmer[8] introduced the concept of a two-dimensional nucleus into Kossel's theory, such an aggregate of atoms or ions being stable on the crystal surface only if bigger than a certain critical size. According to Frank[9] spiral growth proceeds at low supersaturations and a two-dimensional nucleus need not then be formed.

It follows that nucleation must be minimized and growth maximized, if a pure and easily filterable precipitate is to be obtained, and this can be achieved by maintaining a low degree of supersaturation. Several attempts have been made to meet this requirement. Hahn and Otto[10] effected the precipitation from extremely dilute solution, by adding separate solutions of the ion to the precipitated and of the precipitant dropwise to boiling distilled water. The electrolyte concentration is much higher at the end of precipitation than at the beginning. In this way well-formed crystals can be obtained. In contrast, according to Njegovan and Marjanovic[11] precipitation is to be made from cool concentrated solution with a concentrated solution of the precipitant, and the suspension is to be warmed with hot water, during which process recrystallization probably proceeds, but an excessive length of time is required. According to the precision method of Winkler[12] precipitation is best effected from boiling solution with a reagent solution added dropwise. By the use of a known, constant amount of ammonium salt, adsorption can be avoided or reduced. The deviation of the weight of precipitate from the theoretical value can be corrected for. According to the method of Willard and Tang,[13] precipitation from homogeneous solution, the reagent is generated uniformly dispersed throughout the solution of the ion to be precipitated, and so local supersaturation can be avoided. This can be achieved by generating the precipitating reagent *in situ* by a hydrolytic reaction (*e.g.*, hydrolysis of sulphamic acid to produce sulphate), a condensation (*e.g.*, formation of dimethylglyoxime from biacetyl and hydroxylamine), a pH change which itself is brought about by a hydrolytic reaction (*e.g.*, hydrolysis of urea to raise the pH to produce the appropriate 8-hydroxyquinoline species for precipitation of aluminium) *etc*, or the metal ion to be precipitated may be released from a stable complex in the presence of an excess of precipitant (*e.g.*, peroxide oxidation of the bismuth-EDTA complex in the presence of phosphate), or the reaction may be carried out in the presence of an organic solvent (in the case of precipitation with an organic reagent) in sufficient amount to keep the precipitate in solution, followed by slow removal of the solvent by evaporation.

Whatever the method used, it will be affected by such variables as the concentration and temperature of the reagents, of addition or generation or precipitant, length or digestion of the precipitate with the mother liquor, and temperature during filtration. It should be noted that in precipitation from homogeneous solution, in order to avoid unduly prolonged reaction times it is often necessary to take a very large excess (up to 1000%) of the generating reagent, and to quench the reaction by cooling when sufficient precipitant has been produced (a study of kinetic curves will show why).

Solubility of precipitates

Factors affecting the solubility of precipitates can be classified into two groups, according to whether they influence the properties of the solid phase or those of the solution. The precipitate structure, presence of polymorphous modifications and of water of crystallization, particle size distribution, and aging have a remarkable influence on the solubility of precipitates. Of these factors, aging is the most important. By this term is meant those changes which occur in a precipitate on standing in contact with the mother liquor. These changes are discussed in detail in the standard textbooks (*e.g.*, those by Laitinen[14] and by Kolthoff *et al.*[15]) but two of them are of more practical importance than the others. If a species is precipitated in a metastable form and can be transformed into a more stable form with extensive rearrangement of the lattice, then substantial purification will occur in the process (*e.g.*, calcium oxalate dihydrate and trihydrate are metastable with respect to the monohydrate and are converted into it on digestion). Many "hydroxide" precipitates are better described as hydrous oxides, and may undergo slow change in composition on aging. One practical consequence is that hydroxide precipitates left for a considerable length of time may become much more difficult (or even impossible) to redissolve in acid, thus making reprecipitation harder to achieve.

At a certain temperature the mother liquor and precipitate will reach an equilibrium characterized by constancy of the activity product:

$$K_{sp} = a_M{}^m \cdot a_N{}^n$$

where K_{sp} is called the solubility product of the species M_mN_n. The solubility of M_mN_n increases as the activity of its ions in solution decreases (by protonation, hydrolysis, complex formation, oxidation *etc.*). It has been proposed[16] that for direct comparison with stability constants it would be more logical to use an "insolubility product," which would be the inverse of K_{sp}.

Because the object of quantitative analysis is to recover the whole of a particular species, an excess of precipitant must of necessity be used. It follows that the solubility of the precipitate will be decreased by this excess (the common-ion effect), but if the reagent can form charged complexes with the ion of interest, there may be a solubility increase if a very large excess of reagent is used (*e.g.*, silver chloride is soluble in concentrated hydrochloric acid because of formation of $AgCl_2^-$). The wash liquid used may need to contain one of the component species of the precipitate to prevent loss by dissolution in washing, or to contain an electrolyte to prevent peptization of a flocculated colloid, and the salt used must be readily removable from the washed precipitate. Usually an ammonium salt is used, since it will be volatile on suitable heat-treatment of the precipitate. Use of a saturated solution of the precipitate is not to be recommended (positive errors could ensue from precipitation by the common ion excess in the mother liquor still in contact with the precipitate, or if the precipitate is left unduly wet with wash-liquid before ignition or drying, and negative errors if the residual wash-liquid is removed with water).

Factors influencing the properties of the solution can be classified into two groups: those exerting the so-called inert-electrolyte effect because of changes in the ionic strength of the solution, and those causing reactions involving one of the ions of the precipitate, such as hydrolysis of cations, formation of complexes with common or foreign ions, protonation of strongly basic ligands and disproportionation of one of the ions. The extent of all these reactions may markedly depend on the pH, and calculation of their effect is described in the textbooks.[14,15,17]

A particularly insidious influence is exerted by the existence of inert complexes, especially heterobinuclear complexes. The ion to be determined may be initially present in the form of a complex which is thermodynamically unstable relative to the change brought about by addition of precipitant, but kinetically so slow to react that it is effectively stabilized. Worse, it may be present along with a complexing ligand with which it normally forms a labile complex, but which can act as a bridge between it and another ion to form an inert complex, *e.g.*, copper(II)–citrate–chromium(III);[18] the existence of such complexes is often unsuspected. The preliminary history of a solution is often of vital importance, particularly that of the "opening-out" process.

Contamination of precipitates

Contaminations may be classified into two groups: those due to co-precipitation and those caused by post-precipitation. In co-precipitation two types of contamination can be distinguished: adsorption and occlusion. In the case of adsorption, the precipitate particles carry the contaminant on their surface. With colloidal precipitates the coagulated secondary particles may carry in their interior impurities bound by adsorption forces to the primary colloid particles. In occlusion the impurity is inside the primary precipitate particles, whether by mechanical trapping during crystal growth or by formation of solid solutions. The distribution of contaminant in a homogeneous solid solution can be characterized by the Berthelot-Nernst distribution coefficient, D, which describes the thermodynamic equilibrium:[19,20]

$$\frac{[\mathrm{A}]}{[\mathrm{B}]}\ \text{in crystal} = D\,\frac{[\mathrm{A}]}{[\mathrm{B}]}\ \text{in solution.}$$

A homogeneous distribution is obtained for the crystal as a whole and not only for the surface layer, if there is equilibrium between the solution and crystal.

The heterogeneous distribution of a contaminant can be characterized by the coefficient λ in the Doerner-Hoskins equation[19]

$$\log\left(\frac{[\mathrm{A}]_{\text{initial}}}{[\mathrm{A}]_{\text{final}}}\right)\ \text{in solution} = \lambda \log\left(\frac{[\mathrm{B}]_{\text{initial}}}{[\mathrm{B}]_{\text{final}}}\right)\ \text{in solution.}$$

According to this the composition of an elementary layer of the precipitate depends on the ratio of the concentrations of the two components in the solution. λ and D differ in that the former is a kinetic constant while the latter is a thermodynamic equilibrium constant.

Very often all forms of contamination are called occlusion, which can cause confusion, since the exact reason for contamination has to be known if it is to be eliminated. Contaminants bound to the precipitate by adsorption are much easier to remove by washing than those occluded.

It is useful to tabulate the ways in which the purity of precipitates can be improved, and this has been done in Table I. It must be stressed, however, that there are many exceptions to these general guiding rules, and that investigation should always be made of the effect of variation of conditions.

Collection and heat-treatment of precipitates

Precipitates that are to be dried at temperatures up to about 250° are invariably collected in borosilicate sintered-glass crucibles. Those which are to be ignited are

TABLE I.—INFLUENCE OF CONDITIONS OF PRECIPITATION ON PURITY

Condition	Form of impurity			
	Mixed crystals	Surface adsorption	Inclusion	Post-precipitation
Dilute solutions	0	+	+	0
Slow precipitation	+	+	+	−
Prolonged digestion	0/+	+*	+	−
High temperature	−	+†	+	0
Agitation	+	+	+	0
Washing	0	++§	0	0
Reprecipitation	0/+	++	++	+
Adjustment of pH	0	0	0	+
Filtration soon after precipitation	0	0	0	++
PFHS	+	++	++	−

* This would have no effect on gelatinous precipitates.

† There are exceptions. Some crystalline precipitates are affected adversely, *e.g.*, $BaSO_4$ and CaC_2O_4, but digestion improves the situation.

§ Gelatinous and curdy precipitates; crystalline precipitates do not reach the required degree of purity by washing alone.

++ Impurity reduced to negligible amounts, though not necessarily by this means alone; other conditions may have to be used in conjunction.

+ Increased purity, but significant amounts still present.

0 No significant change.

− Decrease in purity.

This table was supplied by Prof. R. Belcher and is based on the one by M. L. Salutsky, in *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. J. Elving eds., Part I, Vol. 1 p. 499, Interscience, New York, 1959.

collected on filter-paper or in crucibles fitted with fritted discs. The latter filters may be made of fused silica or of porcelain. Sometimes use is made of platinum filters fitted with platinum sponge. The use of asbestos (the original Gooch crucible) has largely disappeared. If frits are used, it is essential that the crucibles should be conditioned by repeated heating with solutions of approximately the composition of those with which the crucible is to be used, until the crucible shows no further change in weight on treatment. This is particularly important for work on the micro scale. Because the surface area of the fritted discs is very large, the equilibrium amount of water vapour adsorbed on the surface is also large, and can vary if the humidity changes between weighings. While the effect may not be noticeable on the macro scale (it may amount to one or two hundred micrograms) it is a serious source of error in microanalysis, and microcrucibles should always be used along with a similar crucible as counterpoise. The counterpoise crucible must be given the same heating and cooling treatment as the sample crucibles in order to compensate as far as possible for variation in conditions. Whenever platinum crucibles are used it should be remembered that platinum is appreciably volatile at high temperatures, especially those above 1000°, and an empirically determined correction should be applied for loss, calculated on a temperature and time basis. When silica, glass or porcelain crucibles have been used, the possibility of induced electrostatic charges should not be overlooked,[21] and if necessary a metal crucible can be used to provide a Faraday cage on the balance pan.

The pore-size of the filter must be matched to the particle size of the precipitate. If it is too great there may be loss of material by passage through the filter; if it is too small the filter may clog and filtration be unduly slow.

Once obtained, collected, and washed with a suitable liquid, the precipitate is freed from water by drying or ignition. During this heat-treatment the precipitate may undergo physical or chemical changes which influence its weight and composition. Winkler[12] has drawn attention to the fact that crystalline precipitates can be dried to constant weight even at room temperature if they are not hygroscopic, do not tend to oxidize, do not react with carbon dioxide present in air and do not decompose in air, though naturally this may take a long time. Sometimes water is removed with alcohol *etc.*

However, the last traces of water cannot always be removed from the precipitate by drying at room temperature. Barium sulphate, for example, may retain water at temperatures up to 600°. Duval[22] systematically studied the thermal behaviour of precipitates by automatically recording the dependence of precipitate weight on temperature. Erdey and Paulik[23,24] have developed the technique further by recording simultaneously the mass loss curve and its derivative, and the differential thermoanalytical curve. These "derivatographic" curves provide useful information concerning the transformations of a precipitate during heat treatment. The optimum drying temperature and the temperature range over which the weight is constant can be determined by the method. However, if static heating conditions are to be used in the analysis and the precipitate is to be weighed in the open air at room temperature, it is essential to check the thermal behaviour of the precipitate under the conditions to be used, and the interaction of the ignition product with wet air at room temperature. For instance, the decomposition temperature of silicomolybdic anhydride has been reported from thermobalance measurements to be about 800°, but on static heating there is loss of molybdenum trioxide at temperatures above 600°; again, calcium oxalate can be converted into the anhydrous form and weighed as such at 200°, but on exposure to laboratory air at room temperature it rapidly reverts to the monohydrate.[25]

The advantages of desiccators have long been shown to be largely illusory,[26,27] except for keeping dust out of crucibles and preventing accidental loss from draughts, sneezes, *etc.* Even if a good desiccant and design of desiccator *can* be found, immediately a dry object is removed into moist air it will begin to adsorb moisture on its surface, so there is no real point in keeping it dry in the first place, unless the material within it is markedly hygroscopic (*e.g.*, dry flour or calcium oxide) but can be sufficiently protected from the atmosphere by a close-fitting lid for there to be no appreciable uptake of water by it during the period needed for weighing. If the final product to be weighed in a gravimetric analyses is hygroscopic the method is inferior. For rapid cooling a block of metal is adequate, and it is essential that the object to be weighed should be at the temperature of the balance.[28]

Thermal methods can also be used to solve analytical problems directly, *e.g.*, strontium, calcium and barium can be determined rapidly without separation, by means of the derivatogram of their oxalates.[29] The method also permits determination of polymorphous modifications when present together, which is rather difficult to do by other methods.[30]

THE APPLICABILITY OF A METHOD

As pointed out long ago by Lundell,[31] an analytical method is not much use in isolation; it must be capable of application to a particular problem. The analysis of a pure solution of a single substance is not usually much of a problem, certainly not in comparison with analysis of a complex mixture. It follows that any new method must be assessed for usefulness, and those species which will affect the results adversely must be delineated, and where possible, means suggested for eliminating their effect. It is also essential that the useful scale of operations should be defined, so that the method is used sensibly. Gravimetric analysis is useful only in certain contexts, and is meaningless in others.

Amount of sample

The sample weight to be taken, and the accuracy of weighing, are both determined by the composition of the material, the overall error that can be tolerated, and the desired speed of analysis. It is obviously faster to filter a small volume of liquid than a large, so scaling down of operations should hasten the analysis. Both weights and volumes must be reduced in similar proportions in order to keep concentrations about the same. The error of weighing a 5-mg precipitate on a microbalance with a standard deviation of 3 μg is about the same as that of weighing a 100-mg precipitate on an ordinary balance with a standard deviation of 0·05 mg, but an attempt to collect 5 mg of precipitate from say 250 ml of mother liquor would be much more likely to produce an erroneous result than would collection of 100 mg from the same volume. At the other end of the scale, an attempt to increase accuracy by collection of 10 g of precipitate would be a self-defeating exercise because of the unwieldy amount of precipitate and the very large volume of liquid to be filtered, coupled with the impossibility of washing the precipitate adequately. The scale of operations is therefore defined at one end by purely manipulative considerations, and at the other by the precision and accuracy sought.

If an overall error of not more than 0·1 % is aimed at, the error of the final weighing must be smaller than this, and in conjunction with the known performance of the balance used will set the magnitude of the weight of precipitate to be collected, and hence the minimum size of sample to be taken. If a correction is to be applied for a reagent blank, due allowance must be made for the uncertainty in determining it.

An important factor in assessing the statistical errors is the conversion factor from weight of product to weight of species sought. The higher the conversion factor, the less significant the statistical weighing error. For example, in determination of copper by electrolytic deposition and weighing, the conversion factor is unity, whereas in determination of silicon as silicomolybdic anhydride, the product weighs about 60 times as much as the amount of silicon in it; a weighing error of 0·1 mg represents an error of 0·1 mg of copper and 16 μg of silicon respectively.

Gravimetric analysis is not at all suitable for trace analysis, and is generally applicable only to major components of a sample, *i.e.*, those present to the extent of at least 1 %, though it can be applied to minor components (0·1–1 %) if an amplification reaction[32] is available or the conversion factor is very favourable or a larger relative error is tolerable.

If carbon is to be determined in a steel by ignition to carbon dioxide in a stream of oxygen, followed by collection and weighing of the product to the nearest 0·1 mg, then if a "factor weight" of sample is taken (*i.e.*, 2·729 g, because CO_2 contains 27·28 % of carbon) 1 mg of CO_2 produced is equivalent to 0·1 % of carbon in the steel. If there is not more than 0·2 % of carbon present there is no point in weighing the sample more accurately than to the nearest 5 mg (2·73 ± 0·005 g) because the maximum error so caused would be <0·001 % of carbon, which is the limiting error imposed by the final weighing operation. On the other hand, if chloride in sodium chloride were to be determined as silver chloride it would be necessary to weigh both sample and product with a relative error of not more than 0·05 % if an overall error of <0·1 % were desired.

Selectivity

The value and applicability of analytical methods, particularly of new gravimetric determinations, depend greatly on selectivity. An analytical reaction (in the case of precipitation) is selective if the reagent reacts only with the ion to be determined, or with few other ions. A reaction is called specific if it is characteristic for one ion only. By selecting suitable conditions, *e.g.*, by adjusting the pH or other factors which affect complex stabilities, selectivity can be increased, and a reaction can be made specific for an ion. Several attempts have been made[22,23] to interpret the specific or selective nature of reactions, but these problems have yet not been finally settled. With knowledge of the stability constants concerned, the degree of specificty of a complex-formation reaction can be calculated.[24]

Two quantities, the recovery factor R and the separation factor ($S_{B/A}$) are used for the quantitative description of the efficiency of a separation. In the separation of ion A from ion B the recovery factor R_A gives the fraction of A recovered in the precipitate at the end. A separation is good if the value of the recovery factor is between 0·999 and 1·000 (or 99·9 and 100·0 %) where Q_A is the quantity of A isolated

$$1 > R_A = \frac{Q_A}{(Q_A)_0} > 0{\cdot}999$$

and $(Q_A)_0$ is the original quantity, and if the accompanying ion is left quantitatively in the original phase. The selectivity of separation can be characterized by the separation factor, $S_{B/A}$:[25]

$$S_{B/A} = \frac{Q_B/Q_A}{(Q_B)_0/(Q_A)_0} = \frac{(Q_A)_0}{(Q_B)_0}\cdot\frac{Q_B}{Q_A} = \frac{R_B}{R_A}$$

In a good separation the amount of B going into the new phase, Q_B, is less than 0·1 % of Q_A, the amount of A in this phase. It is rather difficult to meet these requirements in separations based on precipitation, especially if the amount of B is great compared to that of A. Chromatographic and extraction methods are more effective means for separation.

Assessment of error and precision

The generally accepted values of allowable errors have been given as follows:[33]

Constituent, %	Error, parts per 1000
100	1–3
10	10
1	10–20
0·1	50
0·01–0·0001	100

but these are the errors associated with routine analysis, which usually involves a "go/no-go" type of inspection of material to see whether it fulfils a specification. For research work and particularly for evaluation of a new method, rather higher precision is to be expected.

Some new analytical methods are preferred to older ones because of their simplicity, rapidity or other advantages, but preference should also take heed of the error involved, and this should be given besides the other features.

Errors can be classified into two groups:

Random errors are due to the uncontrollable small changes in experimental conditions and do not depend on the observer or analyst.

Systematic errors are those caused by the imperfections of equipment used and by the limitations of the physico-chemical reaction serving as the basis of determination.

In gravimetric analysis systematic errors arise from imperfections in balances and weights, from solubility of precipitates, co-precipitation *etc.* As a result, the average of replicate analyses deviates from the true value, but since the deviation is usually of well defined direction and size, it can be eliminated by properly calculated corrections. Random errors cannot be eliminated in this way, however. They arise from such factors as variation in performance of a balance on repeated weighing of the same object, random variation of sample composition, small random fluctuations in treatment of individual analyses, *etc.* The distribution of such errors is assumed to be Gaussian, and the standard deviation is calculated to assess the magnitude of the random error. It is easier to compare results for different methods if the relative standard deviation is given. The nature and statistics of errors are discussed in standard texts (*e.g.*, refs. 14 and 34).

It is not enough, however, simply to calculate the error on the basis of the weight of the final product. It may happen that the reagents contain some of the species being determined, or that the precipitate contains foreign species. As pointed out by Berman, Semeniuk and Russell,[35] the usual practice is to take a standard solution of a substance, put it through the recommended procedure, and if the amount found is very close to the amount taken, to call the method satisfactory, whereas what *should* be done is to investigate separately the loss of precipitate to the filtrate, the extent of contamination of the precipitate, the size of the blank, and any other sources of error, to ensure that there has not been a fortuitous compensation of errors. In their work on thorium determination they showed that silica collected by the precipitate just about cancelled out the amount of thorium lost.

The question of blanks and corrections is rather complicated and depends mainly on the scale of working. In microanalysis, for example, it may prove necessary to apply a correction for dust or other particulate matter in the reagents. It is quite easy to accumulate 25 μg or so of foreign matter, and this would constitute an error of $+0{\cdot}1\,\%$ in a precipitate weight of 2·5 mg. Such an error is easily assessed by dissolving the precipitate off the filter (if an organometallic complex is weighed) with an organic solvent, and then drying and reweighing. Purely inorganic precipitates of ignition products can often be dissolved by suitable acids or fusions; silica in them can be determined by the Berzelius method of removal with hydrofluoric and sulphuric acids. Reagent blanks cannot be properly assessed by running a blank determination in the absence of sample. It is also unrealistic to try to assess the blank by direct determination by other means (spectrophotometry, polarography *etc.*) of the amount of determinand present in the reagents. The constituents of the apparatus used may be extracted to a greater or lesser extent during the analytical operations, and the history of the apparatus may affect the amount removed.

The two methods most commonly used for assessing blanks are to apply the method to a standard material of *accurately* known composition and to determine the difference between "taken" and "found," or to apply the method to two different sample weights, one of which is a simple multiple of the other (usually a 2:1 ratio is used) and to compare the value obtained for the smaller sample with that obtained from the difference between the two results. By "accurately" we mean with a precision that will give an experimental error much smaller than the amount of blank sought, and the remarks of Berman *et al.*[35] on "taken" and "found" must be heeded. (It is obvious that if the standard has been analysed by chemical means there already exists a method of adequate precision and accuracy!)

Corrections for solubility of precipitates should be applied only if the solubility has been determined under the conditions used. A simple consideration of the kinetics shows that it is unlikely that wash-water will become saturated with precipitate during normal washing operations. Corrections for the ash of filter paper are usually negligible for all but micro or semi-micro work.

Applications

As pointed out earlier in this paper, a method is not useful unless an application can be found for it. It is the author's duty to find applications and to test the performances of the method under real and simulated conditions, that is with samples that are likely to be met with in practice, or with samples synthesized by mixing known amounts of materials of known purity to provide mixtures of compositions similar to those of "genuine" samples. Attention must be paid to the method of bringing the sample into solution, and its possible chemical effects on the procedure being developed.

PREPARATION OF A PAPER FOR PUBLICATION

Useful guidance on the information necessary in a published paper on an analytical procedure will be found in the articles by Wilson[36,37] and by Chalmers.[38,39] The requirements for adequate development and description of a gravimetric procedure are dealt with at length in the earlier parts of this paper, and are summarized here for convenience and emphasis. The points listed are those that *must* be examined and reported on. Factorial design of the experimentation can save considerable effort and increase the amount of useful information obtained (see *e.g.*, ref. 40.) A useful general survey of gravimetric methods has been given by Beamish and McBryde.[41]

1. *The precipitant.* Solubility, stability of the solid reagent and its solutions, methods of preparation and physical characteristics (m.p. *etc.*) if a new reagent, should all be given.

2. *Method of precipitation.* Details must be given of the permissible chemical composition of the solution before precipitation; the range of absolute amount and concentration of the species to be determined; the pH, temperature and volume of the sample solution before precipitation; the pH, volume, temperature and concentration of the reagent and the rate at which it is to be added (or alternatively details of the method of conducting PFHS); final pH of the solution, time and temperature

of digestion; temperature for filtration; type of filter; volume and number of washes; composition of the wash-liquid; temperature and duration of drying or ignition; special precautions.

3. *Selectivity.* The effect of possible interfering elements and of species likely to be found in sample matrices must be investigated at realistic concentration levels, covering the full range of likely ratios of interfering species to determinand, and preferably with a 100% safety margin (twice the maximum ratio expected in practice). Any masking agents used to improve selectivity should be tested over a wide range of concentration ratios relative to determinand.

4. *Accuracy and precision.* Results of replicate tests and of tests for loss, recovery, contamination *etc.* should be statistically analysed and summarized. If possible statistical tests of comparison with other methods should be made.

5. *Applications.* Procedures suitable for various matrices tested should at least be outlined, or suitable references given to standard procedures. Results for standard samples should be given.

6. *General.* Tolerances on the various procedure parameters should be quoted and the evidence given on which they are based.[36,37] The value of the method should be realistically assessed against the background of other methods, speed, accuracy, cost, selectivity, simplicity, *etc.*

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Zusammenfassung—Es wird eine Übersicht über die Faktoren gegeben, die die Genauigkeit gravimetrischer Methoden beeinflussen, und die man bei der Entwicklung neuer Verfahren untersuchen muß. Zur Veröffentlichung solcher Untersuchungen werden Empfehlungen gegeben.

Résumé—On procède à une revue des facteurs affectant l'exactitude de méthodes gravimétriques, et qu'il est besoin d'étudier dans le développement de nouvelles méthodes. On fait des recommandations pour la rédaction de telles études pour publication.

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DETERMINATION OF TRACE CONTAMINANTS IN HYDROGENATION CATALYSTS BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A neutron-activation method has been developed for the determination of the active constituents and contaminants in hydrogenation catalysts. The active constituents of palladium and nickel catalysts (Pd and Ni) and Zn and Co contaminants present in small amount were determined by a direct instrumental method. A NaI(Tl) scintillator and a Ge(Li) semiconductor connected to a multichannel analyser were used for the measurements. A computer was used to evaluate the γ-spectra. Contaminants present in small amount were also determined by means of a radiochemical separation method based on heterogeneous isotopic exchange on mercury(II) sulphide and zinc sulphide precipitates.

THE PROBLEM of the determination of trace contaminants in hydrogenation catalysts arose in connection with caprolactam production. For the hydrogenation of phenol in the gaseous phase, nickel or palladium catalysts are used, on aluminium oxide, graphite or on a mixture of them, as carrier.

Sulphur, selenium, tellurium, phosphorus, arsenic, antimony, bismuth, zinc, mercury, lead and their compounds are catalytic poisons.[1] The activity of the catalyst decreases linearly or exponentially with increasing concentration of the poison, depending on the nature of the bond formed between the active ingredient of the catalyst and poison. Very small amounts of the poison—orders of magnitude smaller than necessary to form a monomolecular layer—may remarkably reduce the activity of the catalyst.[2,3]

It therefore seems reasonable to use an analytical method of very high sensitivity, such as neutron-activation analysis, for determining contaminants which poison hydrogenation catalysts. In the present paper the determination of mercury and zinc will be dealt with. The active ingredients of the catalysts (Pd, Ni) have also been determined, since this is necessary in order to elucidate the mechanism of poisoning.

The nuclear reactions to be taken into account for all components of the system are listed in Table I. The components include the active ingredients, the carrier used to give large surface area (alumina), and the contaminants.

Samples activated with thermal neutrons were evaluated by γ-spectrometry, by direct instrumental measurements with or without radiochemical separation. To separate the radioisotopes of the trace contaminants our method based on heterogeneous isotopic exchange with sulphide precipitates[4,5] has been used.

TABLE I.—NUCLEAR DATA OF ELEMENTS OCCURRING IN PALLADIUM AND NICKEL CATALYSTS

Stable isotope	Isotope abundance, %	Reaction type	Cross section, *barn*	Radioactive isotope formed	$t_{1/2}$	Energy peak, *MeV*
^{27}Al	100	n, γ	0·21	^{28}Al	2·3 min	0·76; 1·27; 1·77
		n, α	0·0006	^{24}Na	15 hr	1·36; 1·74; 2·25; 2·76
		n, p	0·004	^{27}Mg	9·5 min	0·18; 0·84; 1·01
^{64}Ni	1·08	n, γ	1·52	^{65}Ni	2·6 hr	0·37; 1·12; 1·49
^{58}Ni	67·84	n, p	0·073	^{58}Co	71·3 d	0·51; 0·81; 1·31; 1·66
^{60}Ni	26·16	n, p	0·002	^{60}Co	5·27 y	1·17; 1·33; 2·50
^{196}Hg	0·15	n, γ	420	^{197m}Hg	24 hr	0·13; 0·164
		n, γ	880	^{197}Hg	65 hr	0·077; 0·191
^{198}Hg	10·00	n, γ	0·018	^{199m}Hg	43 min	0·16; 0·37
^{202}Hg	29·8	n, γ	3·8	^{203}Hg	47 d	0·073; 0·279
^{204}Hg	6·8	n, γ	0·43	^{205}Hg	5·1 min	0·203
^{59}Co	37·0	n, γ	16	^{60m}Co	10·5 min	0·06; 1·33
		n, γ	20	^{60}Co	5·27 y	1·17; 1·33
^{64}Zn	48·98	n, γ	0·47	^{65}Zn	245 d	0·51; 1·12
^{68}Zn	18·57	n, γ	0·097	^{69m}Zn	13·9 hr	0·44
			1·0	^{69}Zn	55 min	
^{102}Pd	0·96	n, γ	4·8	^{103}Pd	17 d	0·053; 0·065; 0·298; 0·324; 0·362; 0·498
^{108}Pd	26·7	n, γ	0·26	^{109m}Pd	4·8 min	0·19
		n, γ	10·4	^{109}Pd	13·6 hr	0·022; 0·088; 0·307; 0·42
^{110}Pd	13·5	n, γ	0·05	^{111m}Pd	5·5 hr	0·17
		n, γ	0·21	^{111}Pd	22 min	0·45, 0·62
				^{111}Ag	7·6 d	0·023; 0·247; 0·31; 0·340

EXPERIMENTAL

Apparatus

Gamma spectroscopy. NaI(Tl) scintillators, 35 mm and 60 mm diameter and 75 × 75 mm; measuring heads equipped with photomultiplier. Ge(Li) semiconductor detector, 12·5 ml. Multichannel analysers, 256, 512 and 1024 channel, constructed in the Central Research Institute for Physics of the Hungarian Academy of Sciences (CRIP).

For evaluation of the spectra by computer the data from the analyser were put on punched tape with a Facit printer. The computer (ICT-1905, using Algol language, developed in the CRIP) draws the spectrum on the basis of the data, and determines the amplitude, area, width at half-height, and position of the energy peaks as Gauss curves by simulation, and corrects the data for the background.

Activation. Irradiations were made in the experimental atomic reactor of the CRIP: thermal neutron flux: $3{\cdot}8 \times 10^{13}$ neutrons.cm^{-2}.sec^{-1}; fast neutron flux: $0{\cdot}5 \times 10^{12}$ neutrons.cm^{-2}.sec^{-1} in the channel used. Samples and standards were irradiated for 24 hr under similar conditions.

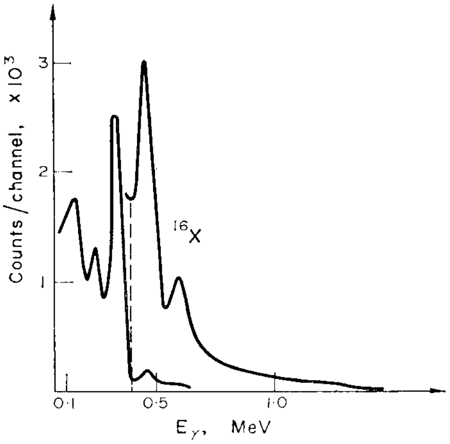

FIG. 1.—γ-Spectrum of palladium standard.

Catalyst samples (5 × 5 mm cylinders of about 150 mg weight) were irradiated sealed in quartz ampoules. Samples were processed after 8–10 days cooling.

Irrespective of the measuring procedure used, catalyst samples were dissolved in 2 ml of nitric acid (1 + 1) in a flask equipped with a reflux condenser, and then diluted to 50 ml with distilled water. Aliquots of the resulting stock solution were used for measurement.

As standards Johnson Matthey's palladium, nickel, cobalt, zinc and mercury compounds of spectral purity were used.

RESULTS AND DISCUSSION

Direct instrumental studies by scintillation detector

Aliquots (1 ml) of the stock solutions of the activated catalyst samples and standards prepared after 10 days cooling were transferred to quartz vessels, evaporated to dryness, and their γ-spectra recorded.

In the γ-spectrum of the palladium standard (Fig. 1) peaks appear at 0·24, 0·34, 0·49 and 0·6 MeV, originating from the radioactive isotopes of palladium and from daughter-isotope ^{111}Ag from ^{111}Pd.

In the γ-spectrum of unused palladium catalyst (Fig. 2) the photopeak of the radioactive isotope ^{65}Zn also appears at 1·12 MeV, as a small amount of zinc was originally present in the catalyst.

In the γ-spectrum of used palladium catalyst appear the photopeaks characteristic of the radioisotopes of zinc and palladium (Fig. 3). On the spectrum obtained with greater amplification (Fig. 4) the 0·279-MeV photopeak of the mercury contaminant

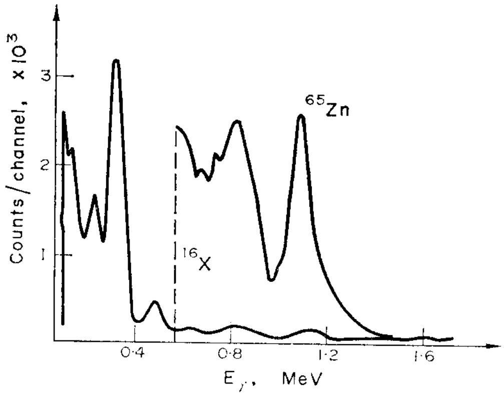

FIG. 2.—γ-Spectrum of unused palladium catalyst.

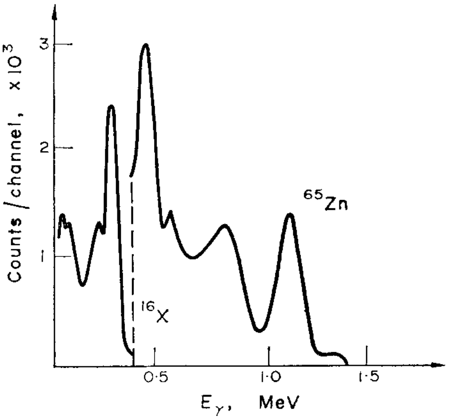

FIG. 3.—γ-Spectrum of used palladium catalyst.

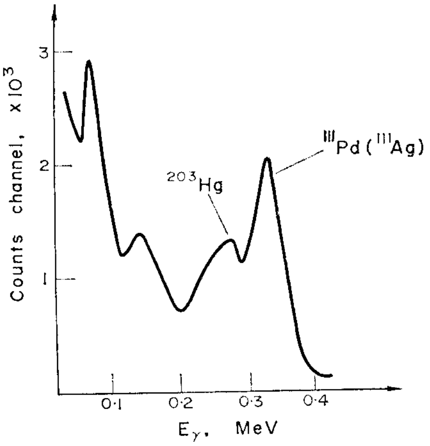

FIG. 4.—γ-Spectrum of used palladium catalyst at higher amplification.

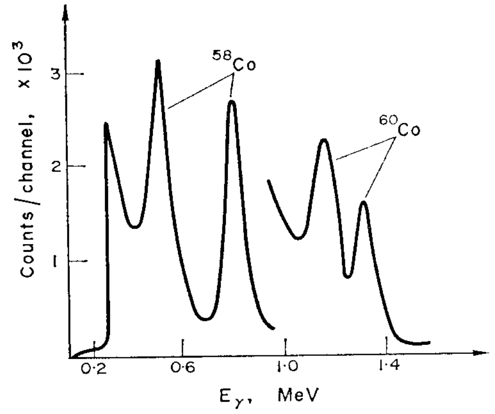

FIG. 5.—γ-Spectrum of unused nickel catalyst.

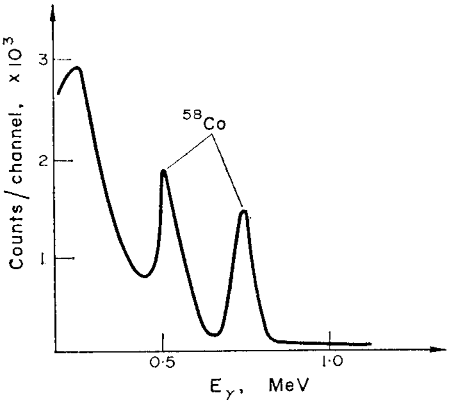

FIG. 6.—γ-Spectrum of nickel standard.

becomes perceptible, but it is not separated from the 0·24-MeV photopeak of palladium.

When scintillation detectors are used, only the palladium active ingredient and zinc contaminant of the catalyst can be determined from the γ-spectra by a direct instrumental method. Before determination of palladium the spectrum of the ^{65}Zn standard was subtracted from the complex spectrum and the 0·34-MeV photopeak of palladium evaluated. In determining palladium and zinc the spectra were evaluated by Covell's method.[6]

In the γ-spectrum of unused nickel catalysts (Fig. 5) the photopeaks of ^{60}Co appeared at 1·17 and 1·33 MeV, and were due to the original cobalt content of the catalyst; in addition there were the 0·51- and 0·81-MeV peaks of radioactive ^{58}Co formed from nickel. In the spectrum of the nickel standard only the 0·51- and 0·81-MeV photopeaks of ^{58}Co appeared (Fig. 6) which indicated that the ^{60}Ni(n, p)^{60}Co nuclear reaction did not proceed to an appreciable extent.

In the γ-spectra of used nickel catalyst obtained with different amplification (Figs. 7 and 8) appeared the peaks of ^{58}Co and ^{60}Co. The photopeak of mercury

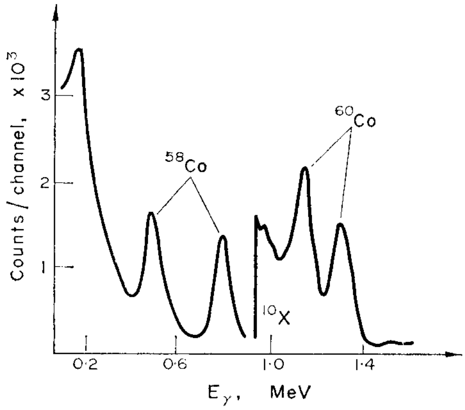

Fig. 7.—γ-Spectrum of used nickel catalyst.

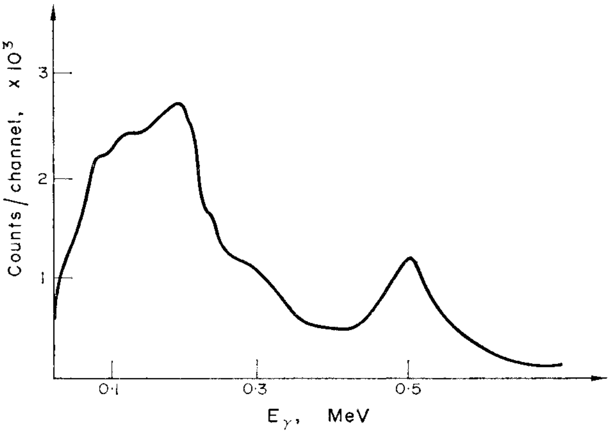

Fig. 8.—γ-Spectrum of used nickel catalyst at higher amplification.

merged in the high-intensity Compton range. On subtraction of the ^{60}Co standard spectrum from the complex spectrum the 1·12-MeV peak of ^{65}Zn appears (Fig. 9), by means of which small amounts of zinc can be determined, although with rather a large error.

Palladium and zinc in palladium catalyst can be determined from the γ-spectra by a direct instrumental method using a scintillation detector.

In the case of nickel catalysts nickel and cobalt can be determined by the method described. The results of the measurements (referred to 150 mg of catalyst, this being the weight of one grain) are presented in Table II.

Direct instrumental measurements with a Ge(Li) semiconductor detector

In the γ-spectrum of the palladium catalyst photopeaks appear at 0·24, 0·31, 0·34 and 1·12 MeV, which are characteristic of the daughter-isotope ^{111}Ag (formed from the radioisotopes of palladium) and of the ^{65}Zn radioisotope. The error of determination by computer-evaluation of the peak areas of the 0·34-MeV peak of

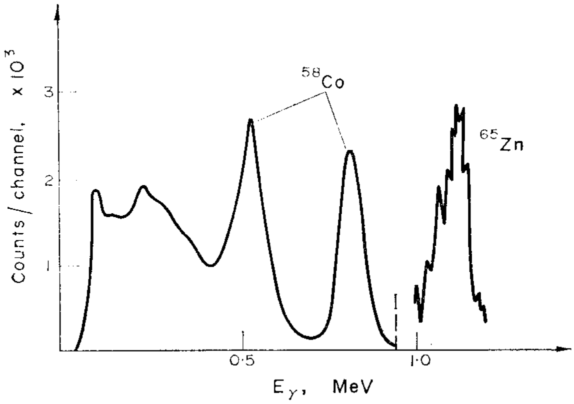

FIG. 9.—γ-Spectrum of used nickel catalyst after subtraction of the γ-spectrum of ^{60}Co standard.

TABLE II.—RESULTS OF STUDIES ON PALLADIUM AND NICKEL CATALYSTS (BY DIRECT INSTRUMENTAL MEASUREMENT)

	Measured Zn		Measured Pd	
Palladium catalyst	Average, *mg/grain**	Max. devn. from the mean, %	Average, *mg/grain*	Max. devn. from the mean, %
Unused	0·057	±8·8	0·059	±17
Used	0·061	±8·1	0·060	±20
	Measured Ni		**Measured Co**	
Nickel catalyst	Average, *mg/grain*	Max. devn. from the mean, %	Average, *mg/grain**	Max. devn. from the mean, %
Unused	48·9	±1·2	0·015	±7·0
Used	46·9	±1·6	0·014	±5·0

* Mean weight of a grain was 150 mg.

palladium and 1·12-MeV peak of zinc is 5–10%, *i.e.*, these elements can be determined from the γ-spectra.

In the γ-spectrum of used palladium catalyst which contains a small amount of mercury the 0·279-MeV peak of ^{203}Hg radioisotope appeared separately only if a biased preamplifier was used in the measuring equipment. By use of this equipment photopeaks differing by 5 KeV can be resolved. The spectrum of the palladium standard was measured with this equipment after activation (Fig. 10) and after 5 days of cooling (Fig. 11). The figures show that the radioisotopes of palladium transform to ^{111}Ag, because the peaks of the latter appear.

The mercury content of palladium catalyst can be determined without destruction only at concentrations higher than 100 ppm, with an error of ±10–15%.

In the γ-spectra of nickel catalyst taken with a semiconductor detector the 0·51 and 0·81-MeV peaks of ^{58}Co, the 1·17- and 1·33-MeV peaks of ^{60}Co and the 1·12-MeV peak of ^{65}Zn all appeared. In the case of used catalyst contaminated with mercury the 0·279-MeV photopeak of ^{203}Hg appeared in the high-intensity Compton region of these isotopes. Accordingly only the nickel, cobalt and zinc could be determined by evaluation by computer, with an error of ±6–10%.

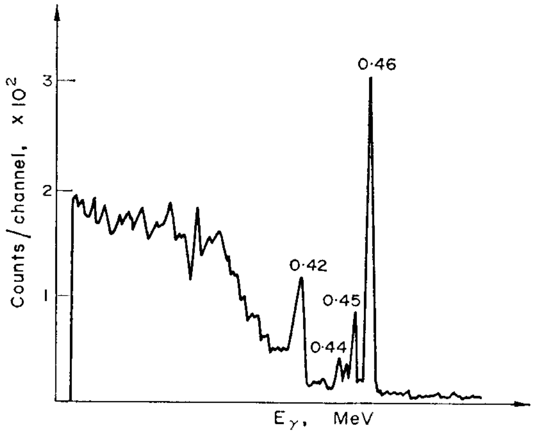

FIG. 10.—γ-Spectrum of an activated palladium standard, made by means of a Ge(Li) semiconductor detector.

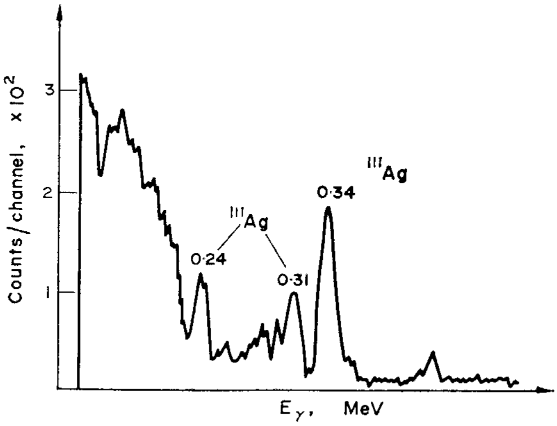

FIG. 11.—γ-Spectrum of palladium standard after 5 days cooling, made by means of a Ge(Li) semiconductor detector.

It can be concluded from the results of direct instrumental studies on catalysts that it is advisable to use a radiochemical separation before determination of trace contaminants, in order to increase sensitivity and accuracy. This is justified, since we wish to determine other trace contaminants for which 8–10 days of cooling are not allowable.

Studies involving radiochemical separation

For the separation of the radioisotopes of trace contaminants the heterogeneous isotopic exchange on metal sulphide precipitates (developed by us[4]) was used. Isotopic exchange was performed on a thin layer (2–3 mm) of the precipitate by a flow technique. The sulphide of an inactive isotope of the ion to be determined was used as the solid phase in each case.

Thus to retain radioactive mercury(II) ions, inactive mercury(II) sulphide was used. Isotopic exchange was carried out in strongly acid solution (1*M* nitric acid), as

TABLE III.—DETERMINATION OF MERCURY AND ZINC IN PALLADIUM AND NICKEL CATALYSTS, AFTER ISOTOPIC EXCHANGE

Sample	Hg		Zn	
	Average, *mg/grain*	Max. devn. from the mean, %	Average, *mg/grain*	Max. devn. from the mean, %
Unused Pd catalyst	—	—	0·061	±4·0
Used Pd catalyst I	0·057	±1·5	0·059	±5·0
II	0·010	±10	0·061	±5·0
III	0·008	±30	0·057	±5·0
Unused Ni catalyst	—	—	0·029	±13
Used Ni catalyst I	0·167	±2	0·030	±13
II	0·137	±3	0·030	±13

the selectivity of separation was found to be highest in this medium. Mercury(II) sulphide precipitate completely retained mercury(II) ions in strongly acid medium, whereas the radioisotopes of zinc, cobalt, palladium, sodium, copper, antimony and arsenic were not retained at all. Radio-zinc ions were separated on zinc sulphide precipitate by isotope exchange. From 0·1*M* nitric acid solution the degree of retention was 99% for radio-zinc, 100% for radio-mercury, 50% for radio-palladium, 7% for cobalt and 0% for sodium. The retention of mercury was to be expected because of the well known precipitate exchange phenomenon.

The retention of palladium and cobalt can be suppressed to 1–2% by adding inactive cobalt or palladium ions to the solution before isotopic exchange.

For the determination of mercury in palladium and nickel catalysts, 1 ml of the stock solution used for the direct instrumental measurements was diluted to 10 ml with 1*M* nitric acid, transferred to a burette and passed at the rate of about 1 ml/min (by dropwise addition and suction) through about 300 mg of mercury(II) sulphide precipitate placed on the filter. The burette was rinsed with about 2 ml of 1*M* nitric acid and this also passed through the precipitate. The γ-spectrum of the mercury (II) sulphide precipitate was recorded with the purpose of evaluation and checking the selectivity of the isotopic exchange.

The mercury present in 1-ml portions of the solutions of mercury standards irradiated under the same conditions as the samples, was retained on mercury(II) sulphide as described above. The products served as a basis for quantitative evaluation of the samples. The isotopic exchange on mercury(II) sulphide is so selective for the components of the samples studied that relative measurements can be made even with an energy-selective scaler.

The zinc content of the catalysts was determined from the filtrate obtained after the isotopic exchange on mercury(II) sulphide. The pH of the filtrate was adjusted to 2, then 10 mg of palladium were added in the case of palladium catalyst and 10 mg of cobalt in the case of nickel catalyst, and the solution was passed through about 300 mg of zinc sulphide at a rate of 0·2–0·3 ml/min by suction. Zinc standard was treated similarly. By the method described the mercury and zinc contents were determined in palladium and nickel catalysts contaminated to different extents. The results of the determinations are presented in Table III. Heterogeneous isotopic exchange, used in the analysis of catalysts, is fast and selective besides having satisfactory accuracy.

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Zusammenfassung—Ein Neutronenaktivierungsverfahren zur Bestimmung der aktiven Bestandteile und der Verunreinigungen in Hydrier-Katalysatoren wurde entwickelt. Die aktiven Bestandteile von Palladium- und Nickelkatalysatoren (Pd und Ni) sowie die in kleinen Mengen anwesenden Verunreinigungen Zn und Co wurden mit einem direkten instrumentellen Verfahren bestimmt. Ein NaJ(Tl)-Szintillator und ein Ge(Li)-Halbleiter wurden in Verbindung mit einem Vielkanalanalysator für die Messungen verwendet. Zur Auswertung der Gammaspektren wurde ein Computer benutzt. In kleinen Mengen anwesende Verunreinigungen wurden auch mit Hilfe eines radiochemischen Abtrennverfahrens bestimmt, das auf heterogenem Isotopenaustausch an Quecksilber(II)sulfid- und Zinksulfid-Niederschlägen beruht.

Résumé—On a élaboré une méthode par activation de neutrons pour la détermination des constituants actifs et des contaminants dans les catalyseurs d'hydrogénation. Les constituants actifs des catalyseurs au palladium et au nickel (Pd et Ni) et les contaminants Zn et Co présents en petites quantités ont été déterminés par une méthode instrumentale directe. Un scintillateur NaI (Tl) et un semi-conducteur Ge (Li) connectés à un analyseur multi-canaux ont été utilisés pour les mesures. On a utilisé une calculatrice pour évaleur les spectres γ. Les contaminants présents en petite quantité ont aussi été déterminés au moyen d'une méthode de séparation radiochimique basée sur l'échange isotopique hétèrogène sur des précipités de sulfure de mercure(II) et de sulfure de zinc.

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APPLICATION OF DISPLACEMENT REACTIONS IN FLAME PHOTOMETRY—I

THE DETERMINATION OF PHOSPHATE BY A FLAME EMISSION METHOD

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Summary—Phosphate ions decrease the flame emission of calcium, but this effect can be partly offset by adding a second metal which partly displaces calcium from the non-excitable species. For the determination of phosphate the sample solution is divided into four equal parts; to each of these, various amounts of calcium and barium ions are added such that the total (molar) concentration of the metals is constant. Plotting the intensity measured at 630 nm *vs.* the calcium content of the solution gives a straight line, the slope of which depends on the concentration of phosphate ions present. The method is suitable for rapid determination of phosphate. Accuracy and precision are within the usual limits characteristic of flame photometric methods.

EMISSION FLAME PHOTOMETRIC methods are frequently applied in chemical laboratories. Their main advantages are simplicity of operation, speed and reasonable precision. The disadvantages, such as chemical and spectral interferences and a certain hazard in manipulation of gases, can easily be overcome by intelligent and careful work. Because the gases used in emission flame photometry offer relatively low energies for excitation, the range of elements which can be determined by flame photometry is rather limited. Though according to the literature,[1] procedures for the determination of more than fifty elements are known, flame photometric determinations are in practice restricted to about ten of these, all metals.

The few methods described for the determination of non-metallic elements fall into two categories. First, some of the non-metals can be determined by measuring the emission of the element or its compounds, *e.g.*, boron can be determined by measuring the emission of the methyl ester of boric acid. On the other hand, some of these elements, mainly in the form of oxo-ions, suppress or enhance the emission of certain metal ions, and this action can, within limits, be proportional to the concentration of the particular ion, so that a quantitative determination can be made. This principle was applied by Dippel, Bricker and Furman[2] for the determination of phosphate by measuring the decrease in emission from calcium. The weakness of this method lies in the fact that the proportionality between the decrease in emission and the concentration of phosphate exists only over a limited concentration range. If the phosphate concentration exceeds a certain value, there is no measurable variation in the calcium emission. Another method suggested more recently for the flame photometric determination of phosphate, by Ratner and Schneider,[3] makes use of the fact that the depressive action does not occur at high flame temperatures. In a first measurement at higher temperature the amount of calcium is measured, this is followed by a measurement of the depressed signal at a lower temperature. From the two results the phosphate content can be determined with an increased accuracy.

Our method makes use of displacement reactions which occur if phosphate, calcium and barium ions are present in one solution. If the phosphate concentration is kept constant, while the relative concentrations of calcium and barium are varied but their total (molar) concentration is kept constant, the measured calcium emission will increase in proportion to the calcium content; the slope of the emission *vs.* concentration (of calcium) curve depends on the phosphate content of the sample.

EXPERIMENTAL

Instruments

Measurements were made both with a simple filter instrument and an instrument with a prism monochromator. The Zeiss Model 3 (Jena) flame photometer was used with the air–acetylene burner. The optimum gas pressures were adjusted according to the manufacturer's recommendation. The calcium interference filter supplied with the instrument was used; this has a maximum transmission at 630 nm with a halfwidth of about 15 nm. The gain was adjusted to obtain a maximum reading of 300 units of the swinging galvanometer (*i.e.*, 30% of full-scale deflection). The Unicam SP 90 combined atomic-absorption and flame-emission spectrophotometer was used in its emission mode. The instrument was equipped with an AEI 10S potentiometer recorder and readings were made using the standard Meker acetylene–air burner. The following parameters were held constant: air flow-rate: 5 l./min, burner height: 20 mm (measured on the scale), slitwidth: 0·1 nm, damping: 4. The acetylene flow-rate was adjusted to give maximum signal in each case, and the gain was adjusted as required.

Reagents

Calcium chloride, 0·5*M*. Prepared by dissolving analytical-grade calcium carbonate in dilute hydrochloric acid.

Barium chloride, 0·5*M*. Prepared from analytical-grade barium chloride dihydrate.

Diammonium hydrogen phosphate, 0·1*M*. Prepared from analytical-grade reagent.

Solutions used for the study of interferences were prepared from the purest available reagents. Metals were added in the form of chlorides; anionic interferences were studied both with the free acids and with their ammonium salts.

Procedure

From 0·5*M* calcium chloride (CA) and 0·5*M* barium chloride (BA) make up four solutions:

Solution *A* 20 parts of CA + 30 parts of BA
Solution *B* 15 parts of CA + 35 parts of BA
Solution *C* 10 parts of CA + 40 parts of BA
Solution *D* 5 parts of CA + 45 parts of BA

These solutions can then be stored indefinitely.

Make up 100 ml of stock solution of the sample to contain 2–8 mmole (200–800 mg) of phosphate, and 20 ml of concentrated hydrochloric acid. In each of four beakers, place 20 ml of the stock solution and 5 ml of one of solutions *A*, *B*, *C* or *D*. Mix the solutions well and measure the flame emission intensities at 630 nm. In a second set of measurements replace the sample solution with 20 ml of water. Plot the emission values *vs.* calcium concentrations (10, 20, 30 and 40 mmole), draw the straight lines and calculate h_0/h_x values as shown in Fig. 4B. Determine the concentration of phosphate in the sample from a calibration curve, obtained in a similar way.

Note. For 0·2–0·8 mmole (20–80 mg) of phosphate use solutions prepared by ten-fold dilution of *A*, *B*, *C* and *D*. By variation of the total concentration of the alkaline earth metals, higher or lower amounts of phosphates can be determined.

DISCUSSION

Under the experimental conditions given, the emission of calcium is strongly depressed in the presence of phosphate, decreasing linearly with increase in the amount of phosphate present until the molar ratio of phosphate to calcium reaches the value 0·67; this corresponds to the formation of tricalcium orthophosphate $Ca_3(PO_4)_2$.[4] If the amount of phosphate relative to calcium is higher than this, the emission becomes almost constant; the signal being only 15–20% of that measured in the absence of phosphate. This type of effect has been widely studied in the past fifteen years, and its explanation has also been attempted.[5–8]

The depressive effect of phosphate on the calcium emission is due to a chemical reaction between calcium and phosphate ions. Since the signal is not completely suppressed, it is obvious that the reaction reaches an equilibrium; there remain free calcium atoms capable of emission. This equilibrium can be shifted by the addition of another metal, which shows similar behaviour to calcium in the presence of phosphate.

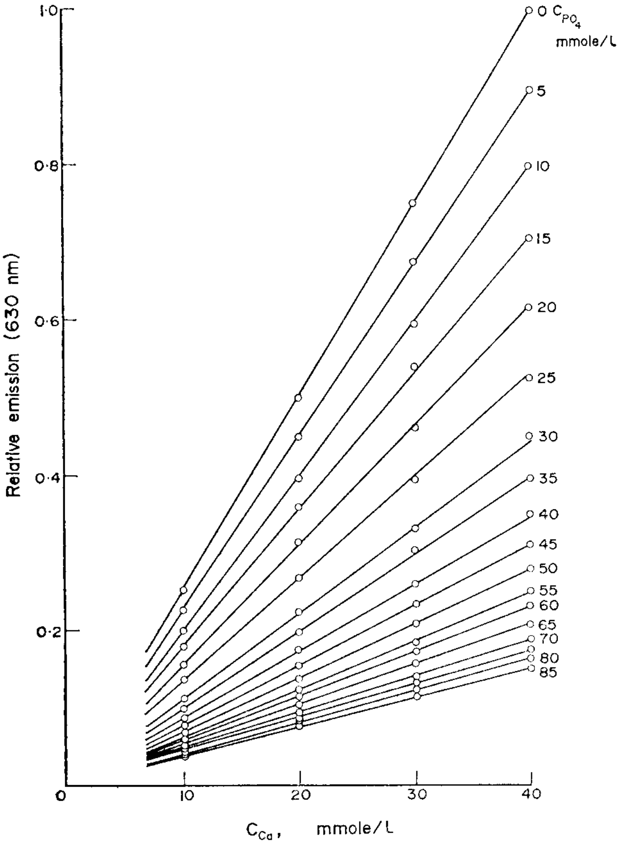


FIG. 1.—Emission for calcium in solutions containing phosphate and barium, such that total metal concentration is always 0·10*M*. Sufficient hydrochloric acid is present to prevent precipitation of the metal phosphates.

The greater the amount of this second metal present, the more calcium will be displaced. If the total metal concentration is kept constant (that is, the metal–phosphate concentration ratio remains unchanged), the signal obtained from the emission of calcium is proportional to the amount of calcium present. This principle can be used for the determination of alkaline earth metals[9] and of lanthanum[10] in the presence of interfering ions.

The slope of the intensity *vs.* calcium concentration plot varies with phosphate concentration; the higher the latter, the smaller the slope of the curve (Fig. 1). The slope depends solely on the concentration of phosphate, and with a suitable calibration curve phosphate concentrations can be determined. The range of phosphate concentration can be narrowed or extended by varying the barium concentration, being extended by using an increased metal ion concentration, and *vice versa.* The set of curves, shown in Fig. 1, behaves like a half-open fan, which can be opened further or closed at will, over a considerable range. Figure 2 shows a set of similar curves with 0·15*M* total alkaline earth metal concentration. The useful range is in this case extended up to 0·07–0·075*M* phosphate. Figure 3 shows narrowing of the range to 0–0·025*M*. As the difference between the slopes of the individual curves becomes larger, the precision of determination increases.

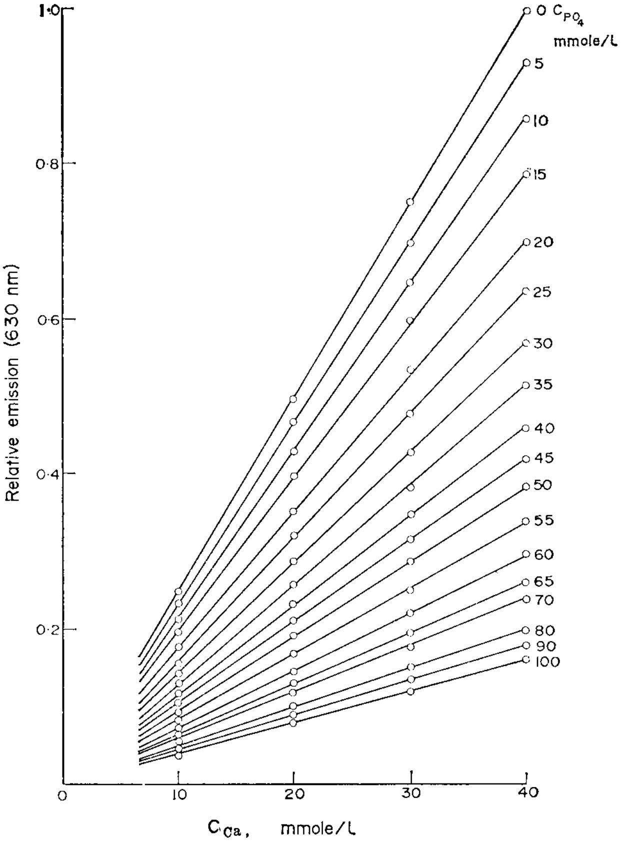


FIG. 2.—As Fig. 1, but total metal concentration = 0·15*M*.

The fact that the extension or contraction of the useful range is achieved by adding more or less barium (but not calcium) to the solution means that the flame photometer is always operated at the same sensitivity, which is an advantage for routine work.

Evaluation of results

Though the set of curves shown in Figs. 1–3 could be used as a chart from which results obtained with unknown samples could be evaluated, it is more practical to use a calibration curve produced from these results. A comprehensive study[11] of the possible variables revealed that the best way to draw the calibration curve was to plot

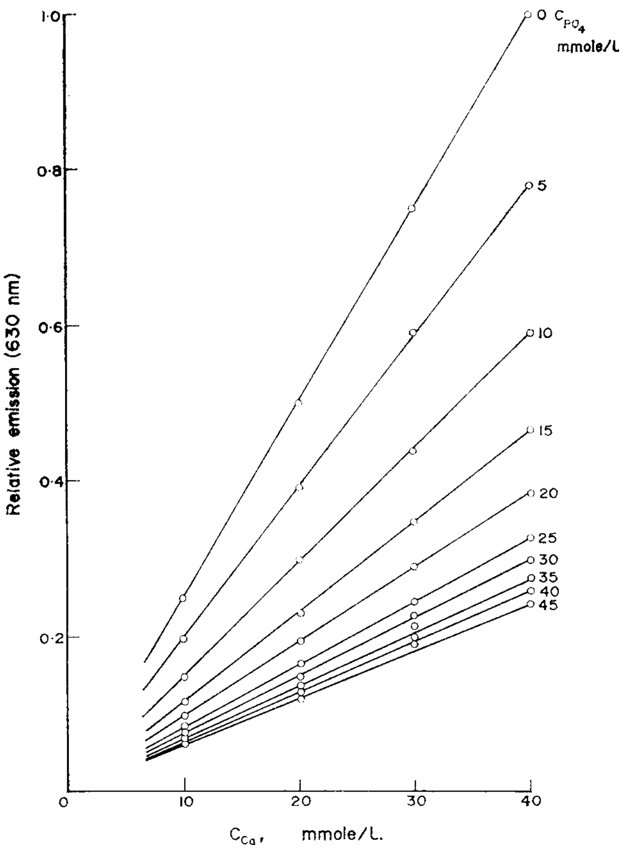
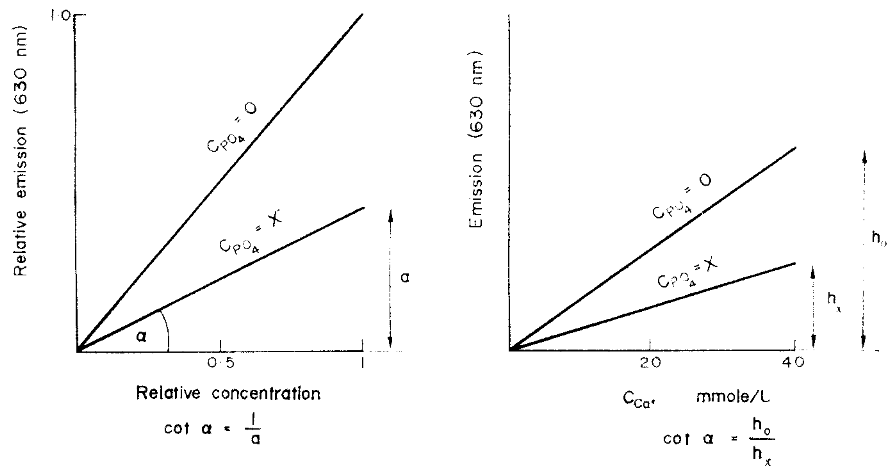


FIG. 3.—As Fig. 1, but total metal concentration = 0·05*M*.

the cotangents of the slope angles of the individual lines as a function of the phosphate concentration. If the relative emissions are plotted (Fig. 4A) the reciprocal value of the height of the line, corresponding to the maximum calcium concentration, gives the required value. If on the other hand, emission readings themselves are plotted against calcium concentration (without calculation of the relative emission values), as shown in Fig. 4B, the two heights, h_0 (which corresponds to the solutions which contain no phosphate) and h_x (the value obtained with the unknown sample) are found, and their ratio then gives the required cotangent. Theoretically it would be sufficient to make two measurements only, that is to use two solutions with equal calcium concentrations, one containing no phosphate at all, the other containing the unknown amount, and to calculate the ratio of their emissions. By using four solutions however, as we suggest, four points on each line (plus the fifth point in the origin) are measured, giving an improved reliability to the results.

Calibration curves, drawn from the graphs given in Figs. 1–3, have a definite S-shape (Fig. 5). Mathematically these can be expressed as

$$y = y_0\left[1 + \exp -\left\{\frac{4b}{y_0} . (C - C_i)\right\}\right]^{-1} + g$$



(A) (B)

Fig. 4.—Measurement of the slope of the curves.

where c is the phosphate concentration, y is the variable (cot α) plotted on the calibration curve and y_0, b, C_i and g are constants. For the middle curve, which corresponds to 0·1M total metal concentration, these constants are $y_0 = 6{\cdot}25$; $C_i = 50$; $b = 0{\cdot}075$ and $g = 0{\cdot}5$. Details of the mathematical analysis of this curve are described elsewhere;[11] they are of little interest for the practical analytical chemist.

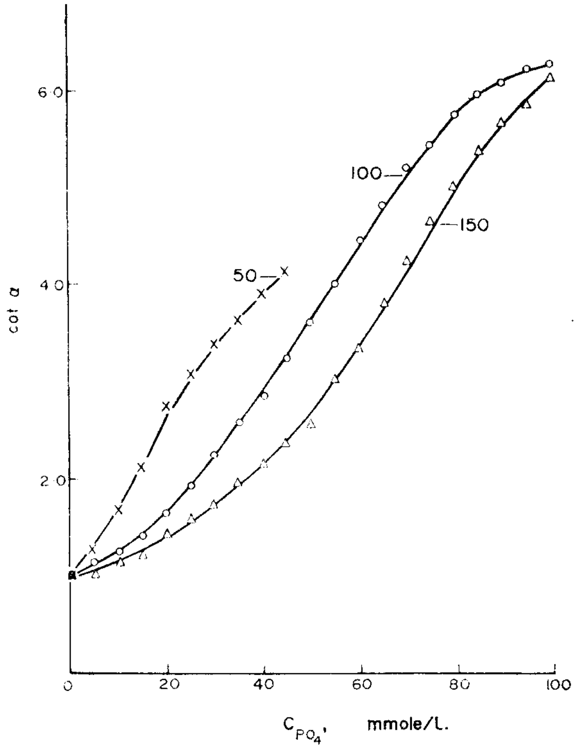


Fig. 5.—Calibration curves for the determination of phosphate at total metal concentrations of 0·05, 0·10 and 0·15M.

The middle parts of the curves are nearly straight lines, and have similar slopes for the different total alkaline earth concentrations; thus the sensitivity of these determinations remains the same for all concentration ranges examined in this study.

Experiments were made with solutions containing 0–0·01*M* phosphate when the total alkaline earth metal concentrations used were 5, 10 and 15 m*M*. The experimental conditions were the same as given above, but the gain of the instruments had to be readjusted appropriately. Results under such circumstances are also satisfactory. With 0–1 m*M* phosphate and 0·5, 1 and 1·5 m*M* total alkaline earth metal, the results are not sufficiently reproducible, mainly because of limitations in the sensitivity of the radiation detector.

Results, accuracy and precision

A typical set of results, obtained with 100 and 10 m*M* total alkaline earth metal concentration, is shown in Table I. The coefficients of variations, obtained by measuring the same samples on 12 different working days (that is, after switching on the flame photometer, and readjusting the parameters), are shown in the last column. As can be seen, these decrease slightly with increase of phosphate concentration. An explanation of this, based on the application of the law of propagation of errors, has been attempted.[11]

TABLE I

Concentration of phosphate, m*M*	Found	Error %	Coefficient of variation %
(a) Total metal concentration: 100 m*M*			
25·0	25·5	+2·2	±4·1
30·0	30·8	+2·6	±3·7
35·0	35·6	+1·7	±3·5
40·0	40·8	+2·0	±3·2
45·0	45·1	+0·3	±3·0
50·0	50·6	+1·2	±2·9
55·0	56·4	+2·8	±2·8
60·0	60·8	+1·3	±2·7
65·0	65·8	+1·2	±2·6
70·0	71·2	+1·7	±2·5
75·0	75·9	+1·4	±2·3
80·0	81·4	+1·8	±2·3
(b) Total metal concentration: 10 m*M*			
3·0	3·15	+5	—
4·0	4·06	+1·5	—
5·0	5·15	+3	±4·4
6·0	6·08	+1·4	—
7·0	7·12	+1·7	—
8·0	8·10	+1·3	—

These results indicate that the method can be applied for a rapid determination of phosphate. The total time required, excluding the switching-on and warming up time of the instrument is less than 10 min, and even this is mainly used for dissolution and preparation of solutions. The method was applied for the rapid assay of fertilizers based on ammonium phosphate.

Effect of foreign ions

Small amounts (not exceeding a 1:1 molar ratio) of antimony, copper, magnesium, manganese, nickel, potassium, sodium and acetate do not cause errors > ±5% in the final result. Ammonium ions, antimony and chloride can be tolerated in amounts 10 times that of the phosphate. Sodium can also be tolerated in 10-fold amounts (relative to phosphate) if an instrument with a monochromator is used with a fairly narrow slitwidth. Medium interference (*e.g.*, an error below 10%) was found in the presence of zinc and mercury in amounts equimolar with the phosphate, and with 10-fold amounts of manganese, potassium and sodium (with a filter instrument). Large errors were caused by the presence of equimolar or 10-fold amounts (relative to phosphate) of aluminium, chromium, cobalt, iron, strontium, tin and nitrate. A 10-fold amount of copper, magnesium, nickel or acetate causes large errors. Cobalt and iron cause negative errors, but all other ions cause positive ones.

Acknowledgements—The authors wish to thank Professor Cecil L. Wilson for his interest in this work and the Government of Northern Ireland for a research grant to P. J. S.

Zusammenfassung—Phosphationen vermindern die Flammenemission von Calcium, aber dieser Effekt kann zum Teil aufgehoben werden, wenn man ein zweites Metall zusetzt, das Calcium zum Teil aus der nicht anregbaren Spezies verdrängt. Zur Bestimmung von Phosphat wird die Probenlösung in vier gleiche Teile geteilt; zu jedem Teil werden verschiedene Mengen Calcium und Bariumionen gegeben, in der Weise, daß die (molare) Gesamtkonzentration der Metalle konstant ist. Trägt man die bei 630 nm gemessene Intensität gegen den Calciumgehalt der Probe auf, so erhält man eine Gerade, deren Steigung von der Phosphationenkonzentration abhängt. Die Methode eignet sich zur raschen Phosphatbestimmung. Genauigkeit und Richtigkeit liegen im üblichen Rahmen flammenphotometrischer Methoden.

Résumé—Les ions phosphate abaissent l'émission de flamme du calcium, mais cette influence peut être partiellement compensée par l'addition d'un second métal qui déplace partiellement le calcium de l'espèce non excitable. Pour le dosage du phosphate, la solution échantillon est divisée en quatre parties égales; à chacune de celles-ci, on ajoute des quantités diverses d'ions calcium et baryum, de sorte que la concentration totale (molaire) des métaux soit constante. Le tracé de l'intensité mesurée à 630 nm par rapport à la teneur en calcium de la solution donne une ligne droite dont la pente dépend de la concentration des ions phosphate présents. La précision et la justesse sont situées dans les limites habituelles caractéristiques des méthodes de photométrie de flamme.

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DETERMINATION OF THE OPTIMUM RESULTANT EFFECT OF FACTORS INFLUENCING HETP-VALUES

THE FOLLOWING OF PARALLEL DIFFUSION AND MASS-TRANSFER PROCESSES

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Summary—One of the most important problems of analytical gas chromatography, both in theory and in practice, is the following of parallel diffusion and mass-transfer processes, with the primary aim of determining the optimum resultant effect of factors influencing the HETP-value. Starting from the work of Costa Neto and collaborators, it is shown that the approximate equation developed by these authors can be deduced from the theory of gas chromatography. Subsequently, by means of the new approximation, the effect of individual factors is determined, and processes proceeding simultaneously are followed.

GAS CHROMATOGRAPHY belongs to the group of multistep operations carried out with continuous contact between two phases, and for want of an exact explicit solution differential equations are used to describe them. These equations cannot in practice be utilized for following the processes occurring, or for the examination of the factors affecting them, though in theory they presumably may describe the processes correctly. This is why the gas chromatographic process is studied and described with the aid of approximative methods which are much simpler, though less exact, than are differential equations.

Among these methods the two best known are the so-called plate theory of Glueckauf[1] and the kinetic or rate theory linked with the name of van Deemter.[2]

Since practical experience has shown that the deviation of the results exceeds the range of experimental errors in the investigation both of the factors influencing the HETP values and of the simultaneous diffusion and mass-transfer processes, the need arose for a new and closer approximation, comprising also van Deemter's equation.

After critical evaluation of pertinent literature, it was thought that the equation published by Costa Neto and co-workers[3] is suitable for this purpose:

$$\mathrm{HETP} = A + \frac{B}{u} + Cu + \frac{D}{u^2} + Eu^2 \tag{1}$$

where HETP is the column length (mm) equivalent to one theoretical plate, and A, B, C, D and E are constants which at constant temperature and under unchanged gas chromatographic conditions are dependent only on the nature of the substance investigated, and u is the linear carrier-gas flow-rate (mm/sec). (It should be mentioned here that in our present work we do not wish to take part in the dispute that has flared up again recently concerning the definition, interpretation, *etc*, of the theoretical plate number or of the HETP value.)

THEORY

Let us write, according to Glueckauf, the theoretical plate number of a substance in a given gas-chromatographic system:

$$n = 16\left(\frac{t_R}{w}\right)^2 \tag{2}$$

where n is the number of theoretical plates of the substance, t_R is the retention time of the substance, w is the width of the chromatographic peak of the substance (in the same units as t_R). On the basis of the theoretical plate number and the column length, the column length corresponding to one theoretical plate, the so-called HETP-value,[4] is obtained, since

$$\text{HETP} = L/n \tag{3}$$

where L is the column length (mm).

Equation (1) can be deduced with the aid of equation (3) from equation (2), by using the following relationships, proved already in one of our earlier works:[5]

$$t_N = m_1/u \tag{4}$$

and

$$w = m_2 \,.\, \zeta + b \tag{5}$$

where t_N is the net retention time (sec), m_1 is the slope of the linear equation (4) (mm), m_2 is the slope of the linear relationship (5) (mm), and b is the intercept with the ordinate (sec).

ζ is the linear rate coefficient (sec/mm) and is given by

$$\zeta = \frac{(u + F)}{u^2}, \tag{6}$$

where F is a constant depending on the gas-chromatographic system and on the nature of the substance (mm/sec).

Equation (2) can be written in the following form from consideration of equations (4) and (5):

$$n = 16\left(\frac{m_1/u}{m_2\zeta + b}\right)^2. \tag{7}$$

The substitution of (7) into (3) results in

$$\text{HETP} = \frac{L}{16}\left(\frac{m_2\zeta + b}{m_1/u}\right)^2. \tag{8}$$

On substitution of (6) into (8), and transformation, the following expression is obtained:

$$\text{HETP} = \frac{L}{16}\left(\frac{bu}{m_1} + \frac{m_2}{m_1} + \frac{m_2F}{m_1u}\right)^2. \tag{9}$$

Expansion gives

$$\text{HETP} = \frac{L}{16}\left[\left(\frac{b}{m_1}\right)^2 u^2 + 2\left(\frac{b}{m_1}\right)\left(\frac{m_2}{m_1}\right) u + \left(\frac{m_2}{m_1}\right)^2 + 2\left(\frac{b}{m_1}\right)\left(\frac{m_2F}{m_1}\right) + \right.$$
$$\left. + 2\left(\frac{m_2}{m_1}\right)\left(\frac{m_2F}{m_1}\right)\Big/u + \left(\frac{m_2F}{m_1}\right)^2\Big/u^2\right]. \tag{10}$$

On introduction of the identities

$$A = \frac{L}{16}\left[\left(\frac{m_2}{m_1}\right)^2 + 2\left(\frac{b}{m_1}\right)\left(\frac{m_2F}{m_1}\right)\right] \tag{11}$$

$$B = \frac{L}{8}\left(\frac{m_2}{m^1}\right)\left(\frac{m_2F}{m_1}\right) \tag{12}$$

$$C = \frac{L}{8}\left(\frac{b}{m_1}\right)\left(\frac{m_2}{m_1}\right) \tag{13}$$

$$D = \frac{L}{16}\left(\frac{m_2F}{m_1}\right)^2 \tag{14}$$

$$E = \frac{L}{16}\left(\frac{b}{m_1}\right)^2 \tag{15}$$

equation (10) becomes

$$\text{HETP} = A + \frac{B}{u} + Cu + \frac{D}{u^2} + Eu^2 \tag{16}$$

which is identical with equation (1), so it can be considered as proved that equation (1) can be deduced from the theory of gas chromatography.

In comparison with the well known equation of van Deemter, (1) and (16) contain two further constants (*D* and *E*). In our opinion, it is due to these two constants that this equation gives a better approximation for description of the gas chromatographic process, which of necessity involves a whole series of complicated interactions and simultaneous processes. Although the interpretation of these two constants is not yet fully clear, it is already certain that the constant *D*, the dimension of which is acceleration of volumetric gas-flow, (mm^3/sec^2) permits a better following of the diffusion processes.

The case is similar with the constant *E*, the dimension of which is reciprocal linear acceleration (sec^2/mm). This latter constant makes possible the better description of mass-transfer processes. Though the investigation and interpretation of both these constants necessitates further experimental work, it promises theoretical results of considerable importance.

On the basis of equation (16), the upper and lower limits of the applicability of the gas-chromatographic process in terms of the carrier gas flow-rate can be more easily interpreted. At high linear gas flow-rates, the value of Eu^2 becomes very large, and makes separation impossible. On the other hand, at very low linear velocities, when u is smaller than 0·001 mm/sec, the term D/u^2 becomes very large and prevents practical work.

HETP$_{\text{min}}$ is obtained by the differentiation of (16):

$$(\text{HETP})' = -\frac{B}{u^2} + C - 2\frac{D}{u^3} + 2Eu = \frac{2Eu^4 + Cu^3 - Bu - 2D}{u^3}\,. \tag{17}$$

Since (HETP)′ = 0 at the minimum, the numerator of the equation must be zero, *i.e.*,

$$2Eu^4 + Cu^3 - Bu - 2D = 0. \tag{18}$$

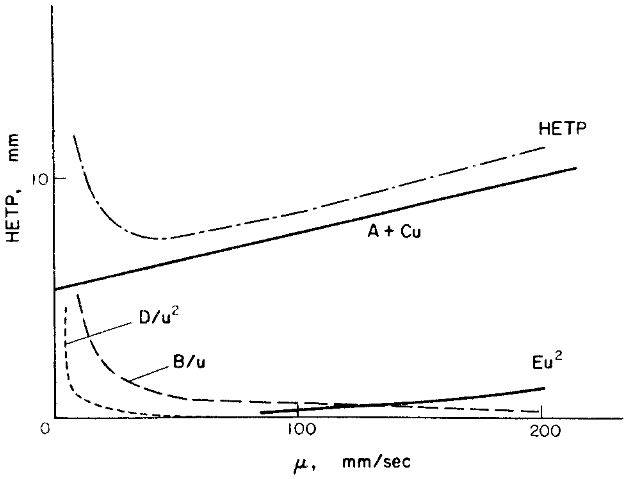

FIG. 1.—The function corresponding to equation (16) for a general case, apportioned to the several constants.

The solution of this fourth-degree equation gives the carrier gas flow-rate corresponding to $\mathrm{HETP}_{\mathrm{min}}$.

The general shape of the function corresponding to equation (16) is shown in Fig. 1, for a particular set of constants.

TABLE I.—VALUES FOR n-BUTANE IN A SPIRAL COPPER COLUMN 3·0 m LONG, 4·0 mm IN DIAMETER, PACKED WITH 12·5% w/w OF SILICONE OIL DC-550 ON 60/80 MESH CHROMOSORB W SUPPORT, AT 40·0 ± 0·1°C, IN NITROGEN AS CARRIER GAS

u mm/sec	A mm	B/u, mm	Cu, mm	D/u^2, mm	Eu^2, mm	HETP mm
10	0·69	1·40	0·16	1·21	0·02	3·48
20	0·69	0·70	0·33	0·30	0·07	2·08
30	0·69	0·47	0·49	0·13	0·15	1·93
40	0·69	0·35	0·66	0·08	0·26	2·03
50	0·69	0·28	0·82	0·05	0·41	2·24
60	0·69	0·23	0·98	0·03	0·59	2·52
70	0·69	0·20	1·15	0·02	0·80	2·85
80	0·69	0·18	1·31	0·02	1·04	3·23
90	0·69	0·16	1·47	0·015	1·32	3·65
100	0·69	0·14	1·64	0·012	1·63	4·10
110	0·69	0·13	1·80	0·010	1·97	4·59
120	0·69	0·12	1·97	0·008	2·34	5·12
130	0·69	0·11	2·13	0·007	2·75	5·68
140	0·69	0·10	2·29	0·006	3·19	6·27
150	0·69	0·09	2·46	0·005	3·66	6·90
160	0·69	0·09	2·62	0·005	4·16	7·56
170	0·69	0·08	2·78	0·004	4·69	8·25
180	0·69	0·08	2·95	0·004	5·27	8·98
190	0·69	0·07	3·11	0·003	5·87	9·74
200	0·69	0·07	3·28	0·003	6·50	10·54

EXPERIMENTAL

Carlo Erba Fractovap Model C, D and GD gas chromatographs were used with classical packed gas-chromatographic columns. The most important gas-chromatographic parameters are listed in connection with the examples given.

Table I shows the applicability of equation (16) to the results obtained for n-butane. The new

TABLE II.—CONSTANTS OBTAINED WITH n-HEPTANE UNDER THE EXPERIMENTAL CONDITIONS SUMMARIZED IN TABLE III

u, *mm/sec*	HETP-value, *mm* nitrogen as carrier	 argon as carrier
10	1·04	0·97
20	0·52	0·47
30	0·41	0·35
40	0·39	0·32
50	0·42	0·32
60	0·45	0·33
70	0·51	0·34
80	0·57	0·38
90	0·64	0·42
100	0·72	0·46
110	0·83	0·51
120	0·92	0·56
130	1·04	0·62
140	1·15	0·67
150	1·28	0·74
160	1·42	0·81
170	1·57	0·88
180	1·72	0·96
190	1·89	1·03
200	2·04	1·13
250	3·02	1·63
500	10·9	5·6
750	23·8	12·1
1200	41·6	21·1

TABLE III.—GAS-CHROMATOGRAPHIC PARAMETERS USED IN THE STUDY OF THE GAS-CHROMATOGRAPHIC BEHAVIOUR OF MEMBERS OF HOMOLOGOUS SERIES

Gas chromatograph: Carlo Erba Fractovap Model D
Detector: FID
Sensitivity: 16 × 100
Sample: 0·3 μl of model mixture introduced by means of a Hamilton syringe
Column: spiral aluminium tube, 2·40 m long, 2·0 mm in diameter
Column packing: 10 % w/w of SE-30 on 60/80 mesh Chromosorb W
Carrier gas: nitrogen at an inlet pressure of 100–300 kN/cm^2
Auxiliary gases:
    hydrogen, inlet pressure 14·2 kN/m^2
    oxygen, inlet pressure 14·9 kN/m^2
Column temperature: 100 ± 0·1°C
Evaporator temperature: 210·0 ± 1·0°C
Recorder: Speedomax G; 2·5 mV final amplitude, 1·0 sec response
Chart speed: 50·8 mm/min

approximation, equation (16), also makes it possible to study the factors affecting separation. As an example of our investigations in this respect, the effect of the nature of the carrier gas on the HETP-value is shown in Table II.

Equation (16) has also been used for study of the gas-chromatographic behaviour of members of a homologous series in terms of HETP-values; n-hexane, n-heptane and n-octane were used as model substances. Gas-chromatographic parameters used in the experimental series are summarized in Table III, and the constants obtained are in Table IV.

The constants determined made possible the comparative investigation and the following of the

TABLE IV.—CONSTANTS OBTAINED FOR n-HYDROCARBONS UNDER EXPERIMENTAL CONDITIONS SPECIFIED IN TABLE III, FOR HETP MEASURED IN mm

Substance	*A*	*B*	*C*	*D*	*E*
n-C_6	2·99	20·52	0·1145	43·86	$1{\cdot}365 \times 10^{-3}$
n-C_7	1·08	6·91	0·0530	13·76	$0{\cdot}811 \times 10^{-3}$
n-C_8	0·35	2·52	0·0210	6·56	$0{\cdot}470 \times 10^{-3}$

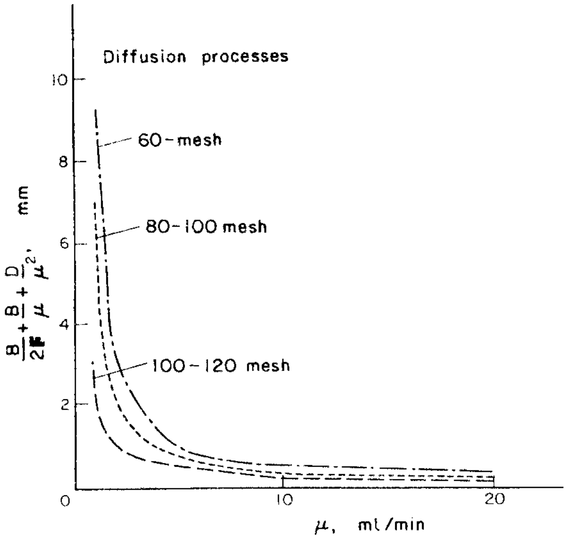

FIG. 2.—Course of the diffusion processes in the case of n-octane with supports of various grain size.

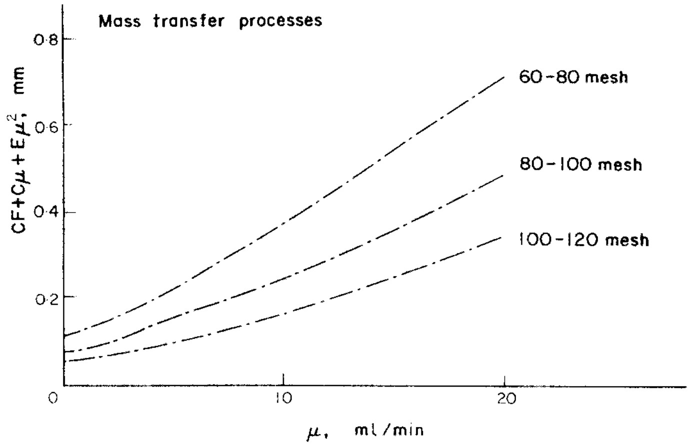

FIG. 3.—Curves characteristic of mass-transfer processes in the case of n-octane.

simultaneous diffusion and mass-transfer processes. Figure 2 shows the course of the diffusion processes, while Fig. 3 illustrates the curves characteristic of the mass-transport processes. Finally, the changes in HETP-value caused by column temperature are presented in Fig. 4.

DISCUSSION

The practical application of the equation discussed in the paper often meets difficulties, although the equation is theoretically correct. There are two reasons for

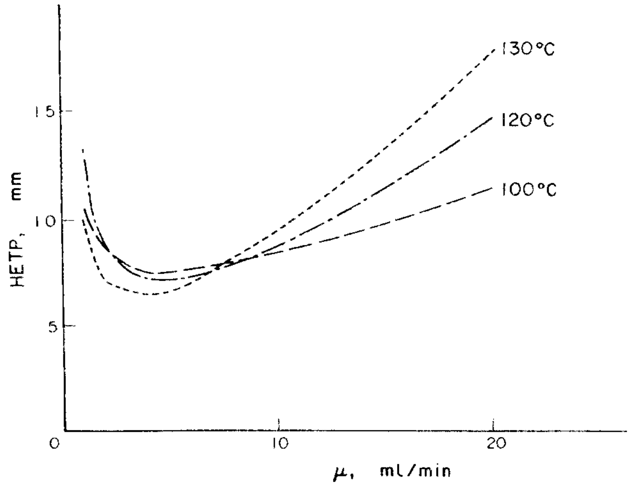

FIG. 4.—The effect of column-temperature on the HETP-value in the case of n-octane.

this. The first is that the conversion of volumetric carrier-gas flow-rate into linear flow-rate poses certain difficulties. The second is the fact that the determination of the constants is reliable only when calculated from the weighted arithmetic mean values of an adequate number of parallel measurements. According to our experience, when the determination of the volumetric carrier-gas flow-rate is made from the average of 11 parallel measurements, the factor necessary for the conversion into linear flow-rate is determined experimentally and then calculated, and the retention data are measured electronically (electronic timer), then very reliable data suitable for a variety of theoretical and practical investigations are obtained, which are worth the time and trouble spent for their determination. The few examples presented are intended rather for demonstration purposes and not to prove the applicability of the new approximation. Its merits will be verified by researchers using it.

Acknowledgement—We thank the firm Carlo Erba (Milan, Italy) for support materials and columns.

Zusammenfassung—Eines der wichtigsten Probleme der analytischen Gaschromatographie in Theorie und Praxis ist die Verfolgung paralleler Diffusions- und Massentransportprozesse, wobei primär der optimale Effekt der verschiedenen Faktoren erzielt werden soll, die den HETP-Wert bestimmen. Ausgehend von den Arbeiten von Costa Neto und Mitarbeitern wird gezeigt, daß man die von diesen Autoren aufgestellte Näherungsgleichung aus der Theorie der Gaschromatographie ableiten kann. In der Folge werden mit Hilfe der neuen Näherung die Einflüsse individueller Faktoren ermittelt und gleichzeitig ablaufende Prozesse verfolgt.

Résumé—L'un des problèmes les plus importants de la chromatographie en phase gazeuse analytique, tant en théorie qu'en pratique, est de suivre les processus parallèles de diffusion et de transfert de masse, avec le but primordial de déterminer l'influence résultante optimale de facteurs influant sur la valeur HETP. Partant du travail de Costa Neto et collaborateurs, on montre que l'équation approchée développée par ces auteurs peut être déduite de la théorie de la chromatographie en phase gazeuse. Par suite, au moyen de la nouvelle approximation, l'influence de facteurs individuels est déterminée, et les processus se développant simultanément sont suivis.

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RETENTION OF RADIONUCLIDES ON METAL SULPHIDE PRECIPITATES

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Summary—The retention of various radionuclides on metal sulphide precipitates has been studied. The sulphide precipitates quantitatively retained the common radionuclides. The condition for 100% retention in a thin layer is small particle size (a few μm) in the precipitate. This can be ensured by pulverization of the dried precipitate of metal sulphide. $^{203}Hg^{2+}$ is retained by mercury sulphide and $^{65}Zn^{2+}$ by zinc sulphide by isotopic exchange. The retention of foreign radioactive ions can be reduced or even eliminated by counter-carrier technique in cases where the retention is not due to chemical reaction, precipitate exchange. The isotopic exchange with mercury(II) sulphide and zinc sulphide enables mercury and zinc ions to be separated rapidly and determined in the presence of a number of interfering ions.

IN CONNECTION with the determination of metal contaminants, especially of zinc and mercury in hydrogenation catalysts by destructive activation analysis, there arose the idea of a systematic study of the possibilities of the separation and determination of traces of metal ions by heterogeneous isotopic exchange, or, speaking more cautiously, by retention on metal sulphide precipitates.

Heterogeneous isotopic exchange with precipitates has only recently been extensively used for quantitative separation or determination in the course of activation analysis. The isotopic exchange of solid silver sulphide with its ions in solution has been studied by Peschanski[1] by means of ^{110}Ag and ^{35}S. The isotopic exchange between radio-silver and silver halides was first recommended for quantitative determination by Langer.[2] Sunderman and Meinke[3] allowed a solution containing radioactive silver ions to react with silver chloride precipitated on a platinum wire. Rai, Nethaway and Wahl[4] have thoroughly studied the conditions under which $^{140}Ba^{2+}$, $^{90}Sr^{2+}$ and $^{113}Sn^{4+}$ are quantitatively retained from aqueous solutions on barium sulphate, strontium carbonate, and tin(IV) or tin(II) sulphide precipitates respectively by (according to their assumption) isotopic exchange. Hamaguchi, Onuma, Watanabe and Kuroda[5] utilized the exchange reaction of strontium between the sulphate precipitate and salt solution for separating carrier-free ^{90}Sr and ^{90}Y. Qureshi, Shahid and Hasany[6] used isotopic exchange with strontium sulphate or oxalate for the radiochemical separation of ^{90}Sr from aqueous solution. Qureshi and Shabbir[7] applied isotopic exchange with antimony trioxide to the radiochemical separation of antimony. In the course of the determination of tin in nickel Csajka[8] adsorbed the radioactive ^{125m}Sn isotope on tin dioxide precipitate after dissolving the activated sample. Girardi, Pietra and Sabbioni[9] studied the retention of different radioactive ions on twelve precipitates of ionic character, mainly on oxides and phosphates, and on ion-exchange resins, with special regard to the radiochemical possibilities of separation.

We have used the reaction

$$ZnS + {}^{*}Zn^{2+} \rightleftharpoons {}^{*}ZnS + Zn^{2+}$$

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as model reaction for the investigation of the isotopic exchange of sulphide precipitates. The asterisk denotes radio-zinc.

EXPERIMENTAL

Isotopic exchange or retention was studied by flow technique, which permitted rapid work, and, as the inactive precipitate was in contact with only a small amount of active solution in unit time, the technique ensured a higher ratio of inactive to active material than that existing if the solution had been shaken with the precipitate until equilibration. Filter paper was placed on the perforated glass plate of the glass funnel shown in Fig. 1 and a known amount of the precipitate placed on the filter paper. The necessary washing liquid and active solutions were poured on the precipitate, and the required rate of filtration was adjusted by suction. The degree of retention can be calculated from the original activity of the active solution poured on, and that of the filtrate (counts n_0 and n respectively). The exchange yield is given by

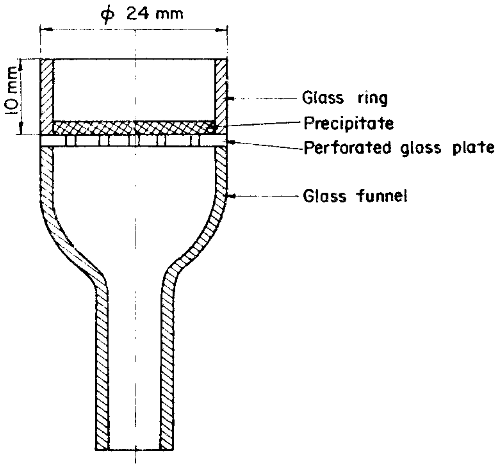

FIG. 1.—Filter for isotopic exchange.

$$Q = \frac{100(n_0 - n)}{n_0}\ \%.$$

For determination of metal traces the activity of the precipitates is measured after the exchange and related to that of a standard. A retention of 99–100% has to be ensured on 350–400 mg of precipitate, since this constitutes a layer thickness small enough not to cause an error due to self-absorption.

In the experiments 10 ml of the active solution at the required pH were passed through the suitably pretreated precipitate by suction, followed by 5 ml of nitric acid solution at the same pH as the active solution. The filtrate was diluted to 20 ml in a volumetric flask. The activity n of n 10-ml aliquot was measured; n_0 was measured at the same dilution. For the activity measurements a measuring head equipped with a hollow NaI(Tl) scintillator and an NK-108 energy-selective scaler produced by the Gamma Works (Hungary) were used, counting the total number of impulses under the corresponding photopeaks, in the differential mode. In this position the signal to noise ratio was so favourable that the counts measured for the filtrate exceeded the background even in the case of 99% retention. Gamma-spectra were recorded on an NTA-256 channel analyser constructed in the Hungarian Academy of Sciences Central Research Institute for Physics.

RESULTS

Isotopic exchange on zinc sulphide: effect of the structure of the precipitate on the exchange yield

The isotopic exchange was made with crystalline and amorphous zinc sulphide.

Preparation of crystalline zinc sulphide. $ZnSO_4 \cdot 7H_2O$ (18 g) and $(NH_4)_2SO_4$ (5 g)

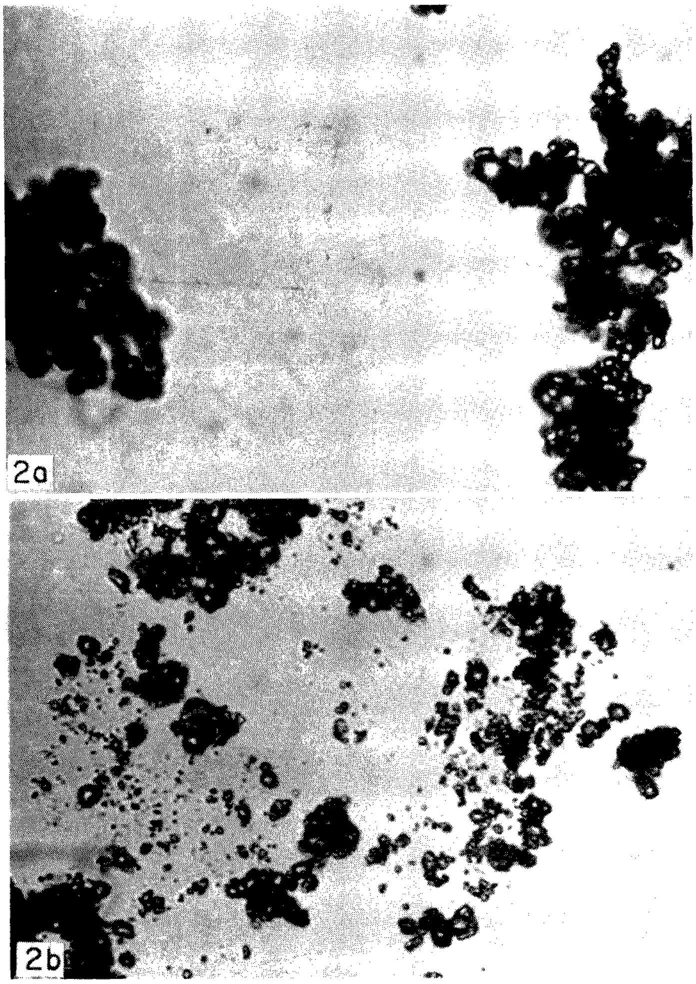

FIG. 2.—Photomicrograph of crystalline zinc sulphide precipitates. Apparatus: Zeiss NF research microscope M-990. (*a*) $Q = 40{\cdot}8\%$; (*b*) the same precipitate after 10 min powdering, $Q \sim 100\%$.

were dissolved in 200 ml of 0·01M sulphuric acid and the solution was heated to 60° and maintained at this temperature for 2·5 hr during which time gaseous hydrogen sulphide was passed through it with stirring. Then heating was stopped and gas passed for a further 0·5 hr. The slurry was stored for four days in a stoppered flask, then filtered on a porosity 4 sintered-glass filter, and the precipitate washed first with 0·01M sulphuric acid saturated with hydrogen sulphide, then with carbon disulphide and benzene to dissolve any sulphur possibly precipitated, then dried at 110° for 1 hr. The washing with carbon disulphide and benzene can be omitted, as, according to our experiments, sulphur precipitated on silica carrier does not bind active zinc ions.

Preparation of amorphous zinc sulphide. $ZnSO_4 \cdot 7H_2O$ (8 g) was dissolved in 100 ml of water. The solution was heated to 60° and 100 ml of freshly prepared ammonium sulphide solution were added with stirring. The precipitate was filtered off after two days' sedimentation, washed with distilled water and dried at 80° for 1 hr.

Solutions containing radioactive zinc. For isotopic exchange, practically carrier-free $^{65}Zn^{2+}$ solutions were prepared from a $^{65}ZnCl_2$ solution with 7 mCi/ml specific activity, by dilution with 0·01M nitric acid in such a way that the activity of the solutions was 480 and 790 cpm/ml.

Zinc sulphide precipitates were in each case treated with inactive zinc sulphate solution. Ten ml of 1M zinc sulphate were passed through the precipitate on the filter. We wished to ensure the retention of active zinc ions by isotopic exchange instead of adsorption on the surface. According to preliminary experiments made with equal portions of crystalline zinc sulphide precipitate taken from the same lot, the values of Q agree within 1 % in the case of equal flow-rates (0·5 ml/min), whereas if the precipitates are taken from different lots, Q varies between 95 and 100 %. The deviations were even greater (40–100 %) if the period of passage of gas and temperature of precipitation were varied.

To elucidate the reasons for the great differences in exchange yield the crystalline structure and morphology of some zinc sulphide precipitates were studied. The X-ray diffraction patterns of precipitates exhibiting different exchange properties were similar, *i.e.*, there was no difference in their crystalline structure. Experimental lattice constants agreed well with literature values taken from A.S.T.M. cards (see Table I). Zinc sulphide crystallizes in the dihexagonal bipyramidal class of the hexagonal system, and so do the precipitates prepared by us. On the other hand, microscopic studies have shown that thin layers of the precipitates have an exchange yield equal to or higher than 99 % only if they consist mainly of particles a few μm in size. Precipitates with poor exchange ability were found to consist of larger agglomerates of the small primary particles. The necessary particle size can be produced by powdering the precipitate in an agate mortar for about 10 min, *e.g.*, see Fig. 2, in which the microscopic image of a poorly exchanging precipitate (*a*) and of one with good exchange properties (*b*) are shown; (*b*) was obtained from (*a*) by powdering. The exchange yield of crystalline zinc sulphide therefore can be made independent of the conditions of precipitation, by subsequent powdering.

The exchange yields of amorphous zinc sulphide precipitates taken from different lots are the same, reaching 100 % in the case of 400–420 mg of precipitate at a flow-rate of 0·5 ml/min. According to microscopic examination, amorphous zinc sulphide precipitates mainly consist of particles some μm in size, and the particle size distribution is more uniform than that of the crystalline modification. The amorphous

TABLE I.—X-RAY DIFFRACTION DATA FOR CRYSTALLINE ZINC SULPHIDE PRECIPITATES

d, nm experimental	*d, nm* literature
0·311	0·312
0·189	0·190
0·162	0·163
—	0·331

Apparatus: Mikrometa 2, X-ray tube: Cu, $\lambda = 0{\cdot}15405$ mm; filter: Ni; diameter of chamber: 57·4 mm; $V = 40$ kV; $i = 20$ mA; exposure time: 2 hr; development temperature: 18°, development time 5 min.

precipitate is, however, very difficult to filter off and the loss of precipitate during isotopic exchange is greater owing to the higher solubility.

By treatment of the active zinc precipitate with 10–20 ml of 2*M* inactive zinc sulphate that is 0·01*M* in nitric acid, part of the active nuclei can be transferred to the solution, which in our opinion supports the assumption that an isotopic exchange takes place on the zinc sulphide precipitate. By the flow technique, a maximum of 53% redissolution could be reached, whereas by the batch technique the redissolution was 55% of this, after 5 hr of shaking. Unfortunately, redissolution of active zinc ions can not be utilized for increasing the selectivity of analysis.

Isotopic exchange with zinc sulphide: effect of experimental conditions on the exchange yield

The effect of the pH, specific activity and flow-rate of the active solution on the exchange yield was studied.

According to the experiments the isotopic exchange can be performed with solutions 0·01*M* or maximally 0·1*M* in nitric acid (see Table II). The precipitate is capable of exchange at even higher acid concentrations—the specific activity of the precipitates is the same at varying acid concentrations—but owing to the high degree of dissolution precipitate particles containing active nuclei may also be dissolved. For studying the effect of pH nitric acid was selected, since the hydrogenation catalysts studied readily dissolve in it, and therefore nitric acid is present during separation by isotopic exchange following dissolution of the samples.

TABLE II.—EFFECT OF ACID CONCENTRATION ON THE ISOTOPIC EXCHANGE WITH ZINC SULPHIDE

Acid concentration, *M*	*Q*%	Weight loss, %	Specific activity of precipitate, *cpm/g*
0·01	100	4·6	5300
0·10	94·6	8·3	5390
1·00	66·3	25·6	5710
2·00	50·9	30·4	4050

As the zinc content of the samples is usually unknown before analysis, it was important to study the relationship between the weight of precipitate required to give

100% exchange yield, and the specific activity and flow-rate of the solution of zinc ions. As reflected by the results in Table III, when the specific activity of the solution increases to 1·7 times that of the original value, the weight of precipitate has also to be increased by a factor of at least 1·7.

A flow-rate of 0·5 ml/min was found to be the optimum for 100% exchange yield with 400 mg of precipitate; doubling the flow-rate reduces the efficiency of isotopic exchange.

Retention of different metal ions on sulphide precipitates

Besides the isotopic exchange of ^{65}Zn the retention of ^{203}Hg, ^{64}Cu, ^{76}As, ^{122}Sb, ^{24}Na, ^{58}Co and ^{103}Pd on sulphide precipitates was studied (see Table IV). The specific activity of the practically carrier-free solutions was about 500 cpm/ml. The sulphides were precipitated with hydrogen sulphide from solutions containing hydrochloric acid.[10]

TABLE III.—EFFECT OF THE SPECIFIC ACTIVITY ON THE ISOTOPIC EXCHANGE WITH ZINC SULPHIDE

Specific activity of solution, *cpm/ml*	Weight of precipitate, *mg*	Q%,	Time of passage of solution, *min*
480	380	100	35
790	380	64·3	35
790	380	65·2	90
790	660	100	35

TABLE IV.—RETENTION OF RADIONUCLIDES ON SULPHIDE PRECIPITATES

Precipitate	Concentration of HNO_3, *M*	Retention of active ions, %							
		Hg^{2+}	Zn^{2+}	Cu^{2+}	Sb^{3+}	As^{3+}	Pd^{2+}	Co^{2+}	Na^{+}
HgS	1·0	100	—	—	—	—	—	—	—
ZnS	0·01	100*	100				50	7	—
CuS	1·0			100					—
Sb_2S_3	1·0 HCl				100				—
As_2S_3	1·0					100			—

* By precipitate exchange.

As shown by the results in the table, sulphide precipitates practically completely retain their own cations. With mercury(II) sulphide the existence of isotopic exchange could be proved experimentally in the same way as for zinc sulphide.

The radionuclides listed in Table IV do not interfere with the determination of mercury(II) ions by isotopic exchange with mercury(II) sulphide. In the γ-spectrum of the precipitate (see Fig. 3) only the photopeak of ^{203}Hg appears.

Zinc sulphide binds mercury(II) ions by a chemical reaction—precipitate exchange:

$$ZnS\downarrow + Hg^{2+} = HgS\downarrow + Zn^{2+}$$

If no precipitate exchange takes place, the interfering effect of foreign radionuclides can be reduced by counter-carrier technique, *i.e.*, by dilution with the inactive isotope. In this way the interference from ^{103}Pd and ^{58}Co in the determination of zinc can be eliminated, or reduced. The peak of ^{58}Co in the γ-spectrum of the zinc sulphide

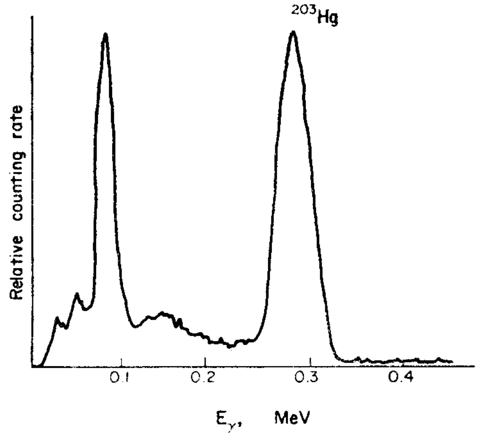

FIG. 3.—Gamma-spectrum of HgS precipitate after isotopic exchange. The original solution contained ^{203}Hg, ^{65}Zn, ^{64}Cu, ^{76}As, ^{122}Sb, ^{58}Co, ^{103}Pd and ^{24}Na.

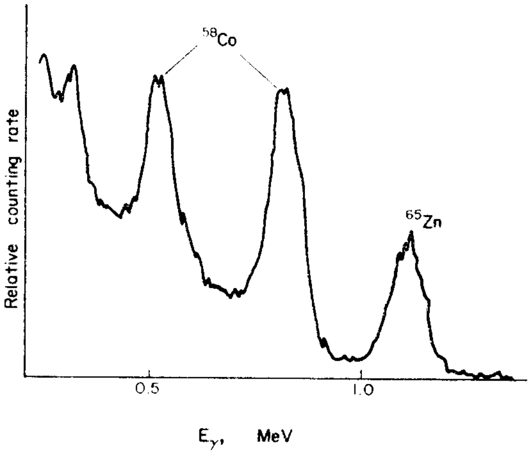

FIG. 4.—Gamma-spectrum of ZnS precipitate after isotopic exchange. The original solution contained ^{65}Zn, ^{103}Pd, ^{58}Co and ^{24}Na.

precipitate taken after isotopic exchange (see Fig. 4) does not disturb the evaluation of the photopeak of ^{65}Zn.

In the case of catalysts on aluminium oxide support ^{24}Na is formed in great amount during activation, owing to the reaction ^{27}Al (n, α) ^{24}Na; however, ^{24}Na is not retained on sulphide precipitates. Thus the method described ensured complete separation from ^{24}Na.[11]

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Zusammenfassung—Die Retention verschiedener Radionuklide an Metallsulfidniederschlägen wurde untersucht. Die Sulfidniederschläge hielten die eingenen Radionuklide quantitativ fest. Bedingung für 100% Retention in einer dünnen Schicht ist eine kleine Teilchengröße (einige μm) im Niederschlag. Das läßt sich durch Pulverisieren des getrockneten Metallsulfidniederschlags erhalten.

$^{203}Hg^{2+}$ wird an Quecksilbersulfid und $^{65}Zn^{2+}$ an Zinksulfid durch Isotopenaustausch festgehalten. Die Retention fremder radioaktiver Ionen kann mit Hilfe von inaktiven Isotop verringert oder gar ausgeschlossen werden; in Fällen, wo die Retention nicht auf chemischer Reaktion Niederschlaganstansch bericht. Der Isotopenaustausch mit Quecksilber(II) sulfid und Zinksulfid ermöglicht die rasche Trennung und die Bestimmung von Quecksilber- und Zinkionen in Gegenwart einer Anzahl störender Ionen.

Résumé—On a étudié la rétention de divers radionucléides sur des précipités de sulfures métalliques. Les précipités de sulfures retiennent quantitativement les radionucléides communs. La condition pour une rétention de 100 % dans une couche mince est une petite dimension de particule (quelques μm) dans le précipité. Ceci peut être assuré par pulvérisation du précipité séché du sulfure métallique. $^{203}Hg^{2+}$ est retenu par le sulfure de mercure et $^{65}Zn^{2+}$ par le sulfure de zinc par échange isotopique. On peut réduire ou même éliminer la rétention d'ions radioactifs étrangers par une technique à contre-support dans les cas où la rétention n'est pas due à une réaction chimique, échange de précipité. L'échange isotopique avec le sulfure de mercure (II) et le sulfure de zinc rend possible la séparation rapide des ions mercure et zinc et leur détermination en la présence d'un certain nombre d'ions gênants.

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STUDIES ON THE MELTS OF ALKALI METAL ACETATES

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Summary—The density, viscosity, and electrical conductivity of alkali metal acetates were measured over the temperature interval between melting and decomposition. The apparent activation energies of the equivalent conductivities and viscosities were calculated. It has been concluded from the results that alkali metal acetates, similarly to alkali metal benzenesulphonates studied earlier, exhibit properties quite unlike those of alkali metal halides. In the dependence of equivalent conductivity on the nature of the cation, the anomalous behaviour of lithium salts appears to be due to association prevailing in the melt phase.

PREVIOUSLY, the changes in properties of alkali metal acetates with increasing temperature have mainly been studied with special regard to phase equilibria, changes in crystalline modification and mechanism of decomposition reactions.[1-6] Relatively few data are available in connection with the temperature interval between melting and decomposition,[7-10] although the investigation of the properties of the molten state is of interest from both a theoretical and a practical point of view.

After studying melts of alkali metal benzenesulphonates[11] we started studies on molten alkali metal acetates in order to compare the behaviour of the two types of compound, and to obtain data characteristic of alkali metal acetate melts.

EXPERIMENTAL

Lithium, sodium, potassium, rubidium and caesium acetates used in the experiments were either commercial products or made by ourselves. The compounds were purified by multiple recrystallization from alcohol-dioxan mixture, and dried to remove water of crystallization. The purity of the products was checked by elemental analysis and melting point measurement. The temperature ranges in which they formed stable melts were determined with a DTA instrument at a low heating rate (1°/min) and by a Paulik-Paulik-Erdey derivatograph (MOM, Hungary). To characterize the molten state, the density, electrical conductivity and viscosity were measured as a function of the temperature. The methods have been described earlier.[11]

RESULTS AND DISCUSSION

The results of DTA and derivatographic measurements are presented in Table I. The data show that all five compounds studied have stable melts, over a relatively wide temperature range depending on the cation, in which no weight or enthalpy change takes place; thus their transport phenomena can be studied easily. The temperature interval between melting and decomposition increases with increasing atomic number of the cation. The data obtained by the two methods do not coincide perfectly, which is due partly to the dynamic nature of the measurements and partly to inaccuracies. This fact, however, did not affect our further experiments, since the

TABLE I

Acetate	Data obtained by DTA, °C			Data obtained by derivatograph, °C						Theoretical change in weight, %
				from the DTA curve			from the DTG curve		from the TG curve	
	Melting point	Decomposition		Melting point	Decomposition		Decomposition		change in weight, %	
		starting	max.		starting	max.	starting	max.		
Li	280	320	425	275	at m.p.	417	320	375	44·0	44·0
Na	332	380	488	340	375	470	350	475	31·5	35·2
K	302	390	477	285	420	485	375	485	28·5	29·6
Rb	241	380	474	228	380	485	340	480	22·0	20·1
Cs	197	380	449	179	325	473	340	476	15·0	15·1

measurements were started below the melting point, and the temperature was raised to the decomposition temperature at a rate of 0·5°/min. The chemical changes proceeding at the decomposition temperature and accompanied by the formation of gaseous product were sensitively indicated by the measuring method used. Heating was stopped at this temperature.

The density of the salt melts as a function of the temperature is shown in Fig. 1. These data were necessary for the conversion of specific conductivities into equivalent conductivities.

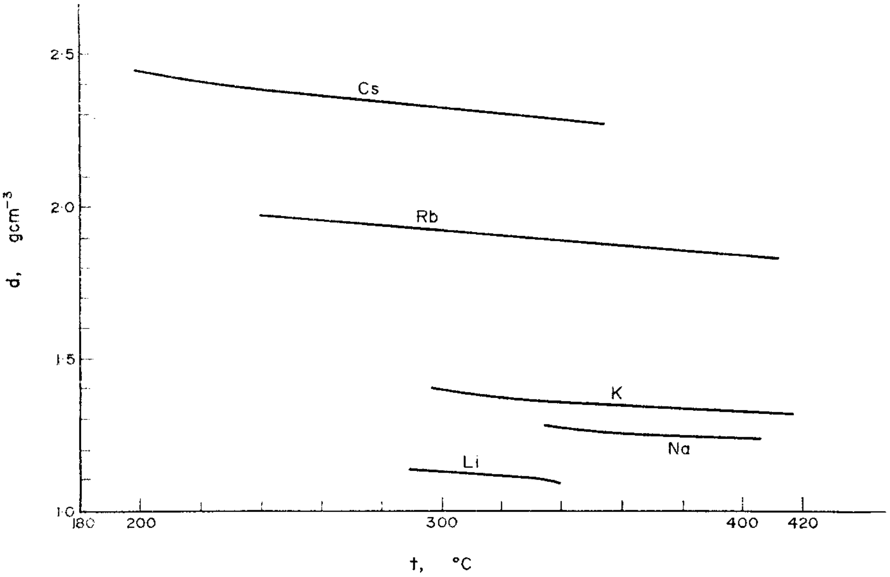

FIG. 1.—Temperature dependence of the density of alkali metal acetates.

The temperature dependence of the equivalent conductivity of the salt melts studied is presented in Fig. 2. The impedance of the measuring cell containing platinum electrodes is only little affected (within the limits of error) by the capacitance of the

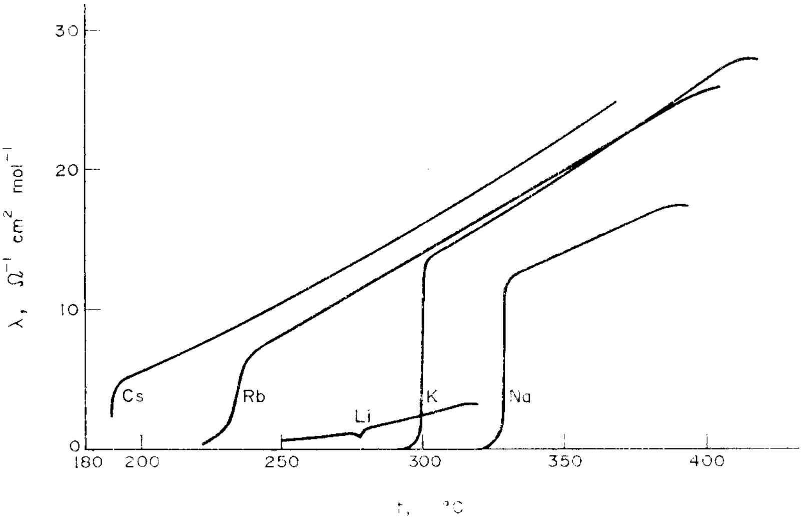

Fig. 2.—Temperature dependence of the equivalent electrical conductivity of alkali metal acetates.

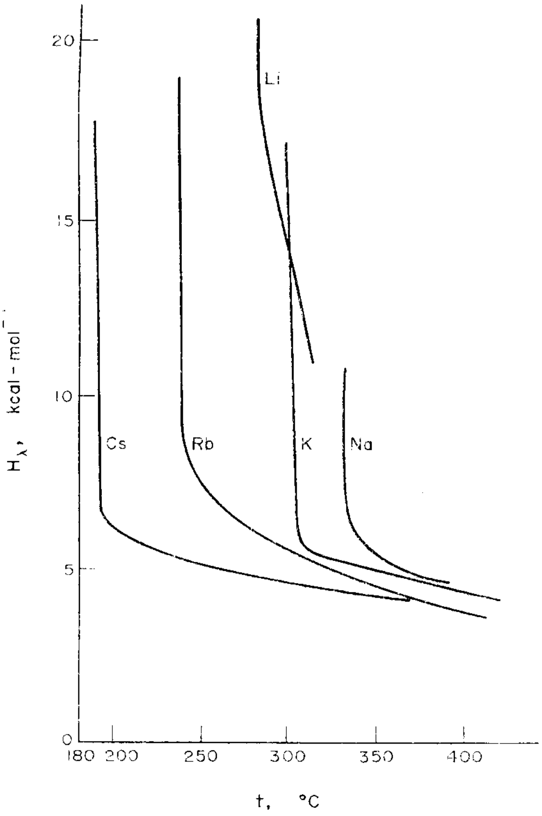

Fig. 3.—Temperature dependence of the apparent activation energy of conductivity of alkali metal acetates.

electrodes, according to our experience and the literature data,[12,13] and therefore a constant-frequency 1-kHz measuring bridge can be used.

The apparent activation energy of conductivity was determined from the Arrhenius equation, from the slope of a plot of the logarithm of the conductivity *vs.* $1/T$. It can be concluded from the measurements and figures that none of the melts studied behaves ideally. The remarkable change of the activation energy with temperature is indicative of complex interactions (Fig. 3). The change of the equivalent conductivity of the salts with the nature of the cation seems unusual when compared with similar data measured for alkali metal halides. The equivalent conductivity of alkali metal halides near their melting point was found to decrease with increasing diameter of the cation for a series of salts of the same halide ion. The case is similar with the different halides, of one cation, the conductivity decreasing with increasing diameter of the anion.[14] With alkali metal acetates, as indicated by the data in Table II, quite different tendencies were observed. The equivalent conductivities measured in the vicinity of the melting point increased with the atomic number of the cation up to potassium, then decreased again. The conductivities measured near the decomposition temperature showed a similar change with the atomic number with the difference that the equivalent conductivities of the potassium, rubidium and caesium salts were practically identical. At a medium temperature the tendencies are intermediary between those at the melting and decomposition temperatures.

The trends were found to be similar in the case of alkali metal benzenesulphonates.[11] The very low equivalent conductivity of the lithium salt, and also the relatively low conductivity of the sodium salt is presumably due to the existence of the dimeric structure above the melting point, owing to polarization by the cations. In other words, the cation–anion bond has a remarkably covalent nature even in the molten phase. The equivalent conductivities of the salts studied not only depend on the diameter of the cation but are also influenced by the associated structure prevailing in the molten phase. The nature of the bond, however, also depends on the anion.

TABLE II

Acetate	Equivalent conductivity, $\Omega^{-1} . cm^2 . mole^{-1}$		
	at melting point, T_{melting}	at decomposition temperature, T_{decomp}	at medium temperature, T_{m}
Li	1·4	3·2	2·3
Na	12·0	16·5	14·3
K	13·4	24·6	18·8
Rb	6·6	23·0	15·1
Cs	4·9	24·6	14·6

$$T_{\text{m}} = \frac{T_{\text{decomp}} + T_{\text{melting}}}{2}$$

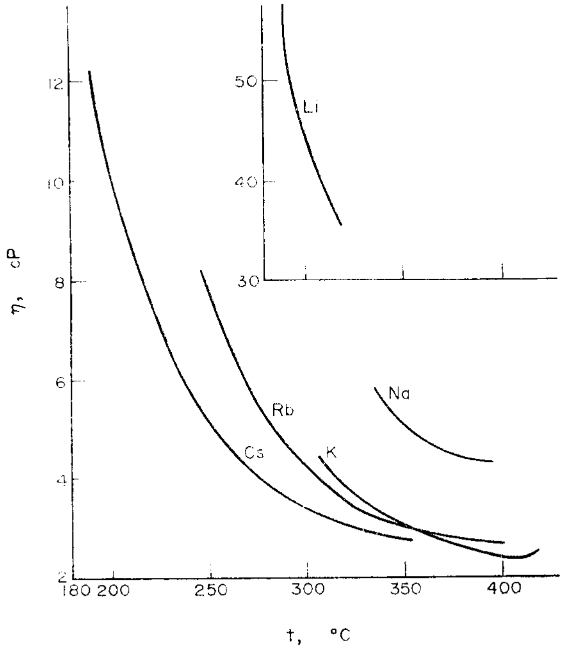

Fig. 4.—Temperature dependence of the viscosity of alkali metal acetates.

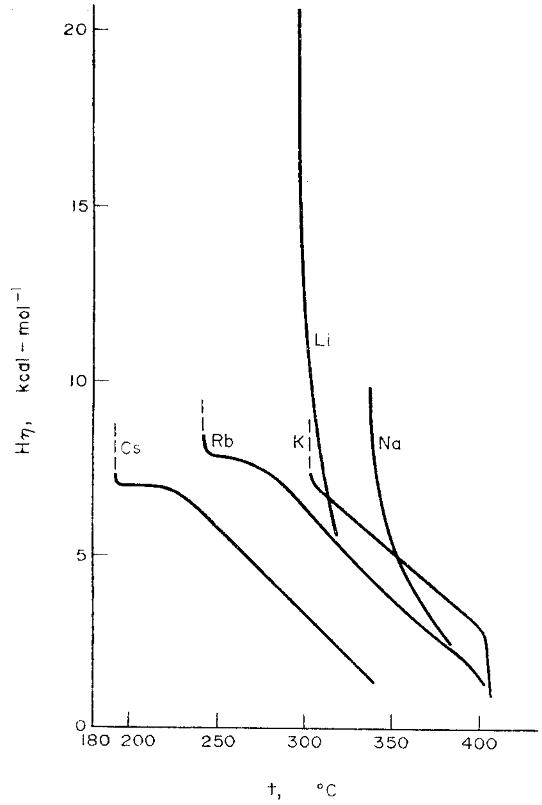

Fig. 5.—Temperature dependence of the apparent activation energy of viscosity of alkali metal acetates.

This statement is supported by the experimental fact (see Fig. 2) that the conductivity of solid lithium acetate does not change much on melting, whereas the conductivities of the other alkali metal acetates change more or less sharply at the melting point. Furthermore, the very high apparent activation energy of the conductivity of the lithium salt in comparison to those of other alkali metal acetates also indicates the high degree of order of the melt of lithium acetate.

The tendencies observed in the change of the viscosities of the melts are in good agreement with the conductivities and the conclusions drawn from them. The temperature dependence of the viscosities of the melts of alkali metal acetates is shown in Fig. 4. The extremely high viscosity of the lithium acetate melt as compared to that of the other acetates studied, and also the high apparent activation energy of viscosity as determined on the basis of the Arrhenius equation is also evidence of the high degree of order of the melt. The temperature dependence of the activation energies of viscosity is shown in Fig. 5. The structure of melts in the ideal case can be characterized by the Walden formula[15] as follows:

$$\eta^n = \text{constant}$$

The condition for ideal behaviour is the constancy of n.

There was found no temperature interval over which this relationship was valid for the data measured by us. The investigation of the molten state of organic salts will be extended to other model compounds in future in order to find further relationships between the properties of the salt and the nature of the constituent ions.

Résumé—On a mesuré les densité, viscosité et conductivité électrique d'acétates de métaux alcalins dans l'intervalle de température compris entre la fusion et la décomposition. On a calculé les énergies d'activation apparentes des conductivités équivalentes et des viscosités. On a conclu, des résultats, que les acétates de métaux alcalins, comme les benzènesulfonates de métaux alcalins étudiés antérieurement, présentent des propriétés tout à fait différentes de celles des halogénures de métaux alcalins. Dans la dépendance de la conductivité équivalente par rapport à la nature du cation, le comportement anormal des sels de lithium paraît dû à une association prévalant dans la phase fondue.

Zusammenfassung—Dichte, Viskosität und elektrische Leit fähigkeit von Alkalimetallacetaten wurden im Temperaturbereich zwischen Schmelzen und Zersetzung gemessen. Die scheinbaren Aktivierungsenergien der Äquivalentleitfähigkeit und der Viskosität wurden berechnet. Es wurde der Schluß gezogen, daß die Acetate der Alkalimetalle, ähnlich wie die früher untersuchten Benzolsulfonate, ganz andere Eigenschaften haben als die Halogenide. Bei der Abhängigkeit der Äquivalentleitfähigkeit vom Kation scheint das anomale Verhalten der Lithiumsalze davon zu rühren, daß in der geschmolzenen Phase überwiegend Assoziate vorliegen.

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SPECTROCHEMICAL ANALYSIS OF HARD METALS BY A ROTATING DISC TECHNIQUE

EFFECT OF IMPREGNATION AND COMPLEXING AGENTS

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Summary—A spectrographic method has been developed for the simultaneous determination of the constituents W, Co, Ti, Ta and Nb and contaminants Fe, Ni, Cr, Mn, Mg and Ca in hard metals. The samples were dissolved in hydrofluoric acid and nitric acid and the solutions stabilized with citric acid. Graphite discs were waterproofed in order to ensure control of the introduction of solution into the source. For the five types of hard metal samples studied no inter-element effect was observed. Titanium has also been determined by means of a double-beam optical spectrometer.

OF THE STANDARD methods for the analysis of hard metals only two will be cited here, in which ion-exchange columns are used for the separation of ions.[1,2] These methods are rather time-consuming, and of low accuracy (2–4% error). Furthermore, they do not permit the quantitative separation of tantalum and niobium.

X-Ray fluorescence methods are commonly used for the simultaneous determination of the constituents of hard metals, by the direct method,[3] powder technique[4] and solution technique.[5] Complex inter-element effects occur during X-ray fluorescence analysis and standards covering a limited concentration range are needed for each type of method.

The inhomogeneity of hard metals is an obstacle to their direct spectrochemical analysis, so solution techniques are required for quantitative analysis. The technique recommended for the spectrographic determination of refractory transition metals was suitable for our work[6] but had not yet been used in the analysis of hard metals.

EXPERIMENTAL

The hard metals analysed represented ten different categories which could be classified into five groups with certain exceptions. The constituents and their concentration ranges are given in Table I.

TABLE I.—HARD METAL TYPES STUDIED

Type	Constituent % WC	TiC	TaC	Co	NbC
I	60–65	25–30	—	3–6	—
II	65–75	13–18	0–5	6–8	0–0·5
III	70–80	5–10	0–4	6–10	0–0·4
IV	80–90	—	0–3	4–7	0–0·3
V	75–85	—	—	18–22	—

Preparation of sample solutions

The basic materials (metal carbide and cobalt powder mixtures), used for making hard metal tips, were freed from paraffin with benzene in a Soxhlet extractor. Tips were broken up by chipping. From the samples so treated, 200 mg were dissolved in a platinum crucible with 10 ml of concentrated hydrofluoric acid, with dropwise addition of nitric acid. It is necessary to remove or neutralize excess of acid after dissolution, in order to prevent corrosion of the instruments used. In the X-ray fluorescence method cited,[5] boric acid was used to complex hydrogen fluoride. In the present case, however, it seemed better to remove free acid because of its possible thermal decomposition during excitation. Evaporation with sulphuric acid[6] could not be used, as tungstic acid was precipitated. Therefore hydrogen fluoride was removed by adding 25 ml of citric acid solution (200 mg/ml) and evaporating to low bulk on a steam-bath. The residue was diluted with water and the evaporation repeated, this step being carried out twice. The final residue was diluted with 10 ml of copper sulphate solution (50 mg of Cu/ml) and then with water to 25 ml in a volumetric flask, and finally transferred to a plastic storage vessel. It has been reported[7] that copper(II) can form a complex with hydrogen fluoride, so any of the latter possibly retained in solution might be masked in this way. In addition, the copper served as internal standard and spectrochemical buffer.[8]

Solutions prepared as described contained 8 mg of sample, 20 mg of copper and 200 mg of citric acid per ml. The solutions remained unchanged for two days if the titanium content was $>10\%$ and for longer periods if it was less. For studying the effect of citric acid on the excitation, solutions containing 100 mg of citric acid per ml were also prepared.

Preparation of standard solutions

Stock solutions were prepared from metals of spectroscopic purity as described for sample preparation. Standard solutions were prepared from the stock solutions by mixing. According to the classification in Table I, five types of reference standards were prepared. Contaminants were added in the form of their solutions in nitric acid (in hydrochloric acid in the case of chromium).

Choice of the electrical parameters of excitation

High-voltage spark excitation was used,[6] and the solution consumption was 0.07 ml/min (averaged over 6 min). In the case of spectrometric determinations low-voltage spark excitation was used with a similar consumption of solution.

Pretreatment of graphite discs

In the residue methods the graphite supporting electrode is water-proofed. The differences in the size and structure of the electrodes and in chromatographic phenomena are less important in the case of the rotating disc technique than with the residue methods.

These effects, however, cannot be neglected.[9] The pretreatment reduces these effects, but also reduces the amount of solution carried into the spark gap. This unfavourable effect can be eliminated by the use of an impregnating agent which decomposes on the surface of the disc during excitation allowing the disc to become absorbent again. The absorption of solution may be controlled by the spark discharge, and a thin layer of solution is formed.[10,11] The impregnating solution used (cellulose nitrate in acetone) has been described previously.[12] Graphite discs were immersed in this solution (a 1:4 solution of "Zapon" lacquer on acetone). The impregnated discs were placed on a glass sheet and dried by means of an infrared lamp.

The effects of the variation in the concentration of citric acid and the impregnation of the discs are demonstrated by the excitation–time studies presented in Fig. 1, where log intensity is plotted *vs.* time for alloy type II. The intensity of the lines decreases with increasing citric acid concentration for both impregnated and non-impregnated discs. Impregnation increases the line intensity in the case of low citric acid concentrations and reduces it at high citric acid concentrations. The thickness of the solution layer is presumably reduced both by increase in citric acid concentration and by impregnation of the discs. In the course of the present work these effects were utilized. Analyses were made under conditions corresponding to curves *B*. These curves are similar in shape, which indicates the absence of selective evaporation. The discs that had not been impregnated previously were rotated in the solution for 90 sec before excitation was started, during which time saturation equilibrium could be established. With impregnated discs this operation is unimportant. Impregnation provides protection against corrosion and contamination of the shaft.

Experimental conditions

In the case of the rotating disc equipment a carbon shaft[13,14] and a plexi-glass solution container were used. The shaft of the motor was connected to the carbon shaft by a flexible steel drive. On the closed electrode stands a 6-mm diameter hole was made in an appropriate position for the flexible shaft. The graphite disc was 10 mm in diameter, and 3.2 mm thick and rotated at 10 rpm: 1 ml of solution was used. The penetration depth of the disc was 2 mm.

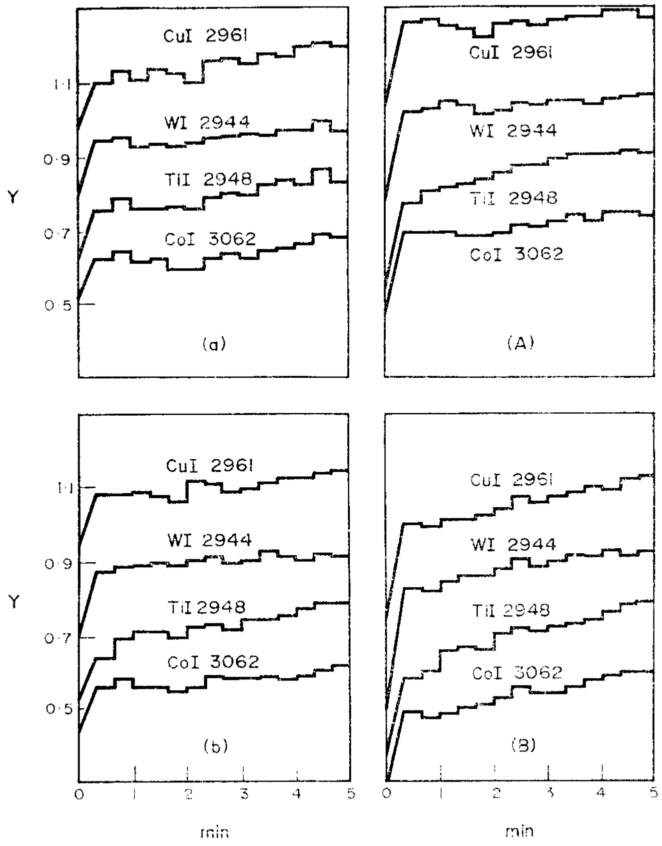

FIG. 1.—Log intensity (Y) *vs.* time.
(*a*) 100 mg of citric acid/ml; without impregnation
(*A*) 100 mg of citric acid/ml; with impregnated disc
(*b*) 200 mg of citric acid/ml; without impregnation
(*B*) 200 mg of citric acid/ml; with impregnated disc.

Spectrographic method

Source. RFT, HFO-1 high-voltage spark generator, 15 kV peak-voltage, 6 nF capacitance, 0·08 mH added self-inductance, 3-mm spark gap, 6·15-mm diameter hemispherical-end graphite counter-electrode; 30-sec presparking, 120-sec exposure.

Spectrograph. Hilger and Watts, Type E 478, quartz optics. Wavelength range 249–360 nm. Slitwidth 0·02 mm. To ensure maximum illumination of the slit the source was placed at the focus (for ultraviolet light) of a quartz lens (Hilger and Watts, F 1509).[15] (Distance of the source from the slit 0·38 m, distance of the lens from the source 56 mm.) With this method of illumination the exposure time necessary to obtain the same line blackening was about 1/7 that with internal focusing. However, this method was unsuitable for spectrograms made by using a step wedge for calibration, so in this case internal focusing was used.

Photographic conditions. Gevaert, Scientia 34 B 50 emulsion, Kodak D 19 developer (4 min, 20°), mechanical agitation during development.

Evaluation of results. A Radelkisz Spectator analogue computer,[16] using the general P-transformation according to Kaiser, was employed. Background correction was applied only for the analytical lines of constituents and impurities.

Spectrometric method

Source. GEU-1 (USSR) low-voltage arc and spark generator with electronic control, 220 V, 10 μF, no added self-inductance, 0·8 A (effective). Spark gap 2 mm; presparking and exposure time 60 sec.

Spectrometer. FESZ-1 (USSR) double-beam spectrometer (visible range, photocell detectors, polychromatic reference light, measurement of integral intensity ratios). Entrance slit 0·04 mm; exit slit 0·06 mm; analytical line Ti I 498·2 nm (adjusted by hand). The intensity of the reference light was reduced by a filter with 17% transmission.

RESULTS

Shape of the analytical curves

The spectrographic analytical curves for all constituents and contaminants were linear and reference standards of all five types gave the same analytical curve. The analytical line pairs used and the corresponding concentration ranges are presented in Table II. Analytical curves were plotted as intensity ratio vs. concentration.

TABLE II.—DATA CHARACTERISTIC OF THE EVALUATION AND ANALYTICAL PERFORMANCE

Analytical line, *nm*	Concentration range %	Coeff. of variation* %	Detection limit, c_d, %
Ti I 498·175†	2–26†	2·2† (15)	—
Ti II 283·216	5–26	3·4 (15)	—
Ti II 316·177	0·5–5	3·2 (3)	—
Ti II 323·452	0·08–0·5	6·2 (0·2)	0·038
W I 294·738	50–85	2·9 (70)	—
Co I 306·182	4–25	3·2 (10)	—
Ta 301·254	1–6	5·4 (4)	0·37
Nb II 295·088	0·2–0·6	5·7 (0·4)	0·084
Fe II 259·957	0·03–0·5	4·3 (0·1)	0·015
Ni I 305·082	0·09–0·3	6·7 (0·2)	0·044
Cr II 284·325	0·02–0·2	7·4 (0·1)	0·013
Mn I 279·482	0·02–0·2	6·5 (0·1)	0·083
Mg II 279·553	0·004–0·02	6·3 (0·01)	0·0023
Ca II 317·933	0·04–0·2	5·6 (0·1)	0·017

* The figure in brackets is the concentration of the element used for determination of the coefficient of variation.

† Data for spectrometric method. All other data refer to the spectrographic method in which the CuI 303·610-nm reference line was used for the determination of all constituents and contaminants.

Precision and sensitivity

To study the precision of the method 20 parallel measurements were made and the coefficient of variation was calculated by means of the usual relationship;[17] the results are also given in Table II.

To characterize sensitivity we wished to calculate the detection limit according to Kaiser's criterion,[18] but its interpretation and application are not consistent in the literature.[19–21] We tried to keep to Kaiser's criterion, however, by using the relationship

$$c_d = \left(\frac{3\sigma_{BU}}{a}\right)^{1/b}$$

where c_d is the limit of detection, a and b are the constants of Lomakin and Scheibe's analytical function, and σ_{BU} the standard deviation of the "relative blank intensity" (blank intensity at the wavelength of the analytical line divided by the intensity of the reference line). The average relative blank intensity and the corresponding standard deviation were determined from 20 spectrograms from a solution of type V (free of contaminants). The constant a is the slope of the analytical curve, and in the cases studied b was equal to unity. The c_d values are given in Table II.

DISCUSSION

The greatest advantage of the method lies in its relative freedom from inter-element effects, which presumably is related to the linear nature of all the analytical curves. These properties can be accounted for by the non-selective evaporation of the constituents during excitation. This is partly due to the formation of a thin solution layer and partly to the similar volatilities of the fluorides of the constituents.

Zusammenfassung—Ein spektrographisches Verfahren zur gleichzeitigen Bestimmung der Hauptbestandteile W, Co, Ti, Ta und Nb und der Verunreinigungen Fe, Ni, Cr, Mn, Mg und Ca in Hartmetallen wurde entwickelt. Die Proben wurden in Flußsäure und Salpetersäure gelöst und die Lösungen mit Zitronensäure stabilisiert. Die Graphitscheiben wurden wasserabstoßend gemacht, um das Einbringen der Lösung in die Lichtquelle zu regeln. Bei den fünf untersuchten Typen von Hartmetallproben wurden keine gegenseitigen Störungen der Elemente beobachtet. Titan wurde auch mit Hilfe eines optischen Zweistrahl-Spektrometers bestimmt.

Résumé—On a développé une méthode spectrographique pour la détermination simultanée des constituants W, Co, Ti, Ta et Nb et des contaminants Fe, Ni, Cr, Mn, Mg et Ca dans les métaux durs. On dissout les échantillons en acide fluorhydrique et acide nitrique et stabilise les solutions avec l'acide citrique. Des disques de graphite ont été rendus étanches à l'eau afin d'assurer le contrôle de l'introduction de la solution dans la source. Pour les cinq types d'échantillons de métaux durs étudiés, on n'a pas observé d'influence inter-éléments. On a aussi dosé le titane au moyen d'un spectromètre optique à double faisceau.

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SHORT COMMUNICATIONS

Selektive Bestimmung in verdünnter Lösung befindlicher Säuren von verschiedener Stärke durch oszillometrische Titration

(*Eingegangen am* 19. *Mai. Angenommen am* 3. *Juni* 1970)

In der Literatur der letzten Jahren sind für die Bestimmung nebeneinander anwesender Säuren von verschiedener Stärke Titrationen in nichtwäßriger Lösungen angegeben.[1–6] Bei diesen Methoden wird die Selektivität durch Auswahl eines geeigneten Lösungsmittels erreicht.

Nach dem von uns ausgearbeiteten Verfahren ist eine Möglichkeit gegeben durch Auswahl einer Maßlösung von geeigneter Basenstärke, Säuren von verschiedener Stärke in wäßriger Lösung nebeneinander zu bestimmen. Die Titration beruht auf folgender Reaktion:

$$\mathrm{HA} + \mathrm{B} \overset{K}{\rightleftharpoons} \mathrm{A} + \mathrm{BH}$$

$$K = \frac{K_\mathrm{B}}{K_\mathrm{A}} \geqslant 10^{1,3}$$

wo K_B und K_A die Protonierungskonstanten der Basen B und A sind.

Ist die Protonierungskonstante der Base B ungefähr 20-mal größer als diejenige der Base A, so verläuft die Reaktion praktisch quantitativ.

Titriert man zwei verschiedene starke Säuren, wo

$$K_{\mathrm{A(I)}} > K_{\mathrm{A(II)}}$$

so verwendet man eine Base B, die eine Protonierungskonstante

$$K_{\mathrm{A(I)}} > K_\mathrm{B} > K_{\mathrm{A(II)}}$$

hat.

In diesem Falle ist die Säure HA(II) mit der Base B selektiv titrierbar. Im Gegensatz zur potentiometrischen Titration ist die oszillometrische Titration für die Bestimmung des Endpunktes auch in denen Fällen geeignet, wo das Verhältnis

$$\frac{K_\mathrm{B}}{K_{\mathrm{A(II)}}}$$

kaum größer als 20 ist. Auf Grund dieses Prinzips haben wir die Titration einiger Säuren durchgeführt. (Siehe Tabelle 1).

EXPERIMENTELLER TEIL

Stammlösungen. Lösungen (0,1*M*) von Trichloressigsäure, Monochloressigsäure, Ameisensäure, Oxalsäure, Maleinsäure. Die Lösungen wurden durch Einwaage bereitet, ihr Titer wurde durch potentiometrische Titration mit einer Natriumhydroxid Maßlösung ermittelt.

Maßlösungen. Molare Lösungen von Kaliumdihydrogenphosphat, Natriumacetat, Natriumformiat und 0,5*M* Lösung von Natriumfluorid. Der Fluoridgehalt der Natriumfluoridlösung wurde nach Erdey[7] als PbClF gravimetrisch bestimmt; der Titer der übrigen Maßlösungen wurde nach Ionenaustausch an einem Kationenaustauscher in H^+-Form mit Natriumhydroxid Maßlösung potentiometrisch bestimmt.

Für die Herstellung der Lösungen wurden in jedem Falle Reagenzien von *p.a.* Qualität verwendet.

Apparate und Instrument

Oszillotitrator, Typ OK 302 der Firma Radelkis; Meßfrequenz *ca.* 140 MHz.
pH-Meter, Typ OP 204 der Firma Radelkis.
Acryl-Bürette, Typ XT 5220 "XLON".

Titration

Eine Portion von 1 bis 10 ml der entsprechenden Säure wurde in einer Meßzelle auf 100 ml verdünnt, daß die Lösung die obere Elektrode erreiche. Nach dem Einschalten und nach entsprechender Einstellung des Apparats wurde der Lösung in 0,05 bis 0,1 ml Portionen, aus einer Mikrobürette—im Falle der Natriumfluoridlösung aus der Acryl-Bürette—die entsprechende Maßlösung

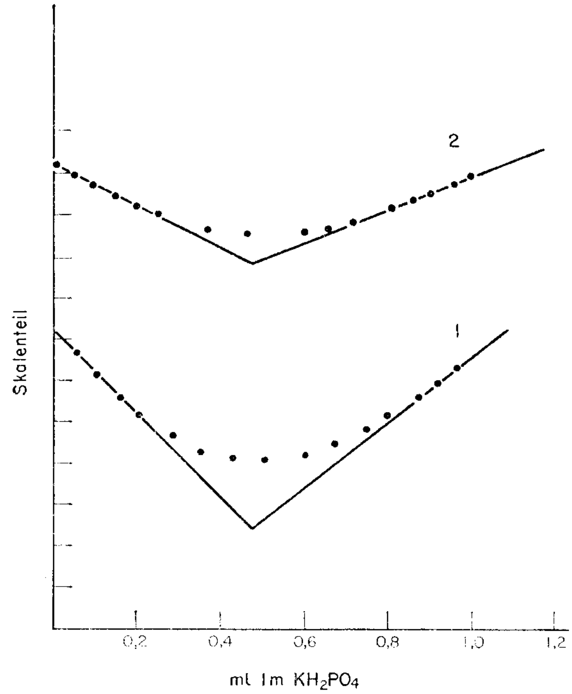

ABB. 1.—1. Titration von 10 ml 0,1*M* Trichloressigsäure in 100 ml Volumen mit 1*M* Kaliumdihydrogenphosphat.

2. Titration von 10 ml 0,1*M* Trichloressigsäure in 100 ml Volumen mit 1*M* Kaliumdihydrogenphosphat in Gegenwart von 10 ml 0,1*M* Monochloressigsäure.

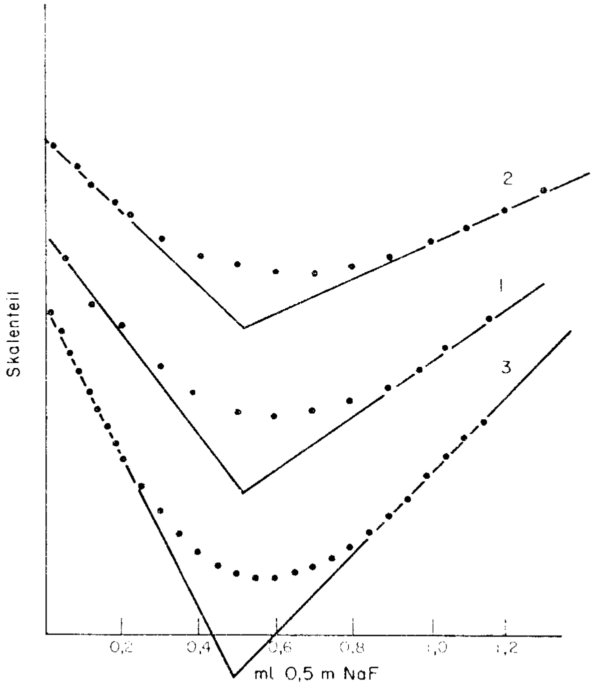

ABB. 2.—1. Titration von 2,5 ml 0,1*M* Oxalsäure in 100 ml Volumen mit 0,5*M* Natriumfluorid.

2. Titration von 2,5 ml 0,1*M* Oxalsäure in 100 ml Volumen mit 0,5*M* Natriumfluorid in Gegenwart von 2,5 ml 0,1*M* Essigsäure

3. Titration von 5,0 ml 0,1*M* Maleinsäure in 100 ml Volumen mit 0,5*M* Natriumfluorid.

zugefügt. Nach dem Erreichen des Äquivalenzpunktes wurde ein etwa 50 bis 100%-iger Überschuß an Maßlösung zugefügt. Der Äquivalenzpunkt wurde graphisch ermittelt.

ERGEBNISSE UND DISKUSSION

Die Analysenergebnisse sind in Tabelle I zusammengestellt.

TABELLE I.—TITRATIONSERGEBNISSE

Bestimmte Säure	$\log K_{A(II)}$	0,1*M* Lösung, ml genomm.	gefund	Begleitsäure, 0,1*M*	$\log K_{A(I)}$	Volumen, *ml*	Abweichung, %
Titrationen mit Kaliumdihydrogenphosphat Maßlösung, $\log K_B = 2{,}12$							
CCl_3COOH	0,89	10,00	9,90	$CH_2Cl\ COOH$	2,86	10,00	−1,0
CCl_3COOH	0,89	10,00	9,96	—		—	−0,4
Titrationen mit Natriumfluorid Maßlösung, $\log K_B = 3{,}45$							
$CH_2ClCOOH$	2,86	2,00	1,98	—		—	−1,0
$CH_2ClCOOH$	2,86	2,00	1,96	CH_3COOH	4,76	2,00	−2,0
$(COOH_2)$	1,19	2,50	2,52	$COOH{\cdot}COONa$	4,21	2,50	+0,8
$(COOH_2)$	1,19	2,50	2,52	$COOH{\cdot}COONa$ CH_3COOH	4,21 4,76	2,50 2,00	+0,8
$C_2H_2(COOH)_2$ Maleinsäure	2,00	5,00	5,00	$C_2H_2COOH{\cdot}COONa$	6,26	5,00	±0,0
Titrationen mit Natriumacetat Maßlösung, $\log K_B = 4{,}76$							
HCOOH	3,75	1,00	0,99	—		—	−1,0
CCl_3COOH	0,89	2,00					
$CH_2ClCOOH$	2,86	2,00	4,04	—		—	+1,0

Da der Unterschied zwischen den Protonierungskonstanten der titrierten und titrierenden Systeme nicht allzu beträchtlich ist, wird sich die Leitfähigkeit in der Umgebung des Äquivalenzpunktes kaum oder gar nicht ändern. Dieser Abschnitt ist desto größer, je näher die Protonierungskonstante der Basen-Maßlösung zur Protonierungskonstante der konjugierten Base der titrierten Säure liegt. In diesem Falle kann man die zur Bestimmung des Äquivalenzpunktes notwendigen Kurven nur dann mit Sicherheit konstruieren, wenn wenigstens etwa 50 bis 100% Überschuß an Maßlösung verwendet wird.

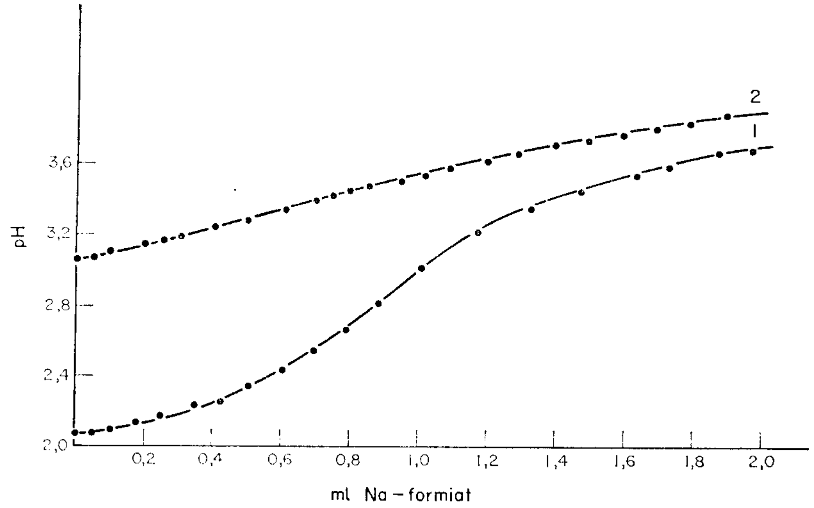

ABB. 3.—1. Potentiometrische Titration von 10 ml 0,1*M* Trichloressigsäure in 100 ml Volumen mit 1*M* Natriumformiat.
2. Potentiometrische Titration von 1 ml 0,1*M* Trichloressigsäure in 100 ml Volumen mit 0,1*M* Natriumformiat.

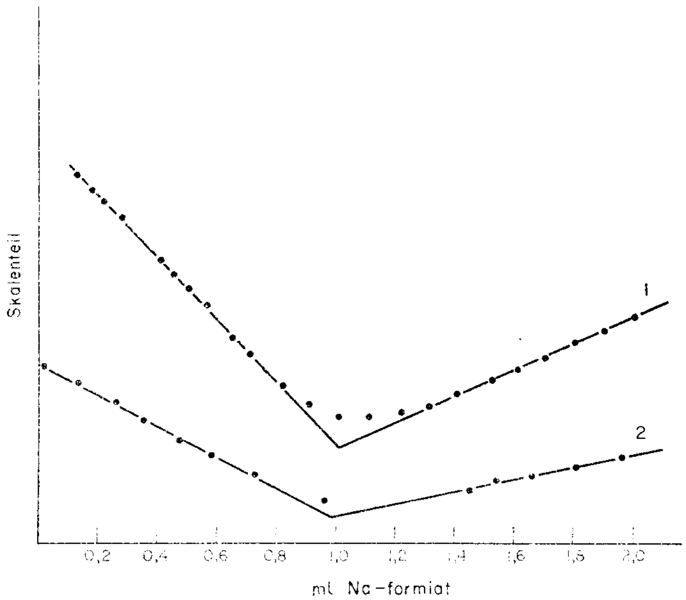

Abb. 4.—1. Oszillometrische Titration von 10 ml 0,1M Trichloressigsäure in 100 ml Volumen mit 1M Natriumformiat.
2. Oszillometrische Titration von 1 ml 0,1M Trichloressigsäure in 100 ml Volumen mit 0,1M Natriumformiat.

Es war festzustellen, daß die anwesende Begleitsäure einer 2 bis 10 fachen Menge der zu bestimmenden Säure keine störende Wirkung verursacht, aber die Kurve wird weniger steil sein (Abb. 1, Kurve 1 und 2; Abb. 2, Kurve 1 und 2). Versuche wurden auch mit 100 facher Menge der Begleitsäure durchgeführt. Ein ml 0,1M Trichloressigsäure wurde in Gegenwart von 100 ml 0,1M Essigsäure titriert, die 20% Mehrverbrauch an Maßlösung verursachte. Ist die Begleitsäure schwächer als Essigsäure, so ist der Fehler selbstverständlich geringer.

Abbildung 2 zeigt die Titrationskurven zweiwertiger Säuren. Oxalsäure und Maleinsäure sind mit Natriumfluorid Maßlösung als einwertige Säuren titrierbar. Auch auf diese Säuren bezieht sich die Feststellung über die zwei einwertigen Säuren verschiedener Stärke.

Vergleichende Titrationen mit der Trichloressigsäurelösung wurden auch potentiometrisch durchgeführt. Abbildung 3 zeigt die potentiometrischen Titrationskurven. Als Maßlösung wurde Natriumformiat verwendet. Dieselben Titrationen mit oszillometrischer Endpunktanzeige sind in Abb. 4 dargestellt. Die Kurven 1 zeigen die Titrationsergebnisse der $10^{-2}M$ Trichloressigsäurelösung, die Kurven 2 sind Ergebnisse mit der $10^{-3}M$ Lösung. Wir benutzten sowohl 1M als auch 0,1M Natriumformiat Maßlösungen. Aus den Abbildungen ist es ersichtlich, daß die potentiometrischen Kurven auch in $10^{-2}M$ Konzentration schwer auswertbar sind, hingegen die Kurven der oszillometrischen Titrationen sind in beiden Fällen gut auszuwerten.

Zusammenfassend kann festgestellt werden, daß im Falle richtiger Auswahl der Titrierbase, die Titrationen der Säuren von verschiedener Stärke durch oszillometrische Endpunktindikation selektiv durchzuführen sind.

$$\text{Im Falle } \frac{K_{A(I)}}{K_{A(II)}} \geqslant 10^2, \quad \text{und} \quad \frac{K_B}{K_{A(II)}} \geqslant 10^{1,3}$$

im Konzentrationsbereich von 10^{-2}–$10^{-3}M$ beträgt der relative Fehler ±1,0%.

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Zusammenfassung—Zur selektiven Titration einer Säure in einem Säuregemisch aus zwei verschieden starken Säuren verwendet man eine solche Basederen Protonierungskonstante zwisschen denen der beiden konjugierten Basen liegt ($K_{A(I)} > K_B > K_{A(II)}$). Im Falle $K_{A(I)}/K_{(II)A} \geqslant 10^2$ und $K_B/K_{A(II)} \geqslant 10^{1,3}$, im Konzentrationsbereich 10^{-2}–$10^{-3}M$, beträgt der relative Fehler für die oscillometrische Titration ±1%.

Summary—The stronger of a pair of weak acids may be selectively titrated in aqueous solution when the conjugate base of a third acid of intermediate strength is used as titrant. Titrations of 10^{-2}–$10^{-3}M$ solutions can be followed by high-frequency oscillometric measurements with an error of about 1%, when the strengths of the two acids differ by a factor of 10^2 or more, and of the acid and titrant by $10^{1.3}$ or more.

Résumé—On peut titrer sélectivement en solution aqueuse le plus fort d'une paire d'acides faibles lorsque la base conjuguée d'un troisième acide de force intermédiaire est utilisée comme agent de titrage. On peut suivre les titrages de solutions 10^{-2}–$10^{-3}M$ par mesures oscillométriques de haute fréquence avec une erreur d'environ 1%, lorsque les forces des deux acides diffèrent d'un facteur de 10^2 ou plus, et celles de l'acide et de l'agent de titrage de $10^{1.3}$ ou plus.

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Investigation of alkali metal and ammonium tetraphenylborates by infrared spectrophotometry

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SODIUM and lithium tetraphenylborates are good precipitating agents used for the gravimetric determination of potassium, rubidium, caesium, and ammonium, and some other metal ions and organic bases containing oxygen and nitrogen,[1-9] according to the equation

$$[B(C_6H_5)_4]^- + X^+ = X[B(C_6H_5)_4]$$

In most cases sodium tetraphenylborate is used as reagent, this being more stable than the lithium salt. Precipitation with tetraphenylborate is widely used in analytical practice since it can be made selective by choosing the experimental conditions appropriately, so that some constituents can be determined in the presence of others relatively simply. Heavy alkali metal and ammonium ions all precipitate together when the reagent is added and they can be separated only by a long procedure.[2] As the determination of these ions in the presence of one another is often necessary, the development of methods for doing this may be of interest.

Ammonium and alkali metal ions can be precipitated with tetraphenylborate in neutral, weakly acidic (acidified with mineral acids or acetic acid) and weakly alkaline solution. Of the procedures described in the literature[2,3,8,10-12] the one given by Kohler[2] was used in the present work. Precipitation was effected at room temperature from solutions 0·1*M* in hydrochloric acid, under which conditions Mg, Ca, Al, Fe(III), Co(II), Ni, Mn, Cu(II), SO_4^{2-} and PO_4^{3-} ions did not interfere. In these circumstances sodium tetraphenylborate is a selective and very good precipitant of alkali metal and ammonium ions. In solutions that are 0·1*M* in mineral acid the precipitate formed consists of coarse crystals which settle quickly. The precipitate is easy to filter off on a porosity-4 sintered-glass filter. As wash-liquid a saturated solution of the precipitate was used.

The infrared spectra of alkali metal and ammonium tetraphenylborate precipitates were taken (in KBr pellets) with a Zeiss UR 10 infrared spectrophotometer from 400 to 4000 cm^{-1}. The spectra are presented in Fig. 1. The bands in the spectra were assigned, and the identity and purity of the precipitates checked by comparing the spectra with those found in the literature.[13-15] The spectra of the alkali metal tetraphenylborates are practically identical. The effect of the different electronegativities of the ions is very small, as is shown by the slightly different positions and intensity ratios of the corresponding bands. The spectrum of ammonium tetraphenylborate contains more bands than those of the alkali metal tetraphenylborates, since it contains the N—H bands from the ammonium ion. The wave-numbers of these bands are characteristic of ammonium tetraphenylborate, so ammonium ions can be determined in the presence of alkali metal ions without separation, by means of infrared spectrophotometry on the basis of these bands.

The bands in the infrared spectra can be assigned as follows.

Aromatic C—H stretching vibrations appear between 2970 and 3080 cm^{-1}, the number of which is equal to the number of hydrogen atoms attached to the ring (five bands). Between 1980 and 1880 cm^{-1} appear the overtones and combination bands of the out-of-plane C—H deformation and C—C deformation vibrations, which are rather weak and not very characteristic.

Aromatic C—C stretching vibrations occur between 1593 and 1400 cm^{-1}, whereas the in-plane deformation vibrations of aromatic C—H groups lie between 1250 and 950 cm^{-1}.

The very strong and sharp bands between 900 and 700 cm^{-1} are the out-of-plane C—H deformation vibrations of five neighbouring hydrogen atoms.

In the spectrum of ammonium tetraphenylborate the stretching and bending vibrations of the NH_4^+ group appear at 3223 and 1405 cm^{-1}. These bands can not be found in the spectra of the alkali metal tetraphenylborates. The intensities of these bands depend only on the amount of ammonium tetraphenylborate, under fixed experimental conditions. It is favourable to use the band at 1405 cm^{-1} for determining ammonium ions, as the results obtained by measuring at 3223 cm^{-1} are less accurate owing to the presence of a small but uncontrollable amount of adsorbed water, as O—H stretching vibrations also appear in this region.

First the possibilities of the determination of ammonium ions in two-component systems were studied. Two-component calibration mixtures were prepared containing ammonium ions and potassium, rubidium or caesium ions, and then two-component precipitates were prepared from the mixtures. From each precipitate KBr pellets were pressed (3 mg of precipitate/1 g of KBr) and the infrared spectra run at a low recording speed (50 cm^{-1}/min) from 1270 to 1500 cm^{-1}; 3 parallel precipitations were made from each mixture and 3 spectra taken of each precipitate. The absorbance for the band at 1405 cm^{-1} was calculated by the base-line technique. The relationship between the absorbance and concentration of ammonium tetraphenylborate was calculated by the method of least squares. The equations of the calibration lines and data concerning the reliability of calculation are presented in Table I.

TABLE I.—DATA FOR CALIBRATION CURVES FOR THE DETERMINATION OF AMMONIUM TETRAPHENYLBORATE

	Equation of the calibration curves	S	S_a	S_b
In the presence of K^+	$A = 0{\cdot}027 + 0{\cdot}0083C$	±0·006	±0·002	±0·0001
In the presence of Rb^+	$A = 0{\cdot}041 + 0{\cdot}0081C$	±0·010	±0·003	±0·0002
In the presence of Cs^+	$A = 0{\cdot}027 + 0{\cdot}0083C$	±0·007	±0·001	±0·0001
In the presence of K^+, Rb^+, Cs^+	$A = 0{\cdot}013 + 0{\cdot}0083C$	±0·012	±0·002	±0·0001

C = concentration of NH_4BPh_4 in wt%.
S = standard deviation of the points of the line.
S_a and S_b = standard deviations of the slope and intercept respectively.

Next the possibility of determining ammonium ions in the presence of all the alkali ions without separation was studied. In order to prepare the calibration series, $0{\cdot}1M$ stock solutions were used in amounts which ensured identical ratios of the alkali metal tetraphenylborates in the precipitates prepared from them. The calibration curve was prepared in a way similar to that used for two-component systems (see Table I).

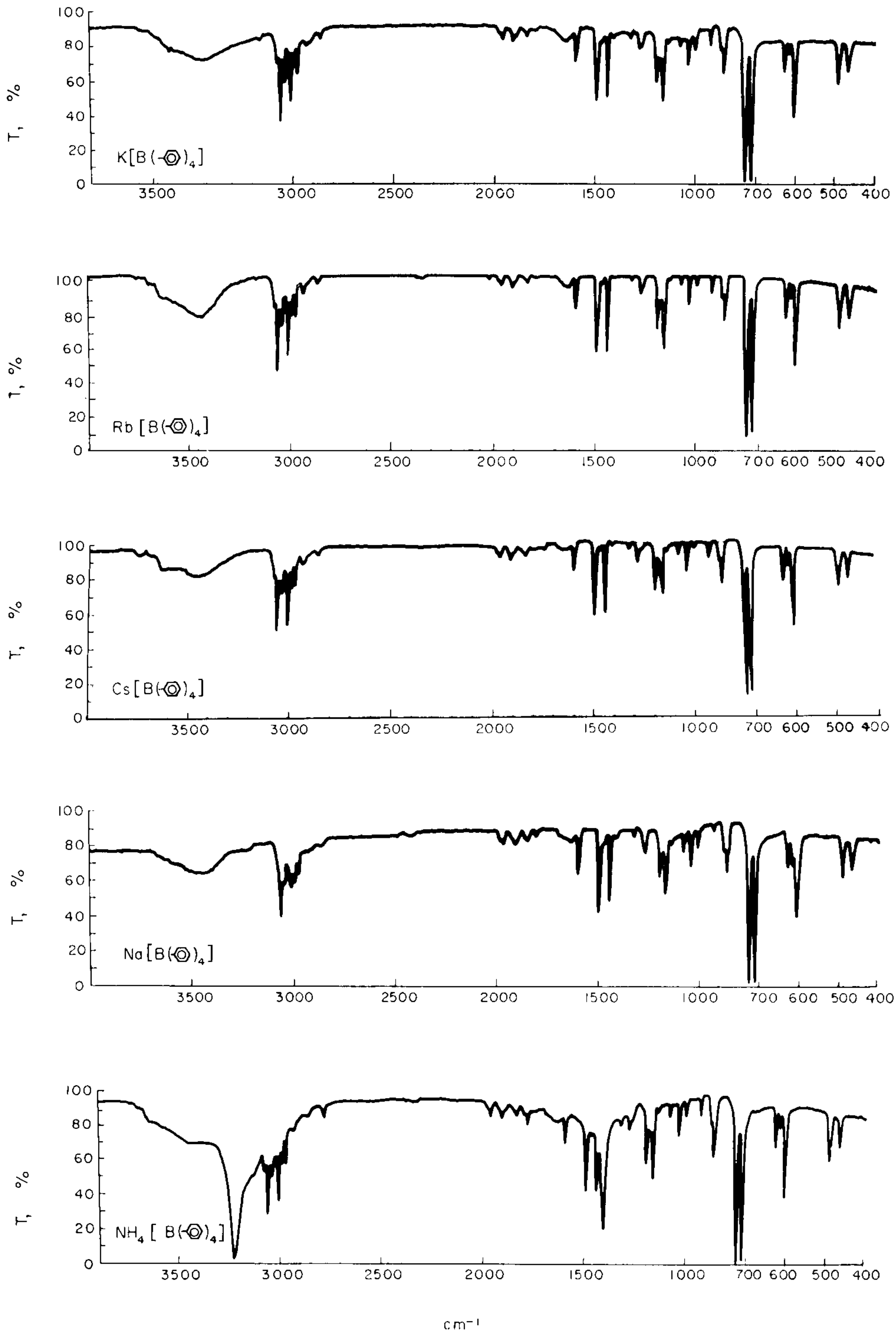

FIG. 1.—Spectra of the tetraphenylborates of (*a*) K^+, (*b*) Rb^+, (*c*) Cs^+, (*d*) Na^+, (*e*) NH_4^+.

TABLE II

In the presence of K^+			In the presence of Rb^+		
NH_4BPh_4, *wt*%	Standard deviation, *wt*%	Error, %	NH_4BPh_4, *wt*%	Standard deviation, *wt*%	Error, %
23·9	1·6	−1·4	21·7	0·9	+1·5
32·0	0·4	+2·2	29·4	1·0	+2·5
48·5	1·9	+1·4	45·5	1·5	−1·8
65·3	1·1	+0·5	62·5	1·4	−1·7
73·8	1·1	−1·5	71·4	0·3	−1·6
In the presence of Cs^+			In the presence of K^+, Rb^+, Cs^+		
NH_4BPh_4, *wt*%	Standard deviation, *wt*%	Error, %	NH_4BPh_4, *wt*%	Standard deviation, *wt*%	Error, %
19·9	4·1	+1·0	10·0	2·4	−3·0
27·1	1·1	+2·8	25·0	1·9	−1·2
42·7	1·2	+0·9	40·0	1·7	+1·8
59·9	1·5	−1·8	57·1	1·0	+1·5
69·1	0·8	+1·1	72·7	0·9	−2·8
			84·2	0·5	−1·7

Finally measurements were made with solutions of known composition in order to estimate the error and standard deviation of the method. The results of these measurements are given in Table II. As shown by the calibration lines, standard deviations and errors, ammonium ions can be determined in the presence of alkali metal ions without preliminary separation, by means of infrared spectrophotometry. The accuracy of the results approaches that of the results obtained by gravimetric analysis involving separation. The method is especially suited to the determination of micro amounts and to routine analyses, owing to its rapidity and simplicity.

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Summary—The infrared spectra of alkali metal and ammonium tetraphenylborates have been studied and an infrared spectrophotometric method developed for the determination of ammonium ions in the form of the tetraphenylborate. The N–H deformation vibration band appearing at 1405 cm^{-1} in the spectrum of ammonium tetraphenylborate has been utilized for quantitative evaluation; the tetraphenylborates of the alkali metals do not exhibit absorption at this frequency. Thus ammonium ions can be determined as the tetraphenylborate in the presence of alkali metal ions without preliminary separation.

Zusammenfassung—Die Infrarotspektren der Alkali- und Ammoniumtetraphenyloborate wurden untersucht und ein infrarotspektrophotometrisches Verfahren zur Bestimmung von Ammoniumionen in Form ihres Tetraphenyloborats entwickelt. Zur quantitativen Auswertung wurde die N-H-Deformationsschwingungsbande verwendet, die im Spektrum von Ammoniumtetraphenyloborat bei 1405 cm^{-1} erscheint; die Alkali-Tetraphenyloborate absorbieren bei dieser Wellenzahl nicht. So können Ammoniumionen in Gegenwart von Alkalimetallionen ohne Abtrennung als Tetraphenyloborat bestimmt werden.

Résumé—On a étudié les spectres infra-rouges des tétraphénylborates de métaux alcalins et d'ammonium, et l'on a élaboré une méthode spectrophotométrique infra-rouge pour le dosage d'ions ammonium sous forme de tétraphénylborate. On a utilisé la bande de vibration de déformation N-H apparaissant à 1405 cm^{-1} dans le spectre du tétraphénylborate d'ammonium pour l'évaluation quantitative; les tétraphénylborates des métaux alcalins ne présentent pas d'absorption à cette fréquence. Ainsi les ions ammonium peuvent être déterminés à l'état de tétraphénylborate en la présence d'ions des métaux alcalins sans séparation préalable.

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Use of complex displacement reactions in photometric analysis

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THE USE of complex displacement reactions in photometric determinations is advantageous if no suitable photometric reagent is available for the direct determination of a metal ion, or where metal ions of similar behaviour are separated chromatographically and the eluate is monitored photometrically by means of the same colour reaction.

The principle of the method, if trace amounts of a metal ion M are to be determined, can be given as follows. Let us consider the case where two chelate-forming agents are used, the one as masking agent and the other as photometric reagent, both forming 1:1 complexes with metal ions.

To the sample solution containing the metal ion M is added excess of a reagent solution containing a stable stoichiometric complex BL and a photometric reagent Y. If the equilibrium conditions are favourable, M replaces B in the complex and the liberated B—the amount of which is equivalent to that of the ion M originally present—forms a coloured compound with Y, which can be estimated photometrically. The reactions are:

$$\mathrm{M} + \mathrm{BL} \rightleftharpoons \mathrm{ML} + \mathrm{B} \tag{1}$$

$$\mathrm{B} + \mathrm{Y} \rightleftharpoons \mathrm{BY} \tag{2}$$

Charges are omitted for simplicity.

To obtain a complete (>99%) displacement reaction between M and BL, the equilibrium constant of reaction (1) must be greater than 100.

$$K_1 = \frac{K_{\mathrm{ML}}'}{K_{\mathrm{BL}}'} > 10^2. \tag{3}$$

K_{ML}' and K_{BL}' are the conditional stability constants of the complexes ML and BL respectively. The conditional stability constants defined and used by Ringbom[1] can be expressed with the side reaction coefficients:

$$K_{ML}' = \frac{K_{ML}}{\alpha_M \cdot \alpha_L} \tag{4}$$

$$K_{BL}' = \frac{K_{BL}}{\alpha_B \cdot \alpha_L}\,. \tag{5}$$

where α_M, α_B and α_L are the side-reaction coefficients for the ions M, B and ligand L respectively. K_{ML} and K_{BL} are the thermodynamic stability constants. By substitution we have:

$$K_1 = \frac{K_{ML} \cdot \alpha_B}{K_{BL} \cdot \alpha_M} > 10^2. \tag{6}$$

In presence of the photometric reagent the main side-reaction of B is presumably reaction (2). Thus

$$\alpha_B \sim \alpha_{B(Y)} = 1 + [Y]K_{BY} \tag{7}$$

Since $[Y]K_{BY} \gg 1$, the first term on the right-hand side can be omitted.

In most cases the photometric reagent is a weak organic acid, and the protonation of the ligand Y must also be considered, by means of the side-reaction function $\alpha_{Y(H)}$:

$$\alpha_{B(Y)} \sim [Y'] \frac{K_{BY}}{\alpha_{Y(H)}} \tag{8}$$

where

$$\alpha_{(Y)H} = 1 + [H^+]k_1 + [H^+]^2 k_1 k_2 + \cdots \tag{9}$$

and k_1, k_2 *etc* are the protonation constants of the ligand Y. By use of equation (8), requirement (6) can be modified:

$$K_1 = \frac{K_{ML} \cdot K_{BY}}{K_{BL} \cdot \alpha_M \cdot \alpha_{Y(H)}} [Y'] > 10^2. \tag{10}$$

The second important requirement is that the displacement reaction between BL and Y

$$BL + Y \rightleftharpoons BY + L \tag{11}$$

should not take place to any appreciable extent (*i.e.*, <1%). Thus the equilibrium constant for this reaction, K_2, must be < 0·01:

$$K_2 = \frac{K_{BY}'}{K_{BL}'} < 10^{-2} \tag{12}$$

or

$$K_2 = \frac{K_{BY} \cdot \alpha_{L(H)}}{K_{BL} \cdot \alpha_{Y(H)}} < 10^{-2}. \tag{13}$$

There is also a third requirement which must be fulfilled for the quantitative photometric determination to be made, namely the completeness of reaction (2), the formation of the coloured complex, *i.e.*,

$$\frac{[BY]}{[B']} = K_{BY}'[Y'] > 10^2. \tag{14}$$

On comparing requirement (10) with requirement (14) it can be concluded that a photometric determination based on a complex displacement reaction can be realized if the two metal ions chosen form with the masking agent L complexes of nearly the same strength, but only one of them (B) reacts with the photometric reagent ($\alpha_{M(Y)} \sim 1$).

By using the deduced requirements (10), (13) and (14) the most favourable conditions for photometric determinations can be found by calculation.

Example

The indirect photometric determination of erbium(III) can be made in a $10^{-1}M$ ammonium lactate buffer solution of pH 4 by using the copper(II)-ethylenediamine tetra-acetate (CuEDTA) complex of stoichiometric composition and 1-(2-pyridylazo)-2-naphthol (PAN) as indicator.

Log $K_{\mathrm{CuEDTA}} = 18{\cdot}8$; log $K_{\mathrm{ErEDTA}} = 18{\cdot}98$;[2] log $K_{\mathrm{CuPAN}} = 16{\cdot}0$;[3] the formation constants of the erbium(III) lactate complexes are log $\beta_1 = 2{\cdot}77$, log $\beta_2 = 5{\cdot}11$, log $\beta_3 = 6{\cdot}70$;[4] those of the copper(II) lactate complexes are log $\beta_1 = 3{\cdot}02$; log $\beta_2 = 4{\cdot}84$;[5] the protonation constant of lactate is log $k = 3{\cdot}76$, those of PAN are log $k_1 = 12{\cdot}2$; log $k_2 = 1{\cdot}9$.[3]

In the calculations requirements (10), (13) and (14) must be considered. In a solution at pH 4

$$\alpha_{\mathrm{lac(H)}} = 1 + 10^{-4}\,.\,10^{3.76} = 10^{0.2}$$

$$\alpha_{\mathrm{Er(lac)}} = 1 + 10^{-1.2}\,.\,10^{2.77} + 10^{-2.4}\,.\,10^{5.11} + 10^{-3.6}\,.\,10^{6.7} = 10^{3.25}$$

$$\alpha_{\mathrm{PAN(H)}} = 1 + 10^{-4}\,.\,10^{12.2} + 10^{-8}\,.\,10^{14.1} = 10^{8.2}$$

According to requirement (10):

$$\log K_{\mathrm{ErEDTA}} + \log K_{\mathrm{CuPAN}} + \log\,[\mathrm{PAN}'] - \log K_{\mathrm{CuEDTA}} - \log \alpha_{\mathrm{Er(lac)}} - \log \alpha_{\mathrm{PAN(H)}} > 2$$

$$18{\cdot}98 + 16{\cdot}0 + \log\,[\mathrm{PAN}'] - 18{\cdot}8 - 3{\cdot}25 - 82 > 2 \qquad \log\,[\mathrm{PAN}'] > -2{\cdot}73$$

The concentration of the PAN reagent must be at least 2 × $10^{-3}M$.

The other two requirements can also be fulfilled by using 2 × $10^{-3}M$ reagent concentration.

$$\alpha_{\mathrm{Cu(lac)}} = 1 + 10^{-1.2}\,.\,10^{3.02} + 10^{-2.4}\,.\,10^{4.84} = 10^{2.53}$$

$$\log K_{\mathrm{CuPAN}} = 16 - 2{\cdot}53 - 8{\cdot}2 = 5{\cdot}27$$

$$\log \alpha_{\mathrm{EDTA(H)}} = 8{\cdot}2 \text{ (at pH 4)}^{1}$$

Requirement (13):

$$\log K_{\mathrm{CuEDTA}} + \log \alpha_{\mathrm{PAN(H)}} - \log K_{\mathrm{CuPAN}} - \log \alpha_{\mathrm{EDTA(H)}} > 2$$

$$18{\cdot}8 + 8{\cdot}2 - 16 - 8{\cdot}6 = 2{\cdot}4 > 2$$

and requirement (14):

$$\log K_{\mathrm{CuPAN}} + \log\,[\mathrm{PAN}'] > 2$$

$$5{\cdot}27 - 2{\cdot}7 = 2{\cdot}57 > 2.$$

The photometric determination can be realized by using the conditions given. This has also been proved by measurements.[6]

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Summary—The theoretical requirements for the quantitative photometric determination of trace amounts of metal ions by use of complex displacement reactions are discussed and a calculation method using conditional equilibrium constants and side-reaction functions defined and used by Ringbom is recommended. As an example, the requirements in the determination of erbium(III) by using copper(II)-EDTA complex and PAN indicator in ammonium lactate buffer solutions are calculated.

Zusammenfassung—Die theoretischen Anforderungen an die quantitative photometrische Bestimmung von Spuren von Metallionen mit Hilfe von Komplexverdrängungsreaktionen werden diskutiert und ein Berechnungsverfahren empfohlen, das die Gleichgewichtskonstanten unter den betreffenden Bedingungen und Nebenreaktionsfunktionen verwendet. Als Beispiel werden die Anforderungen an die Bestimmung von Erbium(III) mit dem Kupfer(II)-EDTA-Komplex und PAN als Indikator in Ammoniumlactat-Pufferlösungen berechnet.

Résumé—On discute des exigences théoriques pour la détermination photométrique quantitative de traces d'ions métalliques par réactions de déplacement de complexe et l'on recommande une méthode de calcul utilisant les constantes d'équilibre conditionnelles et les fonctions de réaction secondaire. A titre d'exemple, on calcule les exigences de la détermination de l'erbium (III) en utilisant le complexe cuivre (II)-EDTA et l'indicateur PAN en solutions tampons de lactate d'ammonium.

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Application of direct thermometric analysis in iodometry

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IODOMETRIC determinations are most often made indirectly, owing to the difficulties of end-point detection. Systems with a standard redox potential more positive than that of the iodine–iodide couple are allowed to react with excess of iodide and the resulting iodine is titrated with standard sodium thiosulphate solution. Similarly, systems with a redox potential less positive than that of the iodine–iodide system are preferably determined by oxidation with excess of iodine and back-titration with sodium thiosulphate.

In the last decade thermometric titration has been used for several redox reactions.[1] Determinations were made in the usual way and order; *e.g.*, copper(II) was determined by adding excess of potassium iodide and titrating with sodium thiosulphate, the temperature change due to the heat of reaction being measured and used to evaluate the amount of copper.[2] The large heat of dilution of sodium thiosulphate, however, renders the determination rather inaccurate.

According to our considerations, two ways present themselves for the more accurate and simple performance of iodometric thermometric determinations.

1. Application of a solution of iodide ions as the titrant.
2. Compensation of the heat of dilution of sodium thiosulphate solution[3] by use of an exothermic process which does not affect the main reaction.

The determination of chlorine in chlorine water was chosen as a model in which no side-reactions had to be considered. Direct determination was used for measurement,[3] *i.e.*, equal amounts of the reagent were added to solutions of equal heat capacities, and the temperature changes were found to be proportional to the concentration of the component to be determined. The amount of reagent added must, of course, be in excess of that required in the reaction.

EXPERIMENTAL

Reagents

Saturated chlorine water. The chlorine content was frequently checked by iodometric titration.[4]

Potassium iodide solution, 20% *w/v* (*about* 1·6*M*).

Acidified potassium iodide solution. Potassium iodide solution (20%, 90 ml) and concentrated hydrochloric acid (10 ml).

Sodium thiosulphate solution, 1*N*.

Sodium thiosulphate solution containing glycerine. Sodium thiosulphate solution (1*N*, 65 ml) + glycerine (d_4^{20} = 1·231; 35 ml).

Apparatus

Directhermom produced by MOM (Hungarian Optical Works).

Procedure

Preparation of the calibration graph. By pipette, 1, 2, 5, 10, 20 ml of chlorine water were transferred to the plastic vessel of the Directhermom and diluted to 200 ml with distilled water. A magnetic stirrer was placed in the vessel and the latter put into the equipment. Next a 2-ml immersion pipette was filled with 20% potassium iodide solution, and mounted on the measuring head. The pipette and the thermistor were immersed in the solution. Stirring was started and 3 min allowed for thermal equililbrium to be set up. The galvanometer was then set to read to 100 scale units at sensitivity 1. The reagent was added first to the blank. In the case studied the galvanometer deflected to −30 scale units, indicating that the dilution of potassium iodide was an endothermic process. When the reagent was added to chlorine water the scale reading was positive, being as high as 500 scale units in the case of a sample containing 20 ml of chlorine water. The heat of dilution of potassium iodide was compensated by adding hydrochloric acid. If 10 ml of concentrated hydrochloric acid were added to 90 ml of 20% potassium iodide solution, and the resulting solution added to the chlorine water samples, the heat effect observed with the blank solution could be eliminated. The calibration line then started from the origin of the graph and was linear.

To prepare an accurate calibration curve the amount of chlorine present at the time of reaction had to be determined—owing to the volatility of chlorine—by measuring the liberated iodine equivalent to the chlorine present in the chlorine water. For this purpose the plastic vessels were removed from the equipment and their iodine contents titrated with dilute sodium thiosulphate solution (1 ml of which was equivalent to about 1 mg of chlorine—*i.e.*, ~0·03*N*) in presence of starch indicator. The scale reading was plotted as a function of mg of chlorine present in 200 ml of sample solution, and gave a linear graph.

The immersion pipette system of the Directhermom allows several determinations to be made successively on the same sample. In the present case both the direct and indirect determinations of chlorine can be made, *i.e.*, after addition of potassium iodide the iodine formed can also be determined on the basis of its reaction with sodium thiosulphate. For the thermometric determination of the liberated iodine 1*N* sodium thiosulphate was used in 2-ml immersion pipettes. The reagent was first added to the blank solution, which already contained 2 ml of potassium iodide acidified with hydrochloric acid. Under these conditions a scale reading of −60 was obtained at sensitivity 1, owing to the endothermic nature of the dilution of sodium thiosulphate. Starting from the well known fact that the dilution of glycerine with water is an exothermic process, a glycerine to thiosulphate solution ratio could be found experimentally, at which no heat effect was observed on adding the mixture to the blank, *i.e.*, the heat of dilution was compensated. The composition of this thermoneutral mixture was 65 ml of 1*N* sodium thiosulphate + 35 ml of glycerine. The calibration line passed through the origin and was linear when this thermoneutral mixture was used.

Another series of measurements was made, for determination of chlorine in chlorine water, as follows. One immersion pipette contained potassium iodide acidified with hydrochloric acid, and another thiosulphate solution containing glycerine. After addition of potassium iodide to the test

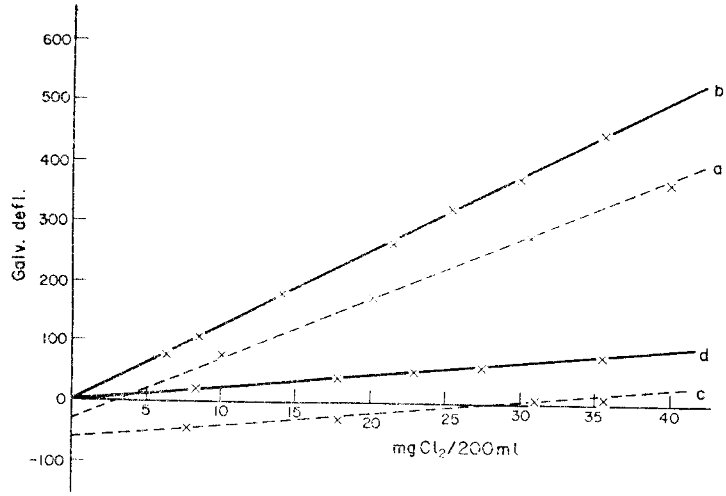

FIG. 1.—Determination of the chlorine content of chlorine water.
a Reagent 20% potassium iodide solution.
b Reagent thermoneutral potassium iodide solution.
c Reagent sodium thiosulphate solution.
d Reagent thermoneutral sodium thiosulphate solution.

solution the galvanometer deflection was read and the galvanometer was set to zero again. Next the thiosulphate solution was added and the temperature change read. The scale reading was equal to the difference in the values given by the two reactions.

Because the slope of the calibration curve is much higher for the iodide–chlorine reaction than for the reaction of iodine with thiosulphate (Fig. 1), the direct determination with iodide is much the more advantageous.

Determination of active chlorine in bleaching powder

As an application of the method described, the active chlorine in commercial bleaching powder was determined.

Procedure. Transfer a 0·1–0·2 g sample of bleaching powder to the plastic vessel of the Directhermom in which 200 ml of distilled water have been placed previously. Fill the immersion pipette with about 2 ml of thermoneutral potassium iodide solution. After stirring for 3 min, add 3 drops of 10% hydrochloric acid to neutralize the solution, switch on the galvanometer and set it to zero. Then add the thermoneutral potassium iodide solution and wait about 100 sec for the galvanometer to reach maximum deflection. Use the chlorine water calibration graph.

Results. For comparison purposes, the results obtained by the thermometric method described are given in Table I, along with those of the conventional iodometric method. The reason why the results of thermometric determinations are lower than those of the conventional iodometric method lies in the non-instantaneous nature of the reaction; as the temperature of the reaction volume becomes higher than that of the surroundings, owing to the exothermic reaction, the cooling effect of the environment which leads the galvanometer deflection being smaller than it should be. The reaction used for the calibration curve is faster, and this difference in rate accounts for the error. The error could be eliminated if the calibration curve were prepared by titrating the iodine liberated by different weights of bleaching powder and plotting galvanometer deflection *vs.* amount of chlorine equivalent to the iodine liberated.

TABLE I.—THE CHLORINE CONTENT OF BLEACHING POWDER

By iodometric titration, %	By Directhermom method, %
30·9	30·4 ± 0·1
30·0	29·5 ± 0·1
28·3	27·8 ± 0·1
26·8	26·3 ± 0·1
25·2	24·8 ± 0·1

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Summary—Elementary chlorine was determined by a thermometric method using potassium iodide as reagent. The temperature rise corresponding to the heat of reaction was proportional to the chlorine content. Iodine formed in the reaction was also determined with sodium thiosulphate. The heat of the chlorine–iodide reaction is about five times that of the iodine–thiosulphate reaction. Direct determination with potassium iodide is simpler and more rapid than the indirect one.

Zusammenfassung—Elementares Chlor wurde thermometrisch mit Kaliumjodid als Reagens bestimmt. Der der Reaktionswärme entsprechende Temperaturanstieg war zur Chlorkonzentration proportional. Das bei der Reaktion freigewordene Jod wurde auch mit Natriumthiosulfat bestimmt. Die Wärmetönung der Reaktion Chlor-Jodid ist etwa fünfmal so groß wie die der Reaktion Jod-Thiosulfat. Die direkte Bestimmung mit Kalium-jodid ist einfacher und geht schneller als die indirekte.

Résumé—On a déterminé le chlore élémentaire par une méthode thermométrique en utilisant l'iodure de potassium comme réactif. L'élévation de température correspondant à la chaleur de réaction est proportionnelle à la teneur en chlorure. L'iode formé dans la réaction a aussi été dosé par le thiosulfate de sodium. La chaleur de la réaction chlore–iodure est environ cinq fois celle de la réaction iode–thiosulfate. Le dosage direct par l'iodure de potassium est plus simple et plus rapide que le dosage indirect.

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Determination of nickel and copper by precipitation from homogeneous solution as their salicylaldimine complexes

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SALICYLALDIMINE was first used for the determination of metal ions by Duke.[1] The procedure recommended by him resulted in a voluminous, gel-like precipitate which was difficult to handle. The composition and thermal behaviour of the precipitate were studied by Pariaud and Labeille[2] and by Marin and Duval.[3] The precipitate was found to have a metal to ligand ratio of about 1:2, but the composition was not reproducible and Duval[3] did not recommend the procedure as an analytical method.

The purpose of the present work has been to produce a crystalline precipitate of well-defined composition by precipitation from homogeneous solution. The reagent was prepared in the solution by the reaction of salicylaldehyde and ammonia, the latter being formed in the solution slowly. The composition and thermal behaviour of the precipitate were studied as well as the pH dependence of its solubility.

EXPERIMENTAL

Reagents

Copper(II) and nickel sulphate solutions. Prepared from analytical grade reagents by accurate weighing. The copper solution was standardized gravimetrically by precipitation of copper(I) thiocyanate and by electrogravimetry, and the nickel solution by the dimethylglyoxime method and by electrogravimetry.

Ammonium carbonate solution, 20% *w/v*. Prepared from the analytical grade reagent.

Urea solution, 20% *w/v*. Prepared from the analytical grade reagent.

Salicylaldehyde solution, 4% *in alcohol.*

Procedure

Two methods have been developed. As salicylaldimine reacts instantaneously with metal ions, the rate of precipitation is controlled in both cases by the rate of formation of the reagent. The two methods differ in the way that the ammonia needed is liberated.

In one method ammonia was produced by hydrolysing a hot (95°) aqueous solution of urea. The ammonia produced reacted with the salicylaldehyde, and the product with the metal ion present.

In the second method solutions of salicylaldehyde and ammonium carbonate were added to the solution of the metal ion to be determined. The solution of ammonium carbonate contains free ammonia in an amount depending on the pH. This free ammonia reacts with the salicylaldehyde. The rate of precipitation can be controlled by adjusting the pH to a suitable value.

Method A. To the solution containing 2–10 mg of nickel or copper in a 400-ml beaker add 10 ml of 4% alcoholic salicylaldehyde solution and 50 ml of 20% aqueous urea solution. Then dilute to 200–300 ml, and warm the solution on a steam-bath for 2–3 hr, during which time a nice crystalline precipitate is formed. Collect the precipitate on a sintered-glass filter, porosity 3, in the cold and wash it with cold water. Dry the precipitate at 110° for 2 hr.

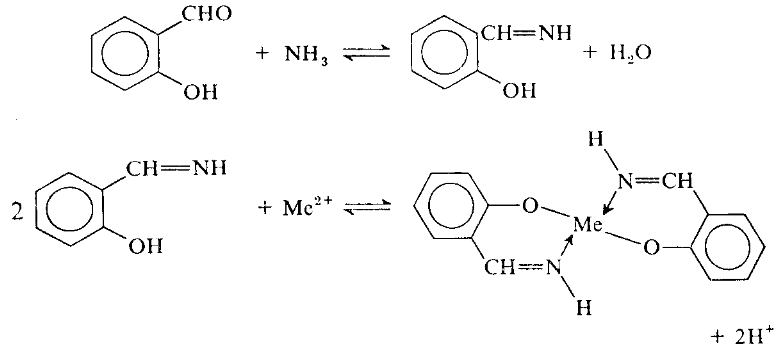
Method B. To the solution containing 2–90 mg of nickel or copper in a 400-ml beaker add 10 ml of 4% alcoholic salicylaldehyde solution and 10 ml of 20% aqueous ammonium carbonate solution. In some minutes a crystalline precipitate forms. Wait for 1–2 hr and then collect the precipitate on a porosity-3 sintered-glass filter and wash it with distilled water.

RESULTS

The organic matter in the filtrates was decomposed with a mixture of hydrogen peroxide and sulphuric acid, then the solution was evaporated to dryness, the residue dissolved in water, and traces of nickel or copper were determined spectrophotometrically. The amount of nickel or copper in the filtrates was found to be smaller than 0.05 mg.

The processes taking place in the course of the determination are accompanied by consumption of ammonia and liberation of acid, so it seemed to be of importance to study the pH-dependence of the solubility of the precipitate. The following reactions take place in the solution:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$



As shown by the equations, two protons are liberated in the reaction of salicylaldimine with the metal ion. The liberated acid must be neutralized in order to carry the reaction to completion. If a constant pH is to be maintained during the reaction (as the rate of reaction is controlled by the pH) the solution must have rather a high buffer capacity. Ammoniacal buffers have highest capacity at pH 9.2. The required buffer capacity could be ensured by increasing the concentrations of both ammonia and ammonium salt.

According to our experiments, to precipitate amounts of nickel or copper smaller than 100 mg at least 2 g of ammonium carbonate are necessary. If the amount of the ammonium salt is smaller the metal salicylaldehyde complex also precipitates.

The pH-dependence of the solubility of the precipitates was studied. Portions (0·5 g) of the dried nickel or copper complex were weighed and transferred to a double-walled vessel and 100 ml of water were added. The temperature of the solution was adjusted to 25·0 ± 1° by means of a VEB U-8 ultrathermostat, the suspension was agitated by a magnetic stirrer, and after 2 hr aliquots were withdrawn at 30-min intervals. The change in the absorbance of the solution was measured spectrophotometrically. When the concentration of the solution did not change further—after about 4–5 hr of agitation—a 50-ml aliquot of the solution was evaporated to dryness and the residue decomposed with a mixture of hydrogen peroxide and sulphuric acid. In the solution so obtained, copper was determined photometrically at 436 nm with sodium diethyldithiocarbamate and nickel at 450 nm with dimethylglyoxime. As shown in Fig. 1, the copper salicylaldimine complex has minimum solubility at pH 8–11 and the solubility of the nickel salicylaldimine complex is lowest in the pH range 8·5–10·5. In the methods described the pH was between 8 and 9.

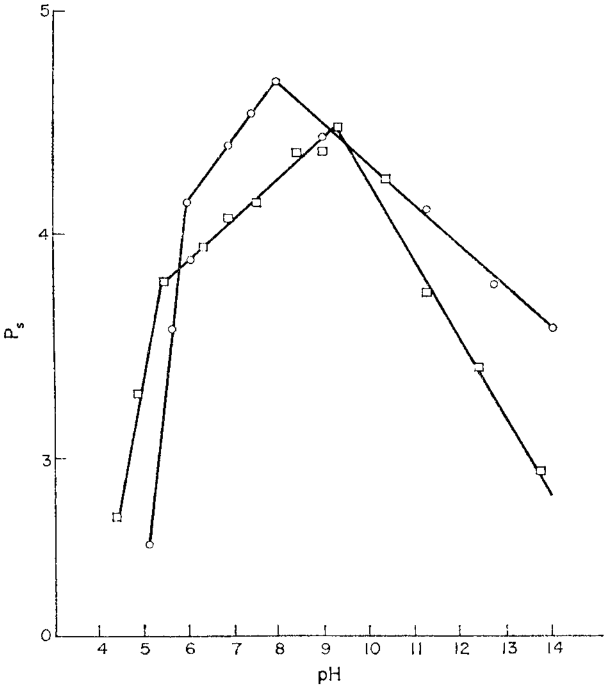


FIG. 1.—Dependence of solubility exponent (p_s) on pH: □ copper complex; ○ nickel complex.

TABLE I

Cu taken, *mg*	Coefficient of variation, %	
	Conventional method	PFHS method
5·86	1·0	0·3
11·72	0·4	0·2
29·32	0·2	0·1
58·60	0·1	0·03

TABLE II

Ni taken, *mg*	Coefficient of variation, %	
	Conventional method	PFHS method
7·81	1·3	0·5
15·62	0·5	0·3
39·05	0·1	0·1
78·10	0·1	0·05

The accuracy of the precipitation from homogeneous medium as compared to that of the conventional method can be judged on the basis of Table I for copper and Table II for nickel. The coefficient of variation was determined from 6 parallel measurements for different sample weights.

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Summary—A method has been developed for the gravimetric determination of copper and nickel as their salicylaldimine complexes, by precipitation from homogeneous solution. The complexes are crystalline precipitates which are very easy to filter off and wash. The accuracy of the determinations is higher than that of the conventional precipitation method.

Zusammenfassung—Ein Verfahren zur gravimetrischen Bestimmung von Kupfer und Nickel durch Fällung aus homogener Lösung als Komplexe mit Salicylaldimin wurde entwickelt. Die Komplexe sind kristalline Niederschläge, die sehr leicht zu filtrieren und auszuwaschen sind. Die Genauigkeit der Bestimmungen ist größer als bei der herkömmlichen Fällungsmethode.

Résumé—On a élaboré une méthode pour le dosage gravimétrique du cuivre et du nickel sous forme de leurs complexes salicylaldimine, par précipitation à partir d'une solution homogène. Les complexes sont des précipités cristallisés qui sont très aisés à filtrer et laver. La précision des dosages est supérieure à celle obtenue par la méthode de précipitation ordinaire.

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Application of chemiluminescent indicators in EDTA titrations

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TWO CHEMILUMINESCENT indicators have so far been used for end-point detection in chelatometric titrations: luminol and lucigenine.[1-3] Both emit intense chemiluminescent light in alkaline medium, in the presence of oxidizing agents (*e.g.*, hydrogen peroxide). The emission reaction is catalysed by heavy metal ions. The mechanism of chemiluminescence is, however, different for the two indicators.

THEORETICAL

In the chemiluminescence of luminol (3-aminophthalic hydrazide), hydroxyl or oxygen free radicals play an important role.[1,4-6] These free radicals are produced during the decomposition of hydrogen peroxide in alkaline medium in the presence of catalysts, *e.g.*, heavy metal ions. From the luminol molecule, which is capable of emission, an unstable peroxide is formed in the presence of free radicals, and is transformed into inactive aminophthalic acid with emission of light. If the heavy metal ions necessary to induce emission are bound by a suitable complexing agent, luminol will not emit light. Luminol can be used as a chelatometric indicator.

In the emission from lucigenine (*N,N'*-dimethyldiacridylium nitrate) perhydroxyl ions play an important part. Perhydroxyl ions are formed during the decomposition of hydrogen peroxide in alkaline medium.[7] In the presence of perhydroxyl ions but the absence of catalysts, lucigenine molecules emit a steady green light; under similar conditions, but in the presence of catalyst ions, a more intense, irreversible emission can be observed for a shorter period of time. This is due to the fast decomposition of perhydroxyl ions in the presence of catalysts. If the heavy metal ions acting as catalyst are bound in the form of complexes the decomposition of perhydroxyl ion can be prohibited and the emission of the indicator stabilized.

Accordingly, if heavy metal ions are titrated with EDTA, the end-point of the titration is indicated by the disappearance of the light of luminol or by the appearance of the steady chemiluminescence of lucigenine. When, in turn, EDTA solution is titrated with, *e.g.*, copper(II), the first excess of titrant is indicated by the appearance of the chemiluminescent light of luminol, or by the disappearance of the luminescence from lumigenine.

TABLE I

Metal taken, μmole		Added 0·01M EDTA, *ml*	Luminol				Lucigenine			
			0·01M $CuSO_4$ used, *ml*	Metal found, μmole	Error, %	Relative std. devn., %	0·01M $CuSO_4$ used, *ml*	Metal found, μmole	Error, %	Relative std. devn., %
Cd^{2+}	48·1	10·00	5·15	48·5	+0·8	0·1	5·19	48·1	0·0	0·1
	96·2	20·00	10·42	95·8	−0·4		10·48	95·2	−1·0	
	192·4	50·00	30·83	191·7	−0·4		31·20	188·0	−2·3	
Zn^{2+}	51·3	10·00	4·75	52·5	+2·4	0·6	4·93	50·7	−1·2	0·1
	102·5	20·00	9·52	104·8	+2·3		9·78	102·2	−0·3	
	205·1	50·00	29·09	209·1	+2·0		29·40	206·0	+1·0	
Ni^{2+}	49·3	10·00	5·00	50·0	+1·4	0·2	5·13	48·7	−1·2	0·1
	98·7	20·00	10·22	97·8	−0·8		10·26	97·4	−1·2	
	197·3	50·00	30·54	194·6	−1·4		30·43	195·4	−1·0	

On the basis of this observation a chelatometric method has been developed by Erdey and Buzás[1] for the direct determination of copper(II) and indirect determination of lead and mercury(II). In the present paper the direct chelatometric determination of cadmium, zinc and nickel will be dealt with.

EXPERIMENTAL

Reagents

Copper(II) sulphate solution, 0·01*M*. Dissolve 2·5 g of $CuSO_4.5H_2O$ in 200 ml of distilled water, add 1 ml of 10% sulphuric acid, dilute to 1 litre and standardize electrogravimetrically.[8]

EDTA solution, 0·01*M*.

Test solutions, 0·01*M*. Solutions of cadmium, zinc and nickel were prepared and standardized gravimetrically.[8]

Luminol solution, 0·01%. Warm (on a steam-bath) 0·1 g of luminol in 500 ml of water containing 5 ml of 1*M* sodium hydroxide until completely dissolved, then dilute to 1 litre.

Lucigenine solution, 0·5%. Dissolve 0·5 g of lucigenine in 100 ml of water with mild warming, then filter the solution. Both indicator solutions can be stored indefinitely without decomposition.

All the reagents used were of analytical purity. Demineralized distilled water was used to prepare standard and reagent solutions.

Procedure

Add excess of 0·01*M* EDTA to an ~0·01*M* solution of the metal ion to be determined. Make the solution alkaline with 20 ml of 4*M* ammonia solution in the case of cadmium and nickel, and with 5 ml of 0·1*M* sodium hydroxide in that of zinc. Then heat the solutions to 90°, add 3 ml of luminol or 1 ml of lucigenine solution and 1 ml of 3% hydrogen peroxide solution and titrate with 0·01*M* copper(II) sulphate in a dark room.

In the presence of luminol the end-point is indicated by the appearance of an intense bluish chemiluminescence, whereas in the presence of lucigenine the green chemiluminescence of the solution suddenly ceases.

Data concerning the reproducibility and standard deviation of the method are presented in Table I. The results for titrations are averages of three parallel measurements and the relative standard deviation was calculated on the basis of six parallel titrations.

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Summary—The chemiluminescent indicators lucigenine and luminol are readily applicable to end-point detection in the EDTA titration of cadmium, zinc and nickel ions. Back-titration with copper(II) gives reproducible results. The end-point is indicated by the disappearance of the green chemiluminescence of lucigenine, or by the appearance of the bluish luminescence of luminol.

Zusammenfassung—Die Chemilumineszenzindikatoren Lucigenin und Luminol lassen sich gut zur Endpunktsbestimmung bei der EDTA-Titration von Cadmium, Zink und Nickel verwenden. Rücktitration mit Kupfer(II) gibt reproduzierbare Ergebnisse. Der Endpunkt wird durch das Verschwinden der grünen Chemilumineszenz von Lucigenin oder durch das Auftreten der bläulichen Lumineszenz von Luminol angezeigt.

Résumé—Les indicateurs chimioluminescents lucigénine et luminol sont aisément applicables à la détection du point de fin dosage dans le titrage à l'EDTA des ions cadmium, zinc et nickel. Le titrage en retour avec le cuivre(II) donne des résultats reproductibles. Le point de fin de dosage est indiqué par la disparition de la chimioluminescence verte de la lucigénine, ou par l'apparition de la luminescence bleuâtre du luminol.

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Combined derivatographic and thermo-gas-titrimetric examination of the thermal decomposition of copper tetra-ammine sulphate monohydrate

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THERMOANALYTICAL methods in general do not furnish unambiguous information on the course of decomposition processes if the thermal decomposition reaction is a complex one and more or less overlapping reactions occur with the release of two or more gaseous decomposition products, as happens in the decomposition of copper tetra-ammine sulphate monohydrate during which water and ammonia escape in the temperature range between 20 and 400°. In such cases even complex thermoanalytical methods, *e.g.*, derivatography[1,2] where the thermogravimetric (TG), derivative thermogravimetric (DTG), differential thermal analysis (DTA) and temperature change (T) curves of a single sample are simultaneously recorded, do not yield an exact picture of the gas-evolution processes. Although TG and DTG curves make it possible to evaluate the whole weight-change quantitatively, they cannot furnish separate information on the partly overlapping processes such as the escape of water and ammonia.

For investigation of such problems we developed our combined derivatographic and thermo-gas-titrimetric method.[3,4] In Fig. 1 the automatically operating combined device is shown schematically. On the basis of an earlier principle[1,2] the device records the TG, DTG, DTA and T curves. By means of inert carrier gas streaming over the sample the evolving gaseous decomposition products (*e.g.*, ammonia and water) are quantitatively transported into an aqueous absorbing solution, the pH of which changes and so alters the potential difference between the glass and calomel electrodes dipping into the solution, whereupon an amplifier coupled to the electrodes sets an automatic burette in operation. The burette feeds titrant to the absorbing solution until the original value of the potential difference between the electrodes has been restored. The slide contact of a potentiometer moves along with the piston of the burette, and the galvanometer coupled to the potentiometer records the thermo-gas-titrimetric (TGT) curve. The derivative device, moving along with the axis of the burette, works on the principle of the derivatograph, and permits recording of the derivative of thermo-gas-titrimetric curve (DTGT)

The thermal decomposition of copper tetra-ammine sulphate monohydrate has already been studied by several investigators. On the basis of dilatometric and thermogravimetric measurements Rencker,[5] and Rencker and Vallet[6] concluded that it gradually decomposes between 125 and 400° with splitting off of ammonia and water. The residue is copper sulphate. Anous[7] found essentially the same. Flóra,[8,9] on the basis of derivatographic measurements, reached similar conclusions but also made suggestions concerning the splitting-off process of water and ammonia.

EXPERIMENTAL

The copper tetra-ammine sulphate monohydrate was prepared according to Berzelius,[10] by adding ethanol to a concentrated ammoniacal solution of copper sulphate, filtering off, washing first with ammoniacal ethanol, then with ethanol and last with diethyl ether. The precipitate was dissolved, the solution made alkaline in a distillation apparatus, and the ammonia collected and titrated.

In the course of the thermal analysis the ammonia released was absorbed in hydrochloric acid absorbing solution at pH 3·6. The automatic titrator maintained this pH during the whole process by addition of hydrochloric acid. After a test was completed, the ammonia contents of the absorbing solution were checked by distillation from alkaline solution and titration.

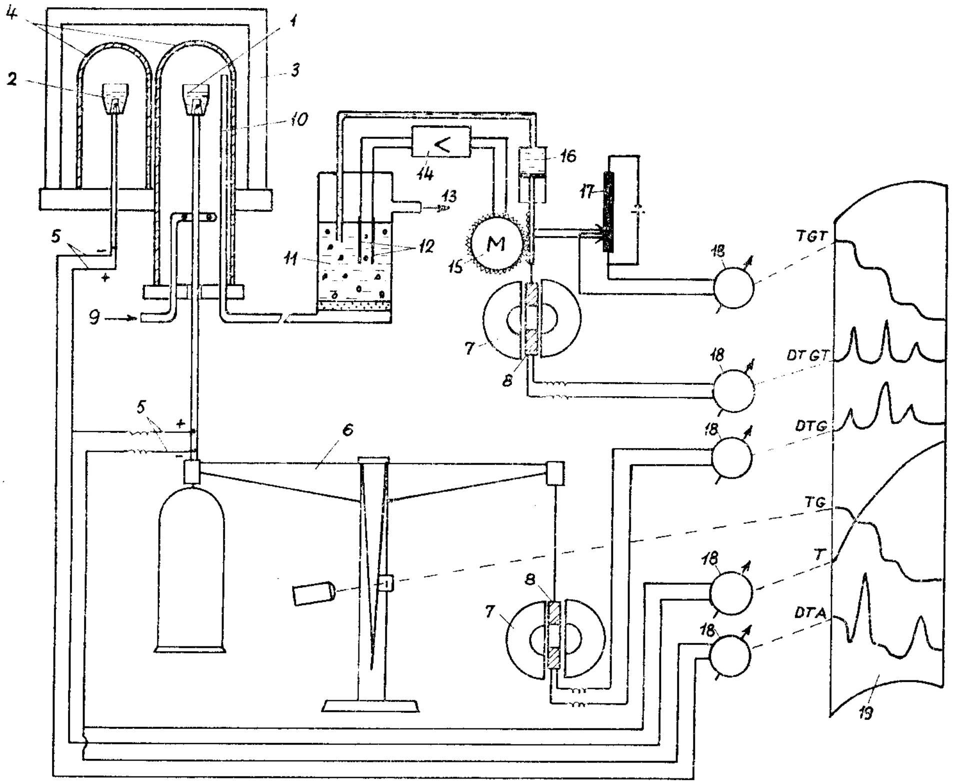

FIG. 1.—Schematic diagram of the combined derivatographic and thermo-gas-titrimetric device.

1—Sample, 2—inert substance, 3—furnace, 4—quartz bulbs, 5—thermocouples, 6—balance, 7—permanent magnet, 8—coil, 9—inlet of inert gas, 10—gas outlet, 11—absorber, 12—electrodes, 13—exhaust, 14—amplifier, 16—motor of the automatic burette, 17—automatic burette, 17—potentiometer, 18—galvanometers, 19—photopaper.

Because during the thermal decomposition a small amount of sulphur trioxide might have been released and absorbed in the absorbing solution, thus affecting the titration, sulphate was determined in the residual solution from the ammonia distillation.

The sample weighed about 130 mg and was heated at a rate of 10°/min. The carrier gas was nitrogen, freed from oxygen by a catalytic reaction, and dried over phosphorus pentoxide. A platinum crucible 16 mm in height and 14 mm in diameter was used.

DISCUSSION

The DTA curve showed that only endothermic reactions occurred, and was in accordance with the DTG curve, showing that apart from processes connected with weight change, no other transformations (*e.g.*, recrystallization) occurred in the sample.

The TG curve shows decomposition processes taking place in three steps. The magnitude of the first step corresponds to a weight loss caused by the joint release of one mole of water and two moles of ammonia, all quantities, here and later, being related to one mole of compound. The second step indicates the release of a further mole of ammonia. The third step shows a greater loss of weight than that corresponding to the last mole of ammonia. There must therefore be loss of some other decomposition product, in the temperature region 300–360°.

The first step of the TGT curve indicates the release of two moles of ammonia, the second one the splitting off of one mole. The third step of the titration curve is smaller than would correspond to the release of one mole of ammonia. Assuming that the sample had the correct stoichiometry, and that all the ammonia was released, there are two possible explanations for this apparent discrepancy. Some acidic decomposition product could be released during the third step and neutralize part of the ammonia, or part of the ammonia released could be thermally decomposed and so not titrated.

The DTGT curve shows the change in the rate of consumption of titrant. On comparing the DTGT curve with the DTA and DTG curves, deviations can be noticed. The DTA and DTG curves indicate by their double peak that between 90 and 210° two decomposition products, water and ammonia, were released. The DTGT curve shows in the same temperature range only a single peak which means that this curve represents the rate of splitting off of one component, ammonia.

The TGT and TG curves represent the release of ammonia and ammonia + water respectively, if formation of other gaseous decomposition products is excluded. It is worth noting that—from among the many possibilities—there is only one way in which the two curves can be brought into agreement without contradiction of the other experimental results, as is shown in Fig. 2. That is, we suppose that in the second period of thermal decomposition only ammonia was released and accordingly the TGT and TG curves were fully in accordance. On the basis of the two curves—by difference calculations—the curve representing the release of water can be constructed (see dotted line in Fig. 2).

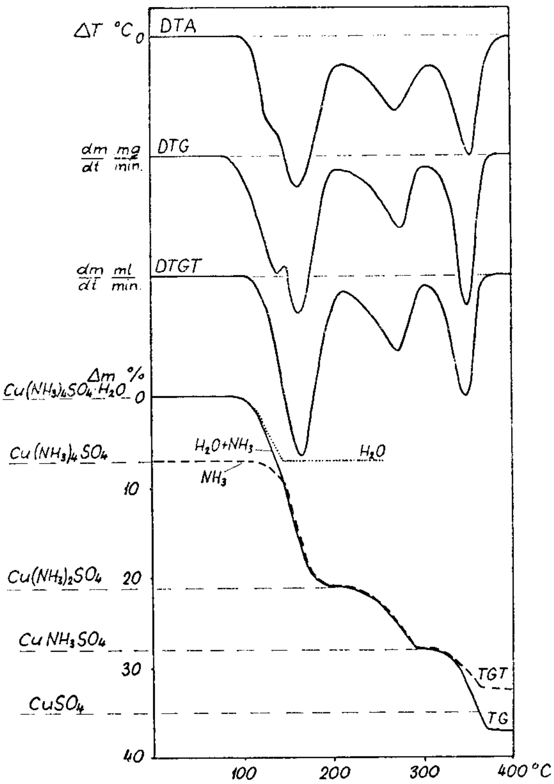

FIG. 2.—Thermogram of the combined derivatographic and thermo-gas-titrimetric examination of copper tetra-ammine sulphate monohydrate.

Examination of the thermal decomposition of copper tetra-ammine sulphate monohydrate under the experimental conditions described above can lead to the following conclusions.

During the first decomposition stage, between 90 and 200°, one mole of water and two of ammonia are released. According to the curves in Fig. 2 decomposition starts with the release of water and only after loss of part of the water does ammonia begin to split off. The two processes overlap to such a degree that the relative amounts of the two decomposition products cannot be determined solely from the TG and DTG curves.

The magnitude of the second decomposition step corresponds to the release of one mole of ammonia. During the third decomposition stage ammonia and a small quantity of sulphur trioxide are released, which is why the third step of the TG curve is bigger, while that of the titration curve is smaller, than is theoretically required. This also explains the 1 % difference in the results in columns 3 and 4 of Table I.

According to the amount of sulphate recovered from the absorbing solution, the titration curve should give only an ammonia content 1·1 % less than the theoretical, but the difference according to columns 2 and 3 of Table I is 2·3 %. Consequently the titration curve gives lower results than the theoretical for loss of 1 mole of ammonia because not only is part of the ammonia neutralized by the sulphur trioxide released, but part of the ammonia also decomposes. The ammonia decomposition starts under the given circumstances only at temperatures above 320°, as proved by the deviation of the TG and TGT curves over this temperature. The amount of ammonia decomposed (difference between columns 2 and 4 of Table I) is 1·3 % relative to the sample weight, or 4·6 % of the total ammonia, or about 20 % of the ammonia released in the last step. These results are essentially in agreement with those obtained by Wendlandt and Southern[11] by a different method.

TABLE I.—TITRIMETRIC RESULTS OF AMMONIA DETERMINATION IN COPPER TETRA-AMMINE SULPHATE MONOHYDRATE AT DIFFERENT STAGES IN THE EXAMINATION

	Ammonia content, %				
	1	2	3	4	5
		27·4	25·3	26·1	1·1
	27·72	27·4	25·0	26·2	1·1
		29·6	25·2	26·4	1·0
Mean		27·5	25·2	26·2	1·1

1. Theoretical ammonia content.
2. Ammonia content of the sample determined by titration.
3. By continuous titration during thermal examination.
4. Results obtained after distillation and titration of the ammonia contents of the absorption solution after completion of the thermal examination.
5. Ammonia equivalent to sulphur trioxide liberated (which yielded 9·7, 10·1 and 8·7 mg of $BaSO_4$ in the respective determinations).

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Summary—The thermal decomposition of copper tetra-ammine sulphate monohydrate has been investigated by a combined derivatographic and thermo-gas-titrimetric method. It has been found that decomposition starts with splitting off of the water of crystallization and only after part of this water has departed does stepwise release of ammonia begin. First two moles, then one and finally again one mole of ammonia (per mole of compound) are released. It has been established that a small amount of sulphur trioxide splits off during the last decomposition step, and that about 20 % of the last ammonia to be released is thermally decomposed.

Zusammenfassung—Die thermische Zersetzung von Kupfertetrammin-sulfat-Monohydrat wurde mit Hilfe eines kombinierten derivatographischen und thermo-gastitrimetrischen Verfahrens untersucht. Es zeigte sich, daß die Zersetzung mit dem Abspalten des Kristallwassers beginnt; erst wenn Teil dieses Wassers ausgetreten ist, beginnt die stufenweise Freisetzung von Ammoniak. Zuerst werden zwei Mol, dann eines und zuletzt nochmals ein Mol Ammoniak (pro Mol Ausgangsverbindung) frei. Es wurde nachgewiesen, daß während des letzten Zerfallsschrittes eine kleine Menge Schwefeltrioxid abgespalten wird und daß etwa 20% des letzten freiwerdenden Mols Ammoniak thermisch zersetzt werden.

Résumé—On a étudié la décomposition thermique du sulfate de cuivre tétrammine monohydraté par une méthode combinée dérivatographique et thermo-gaz-titrimétrique. On a trouvé que la décomposition commence avec le départ de l'eau de cristallisation et le dégagement graduel d'ammoniac ne commence qu'après que soit partie une fraction de cette eau. D'abord deux moles, puis une et finalement de nouveau une mole d'ammoniac (par mole de composé) sont libérées. On a établi qu'une petite quantité d'anhydride sulfurique s'élimine durant le dernier stade de décomposition et qu'environ 20% de l'ammoniac libéré en dernier est thermiquement décomposé.

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Talanta, 1970, Vol. 17, pp. i–iii. Pergamon Press. Printed in Northern Ireland

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Instrumental Analysis Manual: GEORGE G. GUILBAUT and LARRY G. HARRIS. Dekker, New York, 1970. Pp. 444, $7.75.

Printed in offset litho, this book is described as a preliminary edition, to be followed after a year of use and revision by a final version. Some 49 experiments, each described in sufficient detail to ensure success in the hands of students, fall under the six main headings Optical methods, Electronics, Electrochemical methods, Separation methods, Radiochemistry and Miscellaneous. Useful up-to-date references are given and the inclusion of such experiments as those on atomic fluorescence, enzyme kinetics and ion-selective electrodes will make this volume interesting and instructive reading for tutors as well as for students. The discussion points raised after each descriptive section provide a good test of the student's understanding of the work.

Solvent Extraction of Metals: A. K. DE, S. M. KOPKAR and R. A. CHALMERS. Van Nostrand Reinhold, London, 1970. Pp. 259, $6.00.

This very broad field has been efficiently surveyed and the results presented in a concise and readable form, tabulated according to the extracting ligand. The first chapter (40 pages) introduces the field of solvent extraction chemistry. The theory of extraction equilibria is covered briefly and attention is given to more recent developments such as synergism, liquid ion-exchangers (*e.g.*, alkyl amines) and liquid cation-exchangers (*e.g.*, alkyl phosphoric acids). Each succeeding chapter contains a useful discussion on the reagent, its uses and chemistry, the relevant tables of detailed information and an extensive list of references. This is likely to prove a very valuable handbook, and a copy should be in every laboratory concerned with separation chemistry.

Advances in Chromatography, Vol. 9: eds. T. CALVIN GIDDINGS and ROY A. KELLER. Dekker, New York, 1970. Pp. xiv + 358. £8. 18. $18.75.

In introducing this volume the editors rightly lay stress on the importance of dealing with the problems of separating mixtures of totally unknown nature, rather than, as is normally the case in publications on chromatography, dealing with the purification of compounds of predetermined nature. Future volumes will be of greatly enhanced value if the scope is so widened. This remark in no way disparages the present very useful addition to the series of volumes on *Advances in Chromatography* which deals with reversed-phase extraction chromatography in inorganic chemistry, the determination of the optimum conditions to effect a separation by gas chromatography, advances in the technology of lightly loaded glass-bead columns, radiochemical separations and analyses by gas chromatography and analysis of volatile flavour components of foods.

Allied Spectroscopy Reviews, Vol. 3: ed. EDWARD J. BRAME, JR. Dekker, New York, 1970. Pp. xii + 346. £8.7. $17.50.

This latest addition to the series of books on applied spectroscopy is a miscellany of surveys on physical techniques in analytical chemistry. Some have a very restricted scope, as for example the study of the structure of nucleic acids by infrared spectroscopy; others have a more general appeal, as for example the description of the combination of the techniques of gas chromatography and mass spectrometry. Electronic spectra are discussed under the headings of recent advances in emission spectroscopy and the spectra of radical ions. A less familiar topic is a review of the applications of X-ray spectroscopy to clinical analysis.

Complexones: N. M. DYATLOVA, V. YA. TYOMKINA and I. D. KOLPAKOVA, ed. R. P. LASTOVSKY, Khimiya, Moscow, 1970. Pp. 417.

This monograph deals with an important class of organic compounds broadly applied in chemical analysis, chemical engineering and other branches of science and technology, *i.e.*, with complexones. In the first part of the book the fundamental laws of complex formation are described and methods of investigation considered, as well as the main thermodynamic functions characteristic of equilibrium in aqueous solutions, and the kinetics of complex formation.

The second part, the largest, deals with the properties of both well-known and new complexones, and the dependence of complex-forming properties on the structures of these compounds is demonstrated. Carboxyalkyl amines are described, and the influence of the introduction of additional iminoacetic groups and of steric factors on the stability of complexes is explored. Attention is paid to complexones containing hetero-atoms, such as oxygen, nitrogen or sulphur, in their aliphatic or cyclic radicals, which considerably modify the properties of ligands. New complexones with hydroxy- and alkylphosphonic-groups have been extensively studied. Conclusions are reached concerning their specific behaviour and the mechanism of complex formation. Both coloured and fluorescent complexones are described. Special attention is paid to polycomplexones, that is to polymeric ion-exchanges containing carboxyalkyl groups. Polycomplexones have been successfully applied in chemical analysis and chemical engineering.

The third part of the monograph is a review of methods for the synthesis of complexones and their solid metal complexes. The application of complexones in different branches of science and technology is described in the fourth part.

The application of complexones as titrants and masking agents in chemical analysis, for the separation of rare earths, for cleaning of instrument surfaces in heat-power engineering, for preventing chlorosis of plants in agriculture—all these applications of complexones are reviewed in the book. In the appendix the reader will find valuable information on dissociation constants of a large number of complexones and the stability constants of their complexes with a number of cations.

Atomic Absorption Spectroscopy: R. J. REYNOLDS, K. ALDOUS and K. C. THOMPSON. Griffin, London, 1970. Pp. 201. £4.50.

The authors are clearly AAS enthusiasts and try hard to convince the reader that this is *the* method. But why compare it with visual colorimetry to show its superiority? Why emphasize the simplicity of the technique when the problems of matrix effects and non-linear calibration curves (which are adequately discussed) often necessitate special precautions? The "excellent reproducibility" referred to does not seem to be born out by many of the recorder tracings illustrating the text. The inclusion of a wealth of practical details—the tricks of the trade that make the methods succeed—probably justifies the authors' claim that this book is for the operator, to save him time and trouble. A substantial chapter contains useful information for the determinations of the individual elements, similar to the (free) data sheets of some manufacturers. Short but interesting sections discuss Instrumentation, Further Techniques, and Theory.

Undergraduate Instrumental Analysis: JAMES W. ROBINSON. Marcel Dekker, New York, 1970. Pp. 379. £5.50. $11.50.

The title is somewhat misleading—the book is written as an introduction for students, to many of the modern instrumental methods of analysis, and ought to remain on the graduate's bookshelf for further consultation. It is biased towards spectroscopic methods, and rather more to their use by the organic chemist. The tendency to become a critical catalogue of techniques and machines is partly balanced by a good introduction dealing with errors and sampling. Further chapters cover Spectroscopy, NMR, IR, UV, AAS, Spectrophotometry, Flame photometry, Emission Spectrography, X-ray spectroscopy, Chromatography, Thermal methods, Mass spectrometry, and Electrochemistry, the last-mentioned being disproportionately brief and hardly matching the standard of the rest of the book. The clear explanations will make this text easily readable also by trainee technicians, at whom it is aimed, besides students.

Activation Analysis: MILOSLAV RAKOVIC. Iliffe, London, 1970. Pp. 339. £6.00.

This is a useful guide to the method. All aspects of the theory and practice are dealt with briefly in the first two-thirds of the book. The last third is taken up with a summary of methods for elements, usefully grouped according to type of sample e.g. iron, water, plastics *etc.* Several important topics are treated too briefly and the references only go to 1964, with a few in 1965. Then, it was a very good book, but by now it has dated appreciably.

The Application of X-Ray Fluorescence in Ceramic Analysis: Results of some Co-operative Studies on Aluminosilicates and Magnesites: R. P. EARDLEY and G. J. OLIVER. British Ceramic Research Association, Stoke-on-Trent, 1970. Special Publication No. 69. Pp. 51. £1.50.

Analytical Chemistry of Zirconium and Hafnium: ANIL K. MUKHERJI. Pergamon, Oxford, 1970. Pp. xiii + 281. £4.50. $12.00.

A comprehensive account of the literature up to 1967 on the analytical chemistry of these two elements, both by classical and by instrumental methods. The sections on the means of separating the two will be of interest to inorganic as well as analytical chemists. As is usual in this series, the details of procedures add to the general value of the work.

Analytical Chemistry of Nickel: CLYDE L. LEWIS and WELLAND L. OTT. Pergamon, Oxford, 1970. Pp. ix + 233. £5.50. $14.85.

A companion volume to an earlier one entitled "Analysis of Nickel" which dealt with determination of other elements in nickel metal, this book deals with the determination of nickel in various matrices, and gives a thorough survey of the classical and instrumental methods available. There is also a most useful general survey of the chemistry of nickel.

Talanta, 1970, Vol. 17, p. iv. Pergamon Press. Printed in Northern Ireland

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Möglichkeiten und Grenzen bei der Verwendung von Filterpapier als Träger bei der röntgenspektrometrischen Analyse: G. Ackermann, R.-K. Koch, H. Ehrhardt und G. Sanner. (20 *August* 1970)

Cation-exchange separation of uranium in dimethylsulphoxide medium: Gilbert E. Janauer, J. Korkisch and S. A. Hubbard. (21 *August* 1970)

La réaction des nitrilotriacétates métalliques avec la cycloleucine: J. Israeli, J. R. Cayouette and R. Volpe. (10 *September* 1970)

Sensitivity and detectability for manganese(II) determination in solution by kinetic methods of analysis: Horacio A. Mottola and Carl R. Harrison. (21 *September* 1970)

Determination of rare earths in selected rare-earth matrices by spark-source mass spectrometry: D. A. Griffith, R. J. Conzemius and H. J. Svec. (21 *September* 1970)

The "Haltafall" program—some corrections and comments on recent experience: Björn Warnqvist and Nils Ingri. (29 *September* 1970)

Traitement mathématique des resultats du dosage titrimétrique: N. A. Chernova, P. P. Melnicov, L. N. Komissatova and V. I. Spytzin. (2 *October* 1970)

Determination of silver in ores and metallurgical concentrates by a combination of fire-assay preconcentration (using tin as collector) and atomic-absorption spectrophotometry: P. E. Moloughney and J. A. Graham. (5 *October* 1970)

A general computer approach for calculating rate constants from near-equilibrium kinetic studies: V. S. Sharma and D. L. Leussing. (15 *October* 1970)

Extraction with long-chain amines—V. Colorimetric determination of cobalt with nitroso-R salt: Jiří Adam and Rudolf Přibil. (21 *October* 1970)

Potentiometric studies on ternary complex formation. Cu(II), Ni(II), Zn(II) or Cd(II)-iminodiacetic acid-amino acid: Ghanshyam Sharma and J. P. Tandon. (21 *October* 1970)

Oxalato complexes of tervalent thallium: Titrimetric determination of thallium(III): S. R. Sagi and K. V. Ramana. (26 *October* 1970)

Chromatographic separation of vanadium, tungsten and molybdenum with a liquid anion-exchanger: James S. Fritz and Joseph J. Topping. (29 *October* 1970)

Studies on potassium chlorate as a primary oxidimetric reagent: C. Radhakrishna Murty and G. Gopal Rao. (30 *October* 1970)

Thermometric titrimetry: Determination of nickel and selenium by direct injection enthalpimetry, with a thermometric titrator of simple design: A. E. Beezer and A. K. Slawinski. (5 *November* 1970)

Determination of hydrogen in sodium by an amalgamation method: Masao Takahashi. (6 *November* 1970)

A titrimetric method for the rapid determination of carbon in steel with an aqueous titrant: J. M. Ottaway, D. W. Whymark, B. Metters and B. G. Cooksey. (9 *November* 1970)

A new conductivity method for studying reaction kinetics: R. S. Roy and M. M. Misra. (12 *November* 1970)

Study of the oxidation state of plutonium in solution by a flow-coulometric method: Sorin Kihara, Tadashi Yamamoto, Kenji Motojima and Taitiro Fujinaga. (12 *November* 1970)

Determination of plutonium by two-step flow coulometry: Sorin Kihara, Tadashi Yamamoto, Kenji Motojima and Taitiro Fujinaga. (12 *November* 1970)

Iodobenzene dichloride as a new oxidimetric titrant in non-aqueous media: P. N. Krishnan Nambisan and C. G. Ramachandran Nair. (16 *November* 1970)

SUMMARIES FOR CARD INDEXES

Development and publication of new gravimetric methods of analysis: L. Erdey✠, L. Pólos and R. A. Chalmers *Talanta* 1970, **17**, 1143. (Institute for General and Analytical Chemistry, Technical University of Budapest, Budapest XI, Gellért tér 4, Hungary, and Department of Chemistry, University of Aberdeen, Aberdeen, Scotland.)

Summary—A review is made of the factors affecting the accuracy of gravimetric methods, and which need to be investigated in the development of new methods. Recommendations are made for writing up such investigations for publication.

Determination of trace contaminants in hydrogenation catalysts by neutron-activation analysis: L. Erdey, O. Gimesi, E. Szabó and M. Csajka, *Talanta*, 1970, **17**, 1157. (Institute for General and Analytical Chemistry of the Technical University, Budapest, XI, Gellért tér 4.)

Summary—A neutron-activation method has been developed for the determination of the active constituents and contaminants in hydrogenation catalysts. The active constituents of palladium and nickel catalysts (Pd and Ni) and Zn and Co contaminants present in small amount were determined by a direct instrumental method. A NaI(Tl) scintillator and a Ge(Li) semiconductor connected to a multichannel analyser were used for the measurements. A computer was used to evaluate the γ-spectra. Contaminants present in small amount were also determined by means of a radiochemical separation method based on heterogeneous isotopic exchange on mercury(II) sulphide and zinc sulphide precipitates.

Application of displacement reactions in flame photometry—I. The determination of phosphate by a flame emission method: E. Szebényi-Győry, P. J. Slevin, G. Svehla and L. Erdey, *Talanta*, 1970, **17**, 1167. (Chemistry Department, Queen's University, Belfast.)

Summary—Phosphate ions decrease the flame emission of calcium, but this effect can be partly offset by adding a second metal which partly displaces calcium from the non-excitable species. For the determination of phosphate the sample solution is divided into four equal parts; to each of these, various amounts of calcium and barium ions are added such that the total (molar) concentration of the metals is constant. Plotting the intensity measured at 630 nm *vs.* the calcium content of the solution gives a straight line, the slope of which depends on the concentration of phosphate ions present. The method is suitable for rapid determination of phosphate. Accuracy and precision are within the usual limits characteristic of flame photometric methods.

РАЗРАБОТКА И ОПУБЛИКОВАНИЕ НОВЫХ ВЕСОВЫХ МЕТОДОВ АНАЛИЗА:

L. ERDEY, L. POLOS and R. A. CHALMERS, *Talanta*, **17**, 1970, 1143.

Резюме—Приведен обзор факторов влияющих на точность весовых методов, которые нужно исследовать в разработке новых методов. Предложены схемы подготовки таких исследований для опубликования.

ОПРЕДЕЛЕНИЕ ПРИМЕСЕЙ В ГИДРИРУЮЩИХ КАТАЛИЗАТОРАХ МЕТОДОМ НЕЙТРОННОАКТИВАЦИОННОГО АНАЛИЗА:

L. ERDEY, O. GIMESI, E. SZABÓ and M. CSAJKA, *Talanta*, 1970, **17**, 1157.

Резюме—Разработан метод нейтронноактивационного анализа для определения активных компонентов и примесей в гидрирующих катализаторах. Активные компоненты катализаторов на основе палладия и никеля (Pd и Ni) и примеси Zn и Co, присутствующие в небольших количествах, определены непосредственным инструментальным методом. Измерения проведены с использованием NaI(Tl) сцинтиллятора и Ge(Li) полупроводника, соединенных с многоканальным анализатором. Гамма-спектры изучены с применением вычислительной машины. Примеси присутствующие в небольших количествах также определены методом радиохимического разделения основывающегося на гетерогенном изотопном обмене на осадках сульфида ртути(II) и сульфида цинка.

ПРИМЕНЕНИЕ РЕАКЦИЙ ЗАМЕЩЕНИЯ В ПЛАМЕННОЙ ФОТОМЕТРИИ—I. ОПРЕДЕЛЕНИЕ ФОСФАТА МЕТОДОМ ПЛАМЕННОЙ ЭМИССИИ:

E. SZEBÉNYI-GYÖRY, P. J. SLEVIN, G. SVEHLA and L. ERDEY, *Talanta*, 1970, **17**, 1167.

Резюме—Фосфатионы уменьшают пламенную эмиссию кальция, но этот эффект можно избегнуть добавлением второго металла который частично замещает кальций из невозбуждимого соединения. Для определения фосфата раствор пробы разделяют на четыре одинаковых части; каждом из этих частей добавляют различные количества ионов кальция и бария, но так что бы общая молярная концентрация осталась константной. Нанесение интенсивности измеренной при 630 нм в зависимости от концентрации кацьция в растворе дает прямую, уклон которой зависит от концентрации присутствующих фосфатионов. Метод является подходящим для быстрого определения фосфата. Точность и воспроизводимость метода в обыкновенных пределах, характеристических для методов пламенной фотометрии.

Determination of the optimum resultant effect of factors influencing HETP-values. The following of parallel diffusion and mass-transfer processes: J. Takàcs, L. Màzor, M. Kucsera-Pápay and T. Kozma, *Talanta*, 1970, **17**, 1175. (Institute for General and Analytical Chemistry, Technical University, Budapest, Hungary.)

Summary—One of the most important problems of analytical gas chromatography, both in theory and in practice, is the following of parallel diffusion and mass-transfer processes, with the primary aim of determining the optimum resultant effect of factors influencing the HETP-value. Starting from the work of Costa Neto and collaborators, it is shown that the approximate equation developed by these authors can be deduced from the theory of gas chromatography. Subsequently, by means of the new approximation, the effect of individual factors is determined, and processes proceeding simultaneously are followed.

Retention of radionuclides on metal sulphide precipitates: O. Gimesi, É. Bányai, M. Csajka and A. Szabadházy, *Talanta*, 1970, **17**, 1183. (Institute for General and Analytical Chemistry of the Technical University, Budapest, Hungary.)

Summary—The retention of various radionuclides on metal sulphide precipitates has been studied. The sulphide precipitates quantitatively retained the common radionuclides. The condition for 100% retention in a thin layer is small particle size (a few μm) in the precipitate. This can be ensured by pulverization of the dried precipitate of metal sulphide. $^{203}Hg^{2+}$ is retained by mercury sulphide and $^{65}Zn^{2+}$ by zinc sulphide by isotopic exchange. The retention of foreign radioactive ions can be reduced or even eliminated by counter-carrier technique in cases where the retention is not due to chemical reaction, precipitate exchange. The isotopic exchange with mercury(II) sulphide and zinc sulphide enables mercury and zinc ions to be separated rapidly and determined in the presence of a number of interfering ions.

Studies on the melts of alkali metal acetates: Z. Halmos, T. Meisel, K. Seybold and L. Erdey, *Talanta*, 1970, **17**, 1191. (Institute for General and Analytical Chemistry of the Technical University, Budapest, Hungary.)

Summary—The density, viscosity, and electrical conductivity of alkali metal acetates were measured over the temperature interval between melting and decomposition. The apparent activation energies of the equivalent conductivities and viscosities were calculated. It has been concluded from the results that alkali metal acetates, similarly to alkali metal bezenesulphonates studied earlier, exhibit properties quite unlike those of alkali metal halides. In the dependence of equivalent conductivity on the nature of the cation, the anomalous behaviour of lithium salts appears to be due to association prevailing in the melt phase.

ОПРЕДЕЛЕНИЕ ОПТИМАЛНОГО РЕЗУЛЬТАТНОГО ЭФФЕКТА ФАКТОРОВ ВЛИЯЮЩИХ НА ВЕЛИЧИНЧ ВТТ. СЛЕДОВАНИЕ ПАРАЛЛЕЛЬНЫХ ПРОЦЕССОВ ДИФФУЗИИ И ПЕРЕНОСА МАССЫ:

J. Takács, L. Mázor, M. Kucsera-Pápay and T. Kozma, *Talanta*, 1970, **17**, 1175.

Резюме—Проследование параллельных процессов диффузии и переноса массы представляет собой одну из важнейших проблем аналитической газовой хроматографии, как в теории так и в практике, с целью определить оптимальный результатный эффект факторов влияющих на величину ВТТ. Исходя из работы Коста Нето и сотрудников показано что приближенное уравнение выведенное этими авторами может также быть выведено из теории газовой хроматографии. Последовательно, пользуясь новым приближенхем, определен эффект индивидуальных факторов и проследованы одновременно протекающие процессы.

УДЕРЖИВАНИЕ РАДИОНУКЛИДОВ НА ОСАДКАХ СУЛЬФИДОВ МЕТАЛЛОВ:

E. Bányai, M. Csajka and A. Szabadházy, *Talanta*, 1970, **17**, 1183.

Резюме—Изучено удерживание различных радионуклидов на осадках сульфидов металлов. Осадки сульфидов количественно удерживали обыкновенные радионуклиды. Необходимое условие для 100%-тного удерживания в тонком слое—небольшая величина частиц (немногие мкм) в осадке. Это условие получается распылением осушенного осадка сульфида металла. $^{203}Hg^{2+}$ удержан сульфидом ртути а $^{65}Zn^{2+}$—сульфидом цинка путем обмена изотопов. Удерживание посторонних радиоактивных ионов можно уменьшить или даже исключить применением метода противоносителя или в случаях где удерживание не вызвано химической реакцией—обменом осадка. Изотопный обмен с сульфидом ртути(II) и сульфидом цинка позволяет быстро отделять ионы ртути и цинка и определить их в присутствии ряда мешающих ионов.

ИЗУЧЕНИЕ РАСПЛАВОВ АЦЕТАТОВ ЩЕЛОЧНЫХ МЕТАЛЛОВ:

Z. Halmos, T. Meisel, K. Seybold and L. Erdey, *Talanta*, 1970, **17**, 1191.

Резюме—Измерены удельный вес, вязкость и электропроводимость ацетатов щелочных металлов в диапазоне температур между плавлением и разложением. Вычислены кажущиеся энергии активации эквивалентных электропроводимостей и вязкостей. На основе полученных результатов сделан вывод что ацетаты щелочных металлов, подобно раньше изученным бензолсульфонатам щелочных металлов, показывают характеристики различающиеся от характеристик галоидов щелочных металлов. В зависимости эквивалентной электропроводимости от природы катиона, аномальное поведение солей лития кажется результатом ассоциации, преобладающей в расплавленной фазе.

Spectrochemical analysis of hard metals by a rotating disc technique—Effect of impregnation and complexing agents: T. Kántor, L. Erdey and Zs. Szabó-Ákos, *Talanta*, 1970, **17**, 1199. (Institute for General and Analytical Chemistry, Technical University, Budapest, Hungary.)

Summary—A spectrographic method has been developed for the simultaneous determination of the constituents W, Co, Ti, Ta and Nb and contaminants Fe, Ni, Cr, Mn, Mg and Ca in hard metals. The samples were dissolved in hydrofluoric acid and nitric acid and the solutions stabilized with citric acid. Graphite discs were waterproofed in order to ensure control of the introduction of solution into the source. For the five types of hard metal samples studied no inter-element effect was observed. Titanium has also been determined by means of a double-beam optical spectrometer.

Selektive Bestimmung in verdünnter Lösung befindlicher Säuren von verschiedener Stärke durch oszillometrische Titration: Zs. Szabó-Ámos and L. Erdey, *Talanta*, 1970. **17**, 1205. (Institut für Allgemeine und Analytische Chemie, Technische Universität, Budapest.)

Summary—The stronger of a pair of weak acids may be selectively titrated in aqueous solution when the conjugate base of a third acid of intermediate strength is used as titrant. Titrations of 10^{-2}–$10^{-3}M$ solutions can be followed by oscillometric measurements with an error of about 1%, when the strengths of the two acids differ by a factor of 10^2 or more, and of the acid and titrant by $10^{1.3}$ or more.

Investigation of alkali metal and ammonium tetraphenylborates by infrared spectrophotometry. Determination of ammonium ions in the presence of alkali metal ions: K. Kiss-Erőss, L. Erdey and I. Buzás, *Talanta*, 1970, **17**, 1209. (Institute for General and Analytical Chemistry, Technical University, Budapest.)

Summary—The infrared spectra of alkali metal and ammonium tetraphenylborates have been studied and an infrared spectrophotometric method developed for the determination of ammonium ions in the form of the tetraphenylborate. The N–H deformation vibration band appearing at 1405 cm^{-1} in the spectrum of ammonium borate has been utilized for quantitative evaluation; the tetraphenylborates of the alkali metals do not exhibit absorption at this frequency. Thus ammonium ions can be determined as the tetraphenylborate in the presence of alkali metal ions without preliminary separation.

СПЕКТРОХИМИЧЕСКИЙ АНАЛИЗ ТВЁРДЫХ МЕТАЛЛОВ С ИСПОЛЬЗОВАНИЕМ ВРАЩАЮЩЕГОСЯ ДИСКА:—ЭФФЕКТ ПРОПИТЫВАНИЯ И КОМПЛЕКСООБРАЗУЮЩИХ АГЕНТОВ:

T. Kántor, L. Erdey and Zs. Szabó-Ákos, *Talanta*, 1970, **17,** 1199.

Резюме—Разработан спектрографический метод для одновременного определения компонентов W, Co, Ti, Ta и Nb и примесей Fe, Ni, Cr, Mn, Mg, и Ca в твёрдых металлах. Пробы растворяют в фтороводородной и азотной кислотах и растворы стабилизируют лимонной кислотой. Графитовые диски обработаны для придания водонепроницаемости с целью контроллировать введение раствора в источник. Межэлементные эффекты не обнаружены в исследовании пять типов твёрдых металлов. Также определен титан с использованием оптического спектрометра с двойним пучком.

СЕЛЕКТИВНОЕ ОПРЕДЕЛЕНИЕ КИСЛОТ РАЗНОЙ СИЛЫ В РАЗБАВЛЕННОМ РАСТВОРЕ МЕТОДОМ ОСЦЛЛОМЕТРИЧЕСКОЙ ТИТРАЦИИ:

Zs. Szabo-Amos and L. Erdey, *Talanta*, 1970, **17,** 1205.

Резюме—Удается селективно титровать ту более сильную из двух слабых кислот в водном растворе если сопряженная основа третьей кислоты промежуточной силы используется в качестве титрованного раствора. Титрование 10^{-2}–$10^{-3}M$ растворов можно прослеживать высокочастотными осциллометрическими измерениями с ошибкой приблизительно 1%, если силы этих двух кислот различаются в 10^2 раз или больше, а сила кислоты и крепость титрованного раствора—в $10^{1,3}$ раз или больше.

ИССЛЕДОВАНИЕ ТЕТРАФЕНИЛБОРАТОВ ЩЕЛОЧНЫХ МЕТАЛЛОВ И АММОНИЯ МЕТОДОМ ИНФРАКРАСНОЙ СПЕКТРОСКОПИИ:

K. Kiss-Eröss, L. Erdey and I. Buzás, *Talanta*, 1970, **17,** 1209.

Резюме—Изучены инфракрасные спектры тетрафениборатов щелочных металлов и аммония и разработан спектрофотометрический метод определения аммонийиона в форме тетрафенилбората. Полоса деформационного колебания N–H, появляющаяся при 1405 cm^{-1} в спектре тетрафенилбората аммония, использована для количественного определения. Тетрафенилбораты щелочных металлов не поглощают при этой частоте. Поэтому удается определять аммонийион в форме тетрафенилбората в присутствии ионов щелочных металлов без предварительного разделения.

Use of complex displacement reactions in photometric analysis: J. Inczédy, *Talanta*, 1970, **17**, 1212. (Institute for General and Analytical Chemistry, Technical University, Budapest, Hungary.)

Summary—The theoretical requirements for the quantitative photometric determination of trace amounts of metal ions by use of complex displacement reactions are discussed and a calculation method using conditional equilibrium constants and side-reaction functions is recommended. As an example, the requirements in the determination of erbium(III) by using copper(II)-EDTA complex and PAN indicator in ammonium lactate buffer solutions are calculated.

Application of direct thermometric analysis in iodometry: P. Marik-Korda and L. Erdey, *Talanta*, 1970, **17**, 1215. (Institute for General and Analytical Chemistry, Technical University of Budapest, Gellért tér 4, Budapest.)

Summary—Elementary chlorine was determined by a thermometric method using potassium iodide as reagent. The temperature rise corresponding to the heat of reaction was proportional to the chlorine content. Iodine formed in the reaction was also determined with sodium thiosulphate. The heat of the chlorine–iodide reaction is about five times that of the iodine–thiosulphate reaction. Direct determination with potassium iodide is simpler and more rapid than the indirect one.

Determination of nickel and copper by precipitation from homogeneous solution as their salicylaldimine complexes: L. Erdey and L. Pólos, *Talanta*, 1970, **17**, 1218. (Institute of General and Analytical Chemistry, Technical University, Budapest, Hungary.)

Summary—A method has been developed for the gravimetric determination of copper and nickel as their salicylaldimine complexes, by precipitation from homogeneous solution. The complexes are crystalline precipitates which are very easy to filter off and wash. The accuracy of the determinations is higher than that of the conventional precipitation method.

ПРИМЕНЕНИЕ РЕАКЦИЙ ЗАМЕЩЕНИЯ КОМПЛЕКСОВ В ФОТОМЕТРИЧЕСКОМ АНАЛИЗЕ:

J. INCZÉDY, *Talanta*, 1970, **17**, 1212.

Резюме—Обсуждены теоретические необходимые условия для количественного определения фотометрическим методом ионов металлов применением реакций замещения комплексов и предложен метод рассчета основанный на условных константах равновесия и функциях побочных реакций. В качестве примера рассчитаны необходимые условия определения эрбия(III) с использованием комплекса меди(II) с ЭДТА и индикатора ПАН в буферных растворах лактата аммония.

ПРИМЕНЕНИЕ НЕПОСРЕДСТВЕННОГО ТЕРМОМЕТРИЧЕСКОГО АНАЛИЗА В ИОДОМЕТРИИ:

P. MARIK-KORDA and L. ERDEY, *Talanta*, 1970, **17**, 1215.

Резюме—Элементарный хлор определен термометрическим методом с использованием иодида калия в качестве реагента. Соответствующее теплоте реакции повышение температуры было пропорциональное содержанию хлора. Образованный в реакции иод также определяли с тиосульфатом натрия. Теплота реакции хлора с иодидом в пять раз больше чем теплота реакции иода с тиосульфатом. Непосредственное определение с иодидом калия несложнее и быстрее чем косвенный метод.

ОПРЕДЕЛЕНИЕ НИКЕЛЯ И МЕДИ ОСАЖДЕНИЕМ ИЗ ГОМОГЕННОГО РАСТВОРА В ФОРМЕ ИХ КОМПЛЕКСОВ С САЛИЦИЛАЛДИМИНОМ:

L. ERDEY and L. PÓLOS, *Talanta*, 1970, **17**, 1218.

Резюме—Разработан метод весового определения меди и никеля в форме их комплексов с салицилалдимином, осаждением из гомогенного раствора. Комплексы представляют собой кристаллические осадки, легко фильтруемые и промываемые. Точность метода лучше чем обыкновенных методов осаждения.

Application of chemiluminescent indicators in EDTA titrations: L. Erdey, O. Weber and I. Buzás, *Talanta*, 1970, **17**, 1221. (Institute for General and Analytical Chemistry of the Technical University, Budapest.)

Summary—The chemiluminescent indicators lucigenine and luminol are readily applicable to end-point detection in the EDTA titration of cadmium, zinc and nickel ions. Back-titration with copper(II) gives reproducible results. The end-point is indicated by the disappearance of the green chemiluminescence of lucigenine, or by the appearance of the bluish luminescence of luminol.

Combined derivatographic and thermo-gas-titrimetric examination of the thermal decomposition of copper tetra-ammine sulphate monohydrate: J. Paulik and F. Paulik, *Talanta*, 1970, **17**, 1224. (Institute for General and Analytical Chemistry, Technical University, Budapest.)

Summary—The thermal decomposition of copper tetra-ammine sulphate monohydrate has been investigated by a combined derivatographic and thermo-gas-titrimetric method. It has been found that decomposition starts with splitting off of the water of crystallization and only after part of this water has departed does stepwise release of ammonia begin. First two moles, then one and finally again one mole of ammonia (per mole of compound) are released. It has been established that a small amount of sulphur trioxide splits off during the last decomposition step, and that about 20% of the last ammonia to be released is thermally decomposed.

ПРИМЕНЕНИЕ ХЕМИЛЮМИНЕСЦЕНТНЫХ ИНДИКАТОРОВ В ТИТРАЦИЯХ С ЭДТА:

L. Erdey, O. Weber and I. Buzás, *Talanta*, 1970, **17**, 1221.

Резюме—Хемилюминесцентные индикаторы луцигенин и луминол хорошо используемы для обнаружения конца титрования в определении ионов кадмия, цинка и никеля с ЭДТА. Оттитрование избытка с медью(II) дает воспроизводимые результаты. Конец титрования указан исчезновением зеленой хемилюминесценции луцигенина или появлением голубоватой люминесценции луминола.

КОМБИНИРОВАННОЕ ДЕРИВАТОГРАФИЧЕСКОЕ И ТЕРМО-ГАЗОТИТРОМЕТРИЧЕСКОЕ ИСПЫТАНИЕ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ МОНОГИДРАТА МЕДЬ-ТЕТРААММИНСУЛЬФАТА:

J. Paulik and F. Paulik, *Talanta*, 1970, **17**, 1224.

Резюме—Исследовано комбинированным дериватографическии и термо-газотитрометрическим методом термическое разложение моногидрата медь-тетрааминсульфата. Обнаружено что разложение начиняет отшеплением кристаллизационной воды, а только поско после удаления части этой воды начиняет этапное выделение аммиака. Сначала выделяются два моля, затем один моль и конечно еще один моль аммиака для каждого моля соединения. Установлено что в последнем этапе выделяется небольшое количество трёхокиси серы и что около 20% последнего выделяющегося аммиака термически разлагается.

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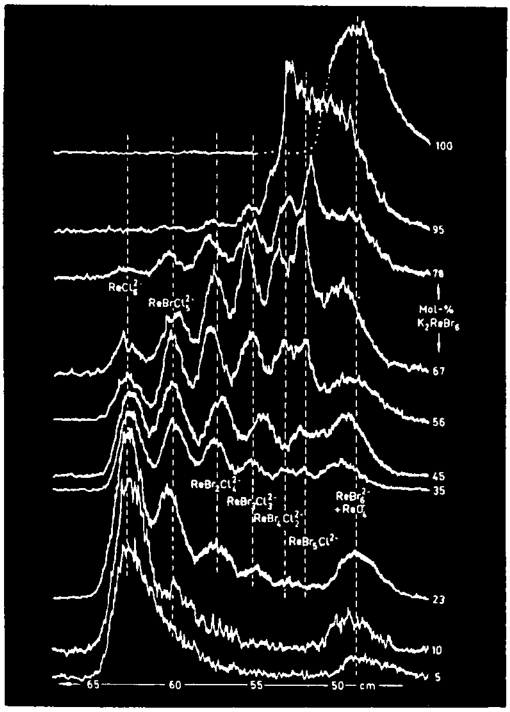
100
95
78
Mol-%
K_2ReBr_6
67
56
45
35
23
10
5
$ReCl_6^{2-}$
$ReBrCl_5^{2-}$
$ReBr_2Cl_4^{2-}$
$ReBr_3Cl_3^{2-}$
$ReBr_4Cl_2^{2-}$
$ReBr_5Cl^{2-}$
$ReBr_6^{2-}$
$+ReO_4^-$
65
60
55
50
cm

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