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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA
Vol. 25, No. 4, October 1961

AN EXAMINATION OF SOME ASPECTS OF INCREASING SELECTIVITY IN
CHELATOMETRY

(Review)

T. S. WEST, *Anal. Chim. Acta*, 25 (1961) 301-312

PAPER SOLUBILIZATION CHROMATOGRAPHY

I. PHENOLS

The R_F values of a series of eleven phenols have been determined using paper-chromatographic techniques on filter paper loaded with ion-exchange resin. The data have been used to predict the separation of various mixtures of these phenols by development with aqueous solutions of acetic acid.

D. LOCKE AND J. SHERMA, *Anal. Chim. Acta*, 25 (1961) 312-316

SEMI-MICRO CRYOSCOPIC MOLECULAR WEIGHT DETERMINATION WITH A
THERMISTOR THERMOMETER

An apparatus for extending the steady state freezing point depression method to small volumes, of the order of 0.3 or 0.4 ml, has been developed. A thermistor is used as the temperature sensing element, in one arm of a Wheatstone bridge. The apparatus is simple and dependable. Accuracies in the order of 2% are easily attainable.

J. A. KNIGHT, B. WILKINS JR., D. K. DAVIS AND F. SICILIO, *Anal. Chim. Acta*, 25 (1961) 317-321

DIFFERENTIAL PRECIPITATION IONOGRAPHY FOR QUALITATIVE CATION
ANALYSIS

A method — differential precipitation ionography — is described for the separation and detection of cations in mixtures in trace amounts. The ions are caused to migrate by application of current to a supporting membrane. The substrate is kept moist with an electrolyte so chosen that its electrolysis provides a pH gradient. The migrating ions form narrow bands of their oxides or hydroxides at the point of their precipitation pH in this field. After this separation the filter is developed with a suitable reagent and examined microscopically. Several metal ions can be detected in a single sample. Materials in amounts as low as 10^{-9} g may be detected.

B. J. TUFTS, *Anal. Chim. Acta*, 25 (1961) 322-327

ORGANIC COMPOSITION ANALYSIS BY COMBINATION OF GAS CHROMATOGRAPHY
WITH INFRARED SPECTROPHOTOMETRY

A technique combining gas chromatography with infrared spectrophotometry for analysis of complex organic mixtures has been described and modes of application discussed. The components are trapped and run as gases. Proper use of the data makes possible qualitative and quantitative analysis.

W. L. SENN JR. AND H. V. DRUSHEL, *Anal. Chim. Acta*, 25 (1961) 328-333

THE ABSORPTIOMETRIC DETERMINATION OF PHOSPHORUS IN IRONS AND STEELS

A critical investigation has been made of the vanadomolybdiphosphate method for the absorptiometric determination of phosphorus in irons and steels. The reaction conditions have been standardised to produce a simple, rapid and reliable control method. The effects of interfering elements have also been studied.

G. LINDLEY, *Anal. Chim. Acta*, 25 (1961) 334-342

OXIMIDOBENZOTETRONIC ACID

A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF IRON(II)

Oximidobenzotetronic acid is proposed for the spectrophotometric estimation of iron. A freshly prepared alcoholic solution of the reagent produces a deep blue water-soluble complex with an aqueous solution of iron(II). The complex is stable and its optical density is constant at pH 2.5-10. Lambert-Beer's law is followed from 0.54-5.4 p.p.m. of iron at 625 m μ ; temperature has no effect between 10° and 50°. The reagent is highly selective for iron.

A. N. BHAT AND B. D. JAIN, *Anal. Chim. Acta*, 25 (1961) 343-347

SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF METALS WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL

PAN(1-(2-pyridylazo)-2-naphthol) is proposed for the solvent extraction and spectrophotometric determination of manganese, iron, cadmium, mercury, gallium and yttrium. The reagent, which is highly specific for iron, has been applied to the determination of iron in clay and anorthosite. The separation of yttrium from lanthanum and the separation of manganese from nickel were successful.

S. SHIBATA, *Anal. Chim. Acta*, 25 (1961) 348-359

STUDIES ON THE EXTRACTION OF ZIRCONIUM WITH ORGANOPHOSPHORUS COMPOUNDS

The extraction of zirconium from nitric acid media with alkyl phosphates, phosphonate, phosphinate and phosphine oxide was studied. The extraction ability is affected by alkyl substituents attached to the phosphoryl group as well as by the solvent structure, the order of efficiency being: tri-*n*-butyl phosphinate > tri-*n*-butyl phosphine oxide > tricyclohexyl phosphate and tri-*sec*-butyl phosphate > diethyl butyl phosphate > normal alkyl phosphates. In the extraction with normal alkyl phosphates, two solvent molecules and four nitrate ions combine with one atom of zirconium. The equilibrium constant and the effect of temperature were studied in the extraction with tri-*n*-butyl phosphate. The infrared spectra of zirconium extracted from 10 *M* nitric acid solution with the organophosphorus solvents were measured; it was confirmed that a covalent complex was formed.

H. UMEZAWA AND R. HARA, *Anal. Chim. Acta*, 25 (1961) 360-365

SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM WITH STANNOUS IODIDE REAGENT

The tin(II) iodide reagent reacts with rhodium to form a stable colored complex with an absorption maximum at 460 $m\mu$. The system obeys Beer's law and exhibits a molar absorptivity of $3.9 \cdot 10^4$ at 460 $m\mu$. Rhodium concentrations between 0.4 and 3 p.p.m. can be determined with an average deviation of only 0.3%. The method compares favorably with the tin(II) chloride and bromide methods for rhodium and is considerably more sensitive. Ir, Pd, Pt, Sb, Ti, Cu, Co, Ni and Fe interfere with the method. Consequently, just as is the case with the chloride and bromide reagent, Rh must be separated from most samples prior to an analysis.

E. W. BERG AND H. L. YOUMANS, *Anal. Chim. Acta*, 25 (1961) 366-370

REFERENCE ELECTRODES FOR VOLTAMMETRY IN ACETONITRILE

The saturated calomel electrode is *the* reference electrode in aqueous polarographic studies. Such is not the case, however, with nonaqueous polarographic studies. In particular acetonitrile has been used as the solvent for many polarographic studies with just as many reference electrodes. An attempt has been made to correct this unfortunate situation. Appropriate measurements have been made to evaluate the potential of the various reference electrode systems used in acetonitrile with respect to the aqueous saturated calomel electrode.

R. C. LARSON, R. T. IWAMOTO AND R. N. ADAMS, *Anal. Chim. Acta*, 25 (1961) 371-374

APPLICATION OF CONTROLLED-POTENTIAL ELECTROLYSIS TO THE ANALYSIS OF LEAD- AND TIN-BASE ALLOYS

II. TIN-BASE ALLOYS

Electrodeposition methods are described for the determination of antimony, copper and lead in tin-base alloys and a method for the determination of tin by controlled-potential electrolysis is discussed.

B. ALFONSI, *Anal. Chim. Acta*, 25 (1961) 374-378

POLAROMETRIC DETERMINATION OF AROMATIC ALDEHYDES WITH 2,4-DINITROPHENYLHYDRAZINE

In the polarometric titration of aromatic aldehydes with a 2,4-dinitrophenylhydrazine solution, the sorption of the reagent on the hydrazone precipitate and the reduction of this precipitate at the mercury dropping electrode have been proved. These effects may be eliminated by the addition of thymol or ethanol to the sample solution, so that most aromatic aldehydes can be determined.

A. BERKA, J. DOLEŽAL, J. JANATA AND J. ZÝKA, *Anal. Chim. Acta*, 25 (1961) 379-385

RAPID DETERMINATION OF ALUMINIUM IN BERYLLIUM METAL BY CATHODE RAY POLAROGRAPHY

A rapid method is presented for the determination of aluminium in beryllium metal by cathode ray polarography using the dye Superchrome Garnet Y. A mercury cathode electrolysis is used to remove heavy metal impurities, but the need for a separation of aluminium from beryllium is avoided. A single determination requiring a 100-mg sample may be completed in little over an hour, with normal polarographic precision.

T. M. FLORENCE AND D. B. IZARD, *Anal. Chim. Acta*, 25 (1961) 386-389

SIMPLE DISTILLATION METHOD FOR TITRIMETRIC DETERMINATION OF CARBON DIOXIDE

(in German)

Carbon dioxide can be distilled at atmospheric pressure if the cooling is properly controlled. A suitable procedure is described. Interference from atmospheric carbon dioxide is prevented by the use of pentane as sealing liquid. Titrations with 0.01-0.1 N solutions allow determination of 0.22-22 mg of carbon dioxide with an accuracy of $\pm 2-0.2\%$.

L. MAROS, E. SCHULEK, I. MOLNÁR-PERLANDM. PINTÉR-SZAKÁCS, *Anal. Chim. Acta*, 25 (1961) 390-399

A SPECIFIC AND SENSITIVE SPOT TEST FOR CADMIUM UTILIZING GLYOXAL-BIS(2-HYDROXYANIL)

A test for cadmium based on the use of glyoxal-bis(2-hydroxyanil) is proposed. The reaction is carried out on beads of an anion exchange resin on which the cadmium has been concentrated as the tetraiodo complex. Separations inherent in the procedure make the test specific. The limit of identification is 0.05 μg .

PH. W. WEST AND J. DIFFEE, *Anal. Chim. Acta*, 25 (1961) 399-402

DETERMINATION OF TRACES OF WATER IN GASES BY MEANS OF A MODIFIED KEIDEL ELECTROLYTIC HYGROMETER

(Short Communication)

E. BARENDRECHT, *Anal. Chim. Acta*, 25 (1961) 402-404

DETERMINATION OF MAGNESIUM AND ALUMINIUM IN ZINC-BASE DIE-CASTING ALLOYS

(Addendum)

L. BLOCH, *Anal. Chim. Acta*, 25 (1961) 404

ReviewAN EXAMINATION OF SOME ASPECTS OF INCREASING
SELECTIVITY IN CHELATOMETRY*

T. S. WEST

Chemistry Department, The University of Birmingham (Great Britain)

(Received March 18th, 1961)

The evolution of ethylenediaminetetraacetic acid and related compounds as analytical reagents by SCHWARZENBACH and his co-workers and the subsequent development by him and many other capable workers, notably PŘIBIL, FLASCHKA, REILLEY AND RINGBOM, has undoubtedly revolutionized the face of inorganic analysis. Rapid, and on the whole, trustworthy titrimetric procedures based on the use of EDTA are available for practically all metal ions except beryllium and some of the platinum metals and indirect methods for many of the non-metals. Yet EDTA is undoubtedly one of the most unselective organic reagents ever proposed for inorganic analysis and it is only by the ingenious use of a large number of auxiliary chemical reactions that such rapid progress has been made possible during the last decade in applying the procedures to the analysis of mixtures and commercial materials. Now the situation may be viewed as consolidated and the chief problem remaining is to simplify matters by increasing the selectivity of reaction wherever possible.

In the following paper some of the newer aspects of complexometry are discussed with particular reference to the problem of increasing selectivity. It should be noted, however, that advantages to be gained by the use of instrumental methods of detecting the end-point have not been taken into consideration nor has the use of polyamines as titrants.

There are three main avenues open to exploration in searching for increased selectivity. Briefly stated, these are as follows:

- (1) The development of more selective reagents of the complexan type.
- (2) The development of selective indicators.
- (3) The development of selective masking agents.

Neither of the first two developments is of much practical use without the other, as will be instanced later on in the discussion, for a selective complexan cannot be of much use in conjunction with the conventional type of metallochromic indicator which is highly unselective. The converse is also true. Most of the progress so far made in obtaining selective complexometric titration without recourse to physical methods of separation has been made possible only as a result of the use of masking agents.

The three major avenues of approach to the problem having been delineated, each may now be investigated in turn.

* Paper presented on 24th January at the 14th Annual Symposium on Analytical Chemistry, Louisiana State University, 1961.

A. Chelating agents

If a complexan is defined as a derivative of iminodiacetic acid (Fig. 1), it will be seen at once that any hopes of obtaining high selectivity of reaction from such a reagent are rather remote, for this group is a complex former *par excellence* by virtue of its

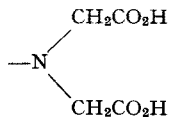


Fig. 1.

multidentate nature, its disposition of lone-pair electrons, steric make-up, etc. Consequently reagents based on it are likely to have a high affinity for the majority of cations, even for the strongly electropositive cations of the alkalis and alkaline earths. Therefore, the best approach appears to be to cut down the reactivity of the group towards certain cations by introducing steric factors which will hinder the reaction of these metals with the complexan centre or, alternatively, to introduce other complex-forming centres in a position such that the metal atoms bound up in the chelate 'claw' of the complexan group can be coordinately bound to the new centre preferably in a five- or six-membered ring structure. This pattern can be traced in some of the following reagents.

First of all, a steric factor has been applied neatly by SCHWARZENBACH and his co-workers¹ who produced homologues of EDTA with the number of carbon atoms between the two complexan centres increasing from 2-8. In EDTA ($n = 2$), the nitrogen atoms are situated so that they form a five-membered ring with the cation across the ethylenediamine bridge, but not unnaturally as the nitrogen atoms are moved further apart the effectiveness of the reagents falls off sharply from $n = 2$ through $n = 4$. As will be seen from Table I from $n = 4$ to $n = 8$ little change results for calcium and cadmium. However, with mercury(II) a different behaviour exists. The stability of the chelates first of all decreases slightly, but thereafter increases till at

TABLE I
HOMOLOGUES OF EDTA

$$\begin{array}{c} \text{HO}_2\text{C CH}_2 \qquad \qquad \qquad \text{CH}_2\text{CO}_2\text{H} \\ \diagdown \qquad \qquad \qquad \diagup \\ \text{N} \text{---} (\text{CH}_2)_n \text{---} \text{N} \\ \diagup \qquad \qquad \qquad \diagdown \\ \text{HO}_2\text{C CH}_2 \qquad \qquad \qquad \text{CH}_2\text{CO}_2\text{H} \end{array}$$

n	Log K		
	Ca ²⁺	Cd ²⁺	Hg ²⁺
2	10.59	16.62	21.8
3	7.12	13.45	19.7
4	5.05	11.87	20.8
5	4.60	—	—
6	4.40	11.70	21.38
8	4.51	11.99	21.83

$n = 8$ the reagent is, if any, more efficient than EDTA. It is also noticeable that a slight increase occurs from $n = 6$ to $n = 8$ for the other metals. This may be due to the degree of flexibility which exists in an 8-membered carbon chain. It is tempting to try and advance a reason for the remarkable specificity of this reagent towards mercury(II). The construction of molecular models reveals no apparent structural difficulty for other metals to form chelates with the reagent equally as well as mercury(II). This rather casts doubt on the view that the selectivity may be due to the ease of deformation of the mercury(II) ion. However that may be, the information currently available points to this reagent, octamethylene diamine-*N,N,N',N'*-tetraacetic acid (ODTA), as being very selective towards mercury(II).

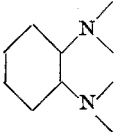
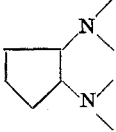
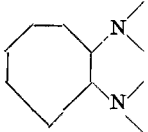
Another interesting series of reagents which illustrates some useful steric and structural effects is shown in Table II (EDTA is included for ease of comparison). In ethylenediamine-*N,N,N',N'*-tetrapropionic acid (EDTP) the size of the primary chelate ring has been increased by one methylene unit, though the five-membered ring across the ethylenediamine bridge remains. It will be seen that in comparison to EDTA the efficiency of chelation towards magnesium, cadmium and nickel falls off very markedly², but a high degree of reactivity is maintained towards copper(II). If now the effect of removing one of the acetic acid groups from each nitrogen atom in

TABLE II
SIZE OF PRIMARY RING/STERIC HINDRANCE IN RING

Complexan	Log K			
	Mg	Cd	Ni	Cu
EDTA →	8.69	16.46	18.2	18.8
$\left(\begin{array}{l} \text{CH}_2\text{CH}_2\text{CO}_2\text{H} \\ \\ -\text{CH}_2\text{N} \\ \\ \text{CH}_2\text{CH}_2\text{CO}_2\text{H} \end{array} \right)_2$	1.8	6.0	9.7	15.4
EDTP →				
$\left(\begin{array}{l} \text{H} \\ \\ -\text{CH}_2\text{N} \\ \\ \text{CH}_2\text{CH}_2\text{CO}_2\text{H} \end{array} \right)_2$	1.6	5.6	9.3	15.1
NN'EDDP →				
$\left(\begin{array}{l} \text{H} \\ \\ -\text{CH}_2\text{N} \\ \\ \text{CH}_2\text{CO}_2\text{H} \end{array} \right)_2$	3.9	8.8	13.5	16.2
NN'EDDA →				
$\left(\begin{array}{l} \text{H} \\ \\ -\text{CH}_2\text{N} \\ \\ \text{CHCO}_2\text{H} \\ \\ \text{CH}_3 \end{array} \right)_2$	2.8	8.1	12.2	16.2
EDDMA →				

EDTA is studied and also a similar procedure for EDTP, then the reagents thus obtained, ethylenediamine-*N,N'*-diacetic acid (EDDA)³ and ethylenediamine-*N,N'*-dipropionic acid (EDDP)², still show a high reactivity towards copper(II) and reduced affinity for the other metal ions. The removal of the propionic acid group from each nitrogen atom in EDTP does not have a marked effect on the stability constants, thus indicating that the second propionic acid group probably plays little part in chelation by EDTP. The removal of an acetic acid group from each nitrogen atom in EDTA, however, does have a very pronounced effect on the stability constants of the magnesium and cadmium and, to a lesser extent, the nickel chelate. This tends to show that the oxygen atom of the carboxyl group plays a vital role in these EDTA chelates. Once more, however, it is apparent that this acetic acid group is unimportant in the chelation of copper(II). It may be concluded from all these results that the ring across the ethylenediamine bridge is a very decisive factor in the chelation of copper(II) and indeed this can readily be explained on the basis of the normal square coplanar habit of the copper(II) ion, for it would not be thus sterically possible for the copper(II) ion to unite with more than one acetyl group on each nitrogen atom as well as with the nitrogen atom itself. Furthermore, the decrease from EDTA to EDTP and from EDDA to EDDP suggests that the strength of the primary ring is of less importance than that of the $N-CH_2-CH_2-N$ ring. Additional evidence for the latter idea may be drawn from the well-known copper reagents, most of which also contain a similar chain. The steric effect of the iso-propyl group in the reagent EDDMA has

TABLE III
COMPLEXANS WITH RESTRICTED ROTATION ABOUT $N-CH_2-CH_2-N$ BOND

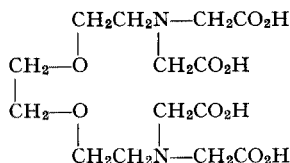
Complexan	Log K			
	Ca^{+2}	Ba^{+2}	Mg^{+2}	Cu^{+2}
EDTA	10.59	7.76	8.69	18.8
 CDTA	12.50	7.99	10.32	21.30
 CPDTA	11.2	—	—	19
 CHDTA	12	—	—	23

been studied by IRVING, SHELTON AND EVANS⁴. Again, there is high stability towards copper(II) and low affinity for magnesium, cadmium and to a lesser extent nickel. The steric hindrance of the —CH₃ group (comparison with EDDA) is negligible. All these reagents show a high degree of selectivity towards copper(II).

One of the most interesting of the complexans is *trans*-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid, first reported by SCHWARZENBACH and co-workers⁵. This reagent, CDTA, differs from EDTA in the attachment of a bulky group, but principally in the restriction of rotation about the ethylene bond. It was until recently, perhaps the most powerful complexan known. Now the cyclohexane ring can exist in boat and chair forms whereas the cyclopentane ring is planar and on the grounds of the entropy significance of this factor in subsequent chelation, MARTELL AND CALVIN⁶ predict that CPDTA (1,2-diaminocyclopentane-N,N,N',N'-tetraacetic acid) should be a yet more powerful reagent. Synthesis⁷ and examination⁸ of the reagent showed that perhaps this factor is less decisive than was originally thought (*cf.* Table III). The trio of reagents was completed by synthesis of the derivative 1,2-diaminocycloheptane-N,N,N',N'-tetraacetic acid⁷ (CHDTA), *i.e.* the higher homologue of CDTA. This proved to be stronger than CDTA for copper(II)⁸ and to have virtually the same affinity for calcium⁹. There is little trend towards selectivity in these reagents, though it is possible that a certain degree of selectivity might be obtained on a kinetic basis, for these reagents are slow to react with some metal ions. However, their synthesis is difficult and costly, and it is not envisaged that they will have much practical importance. It is relevant to subsequent work described in this paper to note in passing that the stability constant gap between the calcium and barium chelates is greater with CDTA ($\Delta^{10}\log K = 4.51$) than with EDTA ($\Delta^{10}\log K = 2.83$). Thus a small measure of selectivity towards calcium relative to barium has been achieved in this particular reagent.

Yet another development is the incorporation of other chelating centres in the ethylenediamine chain. Thus (*cf.* Table IV) we have reagents such as the dioxygen

TABLE IV
COMPLEXANS WITH ADDITIONAL CENTRES



Complexan	Log K			
	Mg	Ca	Cd	Hg ⁺²
EDTA	8.69	10.59	16.46	21.8
EGTA (O)	5.2	11.0	16.73	23.2
EGTA (S)	—	4.87	13.57	23.93
EGTA (N—CH ₃)	4.31	9.42	17.77	27.68

แผนกห้องสมุด กรมวิทยาศาสตร์
กระทรวงอุตสาหกรรม

ether EGTA (O) (1 : 2-bis[2-di(carboxymethyl)aminoethoxy-]ethane)^{1,10}, its sulphur analogue — EGTA (S)¹, and the nearest approach to a nitrogen ether derivative where the oxygen atoms are replaced by N—CH₃ groups, EGTA (N—CH₃)¹. EGTA (O) shows the influence of the oxygen atoms increasing the affinity towards calcium, cadmium and mercury(II) with a depressing effect towards magnesium. The thio ether EDTA (S) shows a depressing action towards all save mercury(II) whilst the =N—CH₃ group notably enhances cadmium and mercury(II). Again, from this series there are trends of selectivity towards mercury(II), cadmium (slight), and calcium, particularly in relation to magnesium. The difference in stability constants between the EGTA (O) chelates of calcium and magnesium is 5.8 ¹⁰log *K* units, whereas for EDTA it is only 1.9 units.

There are many other interesting trends towards selectivity to be observed, but obviously these cannot all be considered, though the high affinity towards iron(III) and copper(II) of ethylenediamine-*N,N'*-di(*o*-hydroxyphenylacetic acid)¹¹ and towards iron(III) of *N,N'*-bis(hydroxyethyl)ethylenediamine-*N,N'*-diacetic acid¹² in alkaline solution deserves special mention.

It should be pointed out, however, that a study of chelation constants can only serve as a useful guide and by no means gives a definitive answer as to what may happen in a solvent medium where other equilibria are involved. An interesting example of this occurs when solutions of the EDTA and NTA (nitrilotriacetic acid) chelates of iron(III) are treated with ammonia and a moderate excess of sodium sulphide. One would expect only to observe a difference in the degree of reaction, whereas, in practice a cherry-red complex is formed with the iron(III)–EDTA chelate and a very intense green complex with iron(III)–NTA. The former colour-body is not particularly stable whereas the latter, once formed, maintains an unchanged transmission for several hours. It may be used for the colorimetric determination of traces of iron, for the colorimetric determination of sulphide ion or as a spot test for either¹³. The results of this examination will be published at a later date.

B. Metallochromic indicators

As mentioned previously, the benefit of selectivity of reagent cannot be reaped in a visual titration unless a selective indicator action is also available. Trends and developments of importance in this direction will now be discussed briefly.

In 1952–54 YOE AND RUSH^{14,15} introduced zincon as a highly selective colorimetric reagent for copper(II) and zinc. Subsequently, KINNUNEN AND MERIKANTO¹⁶ showed that at pH 10 only zinc could be titrated with EDTA and this reagent as indicator. The blue to yellow end-point is an attractive one, but unfortunately this does not provide a selective titration system for zinc, because even metals such as magnesium and strontium titrate partly with the zinc if they are present, whilst others such as calcium, cadmium and lead titrate completely. Obviously, however, if a selective complexan were available, advantage could be taken of the high selectivity of zincon as an indicator. The literature reveals some possibilities in this respect.

Fast Sulphon Black F (Fig. 2) was proposed by BELCHER, CLOSE AND WEST¹⁷ as a highly selective indicator for the EDTA titration of copper. This bis-hydroxy bis-azo dyestuff is selected on the basis of the positioning of the hydroxyl groups with respect to the azo bond. The unusual *ortho-peri* position results in a larger chelate ring, a different stereochemistry across the azo bond and, of course, a different basicity of

the phenolic oxygen. The disposition is such that only nickel and copper(II) react to form coloured chelates in alkaline solution and that only in the presence of ammonia. The indicator action with nickel against EDTA is too sluggish to be of any value, but the action with copper(II) is satisfactory; there again, metals such as calcium, cadmium, cobalt, titrate as copper(II) with EDTA even though they do not react

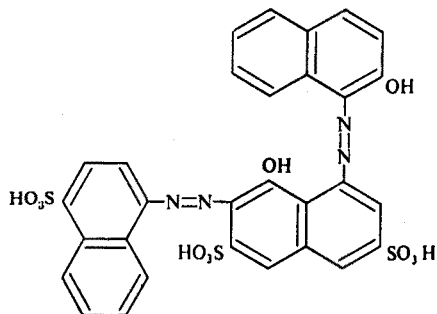


Fig. 2. Fast Sulphon Black F.

with the indicator. Once more, however, a selective complexan would be of benefit and some of these have already been discussed.

Glycine thymol blue, proposed by KÖRBL AND PŘIBIL¹⁸ is not as selective as the two previously mentioned reagents, but it achieves a fair degree of selectivity by utilising a glycine group rather than an aminomethyldicarboxymethyl group substi-

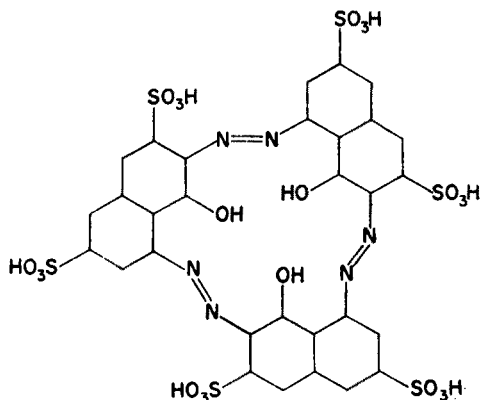


Fig. 3. Calcichrome.

tuted in a position vicinal to the protolysis centres of a conventional acid-base indicator. By this device, a good indicator action is obtained towards copper(II) in weakly acid solution. It does, however, also react with cobalt, cadmium, lead, zinc and mercury(II).

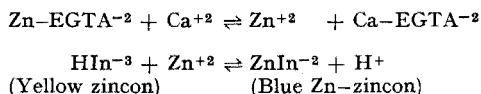
Metallofluorescent indicators have recently received considerable attention. So far they do not show any trend towards specificity of reaction so mention is made only

of two here. These are calcein blue, devised by WILKINS¹⁹, which is a very good indicator for copper(II) ions, but may be used for others such as calcium, etc., and *o*-dianisidine-*N,N,N',N'*-tetraacetic acid synthesised by BELCHER, REES AND STEPHEN²⁰ which has a similar range of utility. These reagents should prove very valuable for the analysis of darkly coloured solutions or the titration of ions which form highly coloured complexan chelates.

Calcichrome (Fig. 3) synthesised and applied by CLOSE AND WEST²¹, embodies most of the attractive features of *o*-hydroxyazo dyestuffs, *e.g.* high chromogenic capacity and low stability of metal complex, and dispenses with their chief drawback, lack of selectivity. This has been achieved by arranging the reactive groups in the centre of the molecule so as to form a chelate cage into which only certain ions can fit. This indicator is specific for calcium at pH 12 in a sodium hydroxide medium. Though chemical affinity may well have a role to play in the specificity of this reaction, the governing factors are undoubtedly (*a*) the ionic size of calcium ($r = 0.99 \text{ \AA}$) as opposed to strontium (1.12 \AA) and barium (1.34 \AA), and (*b*) the fact that at this pH, metal ions other than these exist in an anionic form, or are precipitated out of solution. Calcium forms a red chelate with the molecule whereas barium and strontium do not appear to react. Thus the reagent may be used in a sensitive specific spot-test for calcium or it may be used as a complexometric indicator.

The development of this reagent suggested the possibility of its use as a metallochromic indicator for the titration of calcium in the presence of the other alkaline earths. For EDTA the stabilities of the calcium and barium chelates are $^{10}\log K = 10.59$ and 7.76 respectively (*i.e.* $\Delta^{10}\log K = 2.83$) so that the barium titrates with the calcium. However, for 1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid (CDTA) the corresponding values for $\log K$ are 12.50 and 7.99 ($\Delta^{10}\log K = 4.51$). This separation, though not as much as could be desired, allows the titration by CDTA of calcium in the presence of much barium without the necessity of carrying out a separation. The stability constant of the strontium chelate of CDTA probably lies around $\log K \approx 10$ so that the strontium interferes in the titration of calcium, but a less precise titration may still be effected if some ammonium sulphate is added to precipitate the bulk of the strontium. This method²¹ illustrates the effectiveness of using a selective complexan in conjunction with a specific indicator.

Another interesting example arises from the work of SADEK, SCHMID AND REILLEY²². The EDTA titration of calcium in the presence of magnesium must be carried out at $\text{pH} \approx 12$ when magnesium hydroxide is insoluble, because the separation factor between the two EDTA chelates is only $1.9 \log K$ units. However, for EGTA (Table IV) the separation factor is 5.8 units and this presents a clear-cut possibility for the selective titration of calcium in the presence of soluble magnesium. No direct indicator is available, but REILLEY and his co-workers made ingenious use of a zinc-sensitised zincon indicator system for this purpose. Calcium reacts as follows when treated at pH 9.5 with zincon and a small amount of Zn-EGTA chelate.



Magnesium does not produce a similar reaction. Thus the solution maintains a blue colour till the end-point, when the EGTA titrant removes the free calcium ions. The

experimental conditions for the effective operation of this titration are rather restricted, but it is an interesting example of selectivity based on combined indicator and complexan action.

Another interesting development is based on kinetic effects. A recent example¹⁹ of this illustrates the EDTA titration of nickel in the presence of chromium(III). Chromium(III) forms a much more stable EDTA chelate than does nickel, but it reacts slowly whereas nickel reacts quickly. Thus, it is possible to titrate the nickel before the chromium(III) reacts. Addition of an excess of EDTA and standing or warming allows the combined total of chromium(III) and nickel to be obtained.

C. Masking action

It is largely due to the use of masking agents that the technique of complexometric analysis has advanced to its present status, otherwise the methods would be useless for dealing with anything other than solutions containing only one species of metal ion. Consequently, this pathway towards selectivity is well-known and need not be surveyed in detail here. Some of the more common masking agents which screen selected groups of cations against reaction with EDTA are shown in Table V. The selective demasking of the cyanide complexes of cadmium and zinc is also well-known as a means of further increasing the selectivity, *i.e.*

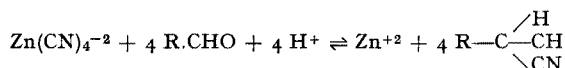
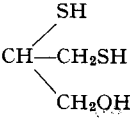
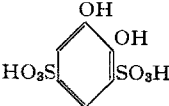
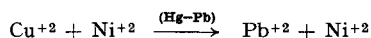


TABLE V
SUMMARY OF MASKING ACTIONS

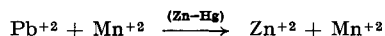
Masking agent	Cations masked
KCN	Ag ⁺ , Cu ⁺² , Fe ⁺² , Hg ⁺² , Co ⁺² , Ni ⁺² , Zn ⁺² , Cd ⁺²
N(CH ₂ CH ₂ OH) ₃	Fe ⁺³ , Al ⁺³ , Mn ⁺³
	Hg ⁺² , Cd ⁺² , Zn ⁺² , As ⁺³ , Sb ⁺³ , Sn ⁺³ , Pb ⁺² Bi ⁺³
NH ₄ F	Mn ⁺² , Fe ⁺³ , Al ⁺³ Ca ⁺² , Mg ⁺² , Al ⁺³ , Ti ⁺⁴ (Nb and Ta)
	Al ⁺³ , Ti ⁺⁴ , Fe ⁺³
KI	Hg ⁺²
H ⁺	Various cations, <i>e.g.</i> Ca ⁺² , Ba ⁺² , Sr ⁺² (pH < 7) Zn ⁺² , Cd ⁺² , Mn ⁺² (pH < 2)
Ascorbic acid	Fe ⁺³ , Cu ⁺²

Amongst many newer masking agents not cited in Table V, the following deserve special mention: thiosemicarbazide²³ used to screen mercury(II) in presence of bismuth (pH 1–2), cadmium, zinc and lead; hydrogen peroxide²⁴ used for titanium(IV) in strongly alkaline solution; sulphosalicylic acid²⁵ used for aluminium and uranium (VI); acetyl acetone²⁵ used for aluminium. *o*-Phenanthroline²⁶ is useful for copper(II), cadmium, zinc, cobalt, nickel and manganese at pH 5–6; it does not complex lead or the rare earths.

Another useful and instructive adjunct towards increased specificity arises out of the use of liquid amalgams by SCRIBNER AND REILLEY²⁷. For example, practically the only way to resolve a mixture of copper(II) and nickel by EDTA is to apply a reducing agent such as ascorbic acid. The use of a lead amalgam results in the reaction



by which copper(II) is replaced by an equimolar amount of lead. The mixture of nickel and lead is easy to resolve by normal procedures. Conversely, difficult-to-mask ions can be replaced by others which are readily masked. Thus a mixture of lead and manganese(II) is difficult to resolve, but treatment with a zinc amalgam results in replacement of the lead by zinc in equimolar amount.



This mixture is now easily resolved. Yet again, advantage may be taken of the difference between redox and complexometric equivalent weights which exists with metals such as bismuth. For example, both lead and bismuth react in 1 : 1 proportion with EDTA. If the solution is reduced with zinc amalgam and then titrated with EDTA, a different titre results because each lead ion is replaced by one of zinc and each bismuth ion is replaced by 1.5 zinc ions. Hence solution of the two simultaneous equations allows a complete resolution of this otherwise difficult mixture.

$$T_1 = [\text{Pb}^{+2}] + [\text{Bi}^{+3}] \quad \text{direct titration with EDTA}$$

$$T_2 = [\text{Pb}^{+2}] + 1.5 [\text{Bi}^{+3}] \quad \text{titration with EDTA following reduction}$$

Finally, it is not inappropriate here to draw attention to one of the most selective reactions devised in the study of complexometry even though this is not a direct complexometric procedure in the normal sense of the word.

In 1954, ANDEREGG, FLASCHKA, SALLMANN AND SCHWARZENBACH²⁸ conceived the neat idea of utilising the acid–base properties of a conventional acid–base indicator (*o*-cresolphthalein) for complexometric purposes by introducing a complexan group in a position vicinal to the protolysis centre of the molecule. This produced the reagent commonly known as ‘phthalein complexone’ or ‘metalphthalein’. Others subsequently explored this region, notably KÖRBL AND PŘIBIL²⁹ with their reagent Xylenol Orange. A similar group of reagents is based on the hydroxyanthraquinone series. One of these, commonly known as Alizarin complexan³⁰ (Fig. 4) has properties similar to Xylenol Orange, but may be used in the basic region as well, and functions best at a slightly

lower pH than Xylenol Orange in acid solution where, for example, it is a particularly effective indicator for copper(II).

The reagent forms a red 1:1 chelate with cerium(III) which is not broken down by EDTA and in the course of further examination it was found not to be broken down by fluoride but indeed to form a new blue-coloured complex with it.

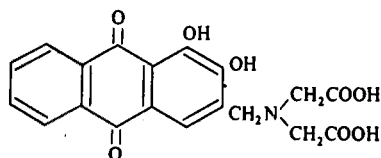


Fig. 4. Alizarin complexan (3-amino-methylalizarin-N:N-diacetic acid).

This complex has a composition corresponding to one part each of fluoride, cerium(III) and Alizarin complexan. The colour reaction is very sensitive and may readily be used for the spot-test detection of $0.2 \mu\text{g}$ of fluoride at a dilution limit of 1:1,800,000³¹ or for the quantitative absorptiometric determination of μg ³² to mg ³³ amounts (pH 5.2) of fluoride. This is probably the first reaction of the fluoride ion known in which a new coloured entity has been produced. All previous tests depend on bleaching or liberation of a free dyestuff from a metal-lake. However, the most surprising thing is the specificity of the reaction, for no other anion save fluoride is effective and the only metals to produce the reaction with fluoride and Alizarin complexan are the elements at the beginning of the lanthanon series, *viz.* La (At. No. 57), Ce (At. No. 58), Pr (At. No. 59) when the entry of the first 5d electron in La leads to subsequent filling of the 4f level throughout the lanthanon series. The mechanism of the reaction has been discussed elsewhere³⁴ and it has been shown that the blue complex produced by fluoride owes its colour to induced deprotonation of the organic part of the molecule following entry of the fluoride ion into one of the two remaining free (H_2O) coordinate positions of cerium(III) ion bound to the alizarin complexan.

None of the common anions interferes seriously with the procedure and though most metal cations do, their interference at the 1/1 level can be eliminated³³ by masking with cyanide, sulphide or iodide. Only in a few cases is it necessary to resort to solvent extraction with 8-hydroxyquinoline and chloroform. Preponderant amounts of metal ions would, no doubt, require physical separation in almost all cases.

REFERENCES

- 1 G. SCHWARZENBACH, H. SENN AND G. ANDEREGG, *Helv. Chim. Acta*, 40 (1957) 1886.
- 2 R. C. COURTNEY, S. CHABEREK AND A. E. MARTELL, *J. Am. Chem. Soc.*, 75 (1953) 4814.
- 3 S. CHABEREK AND A. E. MARTELL, *J. Am. Chem. Soc.*, 74 (1952) 6228.
- 4 H. IRVING, R. SHELTON AND R. EVANS, *J. Chem. Soc.*, (1958) 712.
- 5 G. SCHWARZENBACH AND H. ACKERMANN, *Helv. Chim. Acta*, 32 (1949) 1682; also G. SCHWARZENBACH, R. GUT AND G. ANDEREGG, *Helv. Chim. Acta*, 37 (1954) 937.
- 6 A. E. MARTELL AND M. CALVIN, *Chemistry of the Metal Chelate Compounds*, Prentice Hall, New York, 1952, p. 180.
- 7 R. BELCHER, W. HOYLE AND T. S. WEST, *J. Chem. Soc.*, (1961) 667.
- 8 W. HOYLE AND T. S. WEST, *Talanta*, 2 (1959) 158; 3 (1959) 47.

- ⁹ W. HOYLE AND T. S. WEST, unpublished work.
- ¹⁰ G. SCHWARZENBACH, *Die Komplexometrische Titration*, Ferdinand Enke, Stuttgart, 1955, p. 86.
- ¹¹ H. FREEDMAN, A. E. FROST, S. WESTERBACK AND A. E. MARTELL, *J. Am. Chem. Soc.*, 80 (1958) 530.
- ¹² S. CHABEREK AND F. C. BERSWORTH, *Science*, 118 (1953) 280.
- ¹³ P. SANDERSON AND T. S. WEST, unpublished work.
- ¹⁴ J. H. YOE AND R. M. RUSH, *Anal. Chim. Acta*, 6 (1952) 526.
- ¹⁵ R. M. RUSH AND J. H. YOE, *Anal. Chem.*, 26 (1954) 1345.
- ¹⁶ J. KINNUNEN AND B. MERIKANTO, *Chemist Analyst*, 44 (1955) 50.
- ¹⁷ R. BELCHER, R. A. CLOSE AND T. S. WEST, *Chem. & Ind. (London)*, (1957) 1647.
- ¹⁸ J. KÖRBL AND R. PŘIBIL, *Chem. listy*, 51 (1957) 1061.
- ¹⁹ D. H. WILKINS, *Talanta*, 4 (1960) 182.
- ²⁰ R. BELCHER, D. I. REES AND W. I. STEPHEN, *Talanta*, 4 (1960) 78.
- ²¹ R. A. CLOSE AND T. S. WEST, *Talanta*, 5 (1960) 221.
- ²² F. S. SADEK, R. W. SCHMID AND C. N. REILLEY, *Anal. Chem.*, 29 (1957) 264.
- ²³ J. KÖRBL AND R. PŘIBIL, *Chem. listy*, 51 (1957) 667.
- ²⁴ P. WEHBER, *Z. anal. Chem.*, 154 (1957) 182.
- ²⁵ J. S. FRITZ, M. J. RICHARD AND S. K. KARRAKER, *Anal. Chem.*, 30 (1958) 1347.
- ²⁶ R. PŘIBIL AND F. VYDRA, *Collection Czechoslov. Chem. Commun.*, 24 (1959) 3103.
- ²⁷ W. G. SCRIBNER AND C. N. REILLEY, *Anal. Chem.*, 30 (1958) 1452.
- ²⁸ G. ANDEREGG, H. FLASCHKA, R. SALLMANN AND G. SCHWARZENBACH, *Helv. Chim. Acta*, 37 (1954) 113.
- ²⁹ J. KÖRBL AND R. PŘIBIL, *Chemist Analyst*, 45 (1956) 162.
- ³⁰ R. BELCHER, M. A. LEONARD AND T. S. WEST, *J. Chem. Soc.*, (1958) 2390.
- ³¹ R. BELCHER, M. A. LEONARD AND T. S. WEST, *Talanta*, 2 (1959) 92.
- ³² R. BELCHER, M. A. LEONARD AND T. S. WEST, *J. Chem. Soc.*, (1959) 3577.
- ³³ T. S. WEST, unpublished work.
- ³⁴ M. A. LEONARD AND T. S. WEST, *J. Chem. Soc.*, (1960) 4477.

Anal. Chim. Acta, 25 (1961) 301-312

PAPER SOLUBILIZATION CHROMATOGRAPHY

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INTRODUCTION

Solubilization chromatography, a technique whereby water-insoluble non-electrolytes are separated by elution with aqueous solutions of organic solvents through a column of ion-exchange resin, has been used to separate mixtures of alcohols and phenols¹; ketones²; and ethers, carboxylic acids, and hydrocarbons³. This paper is the first in a series in which the methods of solubilization chromatography and conventional paper chromatography have been combined and applied to the separation of such compounds. It demonstrates the separation of various phenols on filter paper impregnated with ion-exchange resin by development with aqueous solutions of acetic

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acid. Future papers in the series will deal with separations of the other classes of compounds, not as derivatives, as well as studies of the effects of many of the variables involved in the process.

EXPERIMENTAL

Chromatograms were developed by the downward flow of solvent in a bench-top Chromatocab (Research Specialities Co., Model C-350). Amberlite SA-2 ion-exchange papers (batch No. 7802) were used in sheets 18 in. long by about 8 in. wide exactly as supplied in most cases (Rohm and Haas Co.). This paper contains about 45% by weight of Amberlite IR-120 strong-acid cation-exchange resin in the sodium form. For the few runs in which hydrogen-form paper was used, the sodium-form paper was soaked overnight in a 4% solution of reagent-grade hydrochloric acid, rinsed with distilled water, and dried before using.

All the phenols used in this study were of the best grade commercially available. All were used without further purification except catechol and *p*-hydroxybenzoic acid, which were recrystallized from ethanol, and the cresols, which were distilled. Developing solvents were prepared by dilution of reagent-grade glacial acetic acid and reagent-grade methanol.

Samples were transferred to the paper by means of a loop of platinum wire which delivered 5 μ l of test solution (0.2 g/100 ml). The spots were dried after application by hanging the paper in a hood and using a hair drier. The R_F values of Table I were determined by developing samples of each phenol with each of the different solvents. One chromatogram was sufficient to obtain the R_F values of all eleven phenols at any given concentration of acetic acid by spotting the individual phenols across the top of the paper three-quarters of an inch apart; 3.5–4.5 h were required for the solvent front to travel to within one inch of the bottom of the paper sheet. Pre-equilibration of the chamber prior to development was not necessary since only one-phase solvents were used. Using the data of Table I, it was possible to calculate any possible separations. Several such separations of synthetic mixtures (10 μ g of each component) were accomplished. Positive identification of the constituents was guaranteed by developing reference spots on the same piece of paper.

At the end of the solvent development, the chromatogram was removed from the tank and the solvent front marked. The solvent was dried off with the hair drier. To visualize the spots on the paper, it was sprayed with a reagent consisting of equal volumes of 5% ferric chloride and 1% potassium ferricyanide (by weight, in water). This solvent was found to be better than the one containing equal volumes of 1% solutions of each salt as suggested by BARTON *et al.*⁴ The paper was then steamed for 5 min after which time a blue color appeared to mark the location of the phenols. After a period of time, the entire background turns blue so that the positions of the spots should be immediately marked. The blue spots are the result of the reaction of ferricyanide with the divalent 1:1 complex formed between ferric ion and the phenol⁵.

RESULTS AND DISCUSSION

In the interpretation of results, use is made of the familiar equation

$$R_F = \frac{\text{distance travelled by leading edge of solute zone}}{\text{distance travelled by solvent front}} \quad (1)$$

Table I lists the R_F values as calculated by eqn. (1) for each of the phenols studied at different molarities of acetic acid. For most of the phenols, the spots measured one inch in length at all concentrations of acetic acid; resorcinol and *p*-hydroxybenzoic acid measured $1\frac{1}{4}$ in. and *p*-cresol and *m*-cresol measured $1\frac{1}{2}$ in. at all concentrations. Phloroglucinol and pyrogallol cometed over the entire length of the paper with all solvents and so could not be included in any of the synthetic mixtures later separated.

An inspection of the data of Table I indicates that the series of solvents studied tends to have a similar effect on any given phenol. That is to say, plots of R_F vs.

TABLE I

Compound	Values of R_F for [HAc]:								
	0.0 M	1.0 M	2.0 M	3.0 M	4.0 M	5.0 M	6.0 M	7.0 M	8.0 M
catechol	0.36	0.41	0.47	0.52	0.57	0.60	0.63	0.71	0.72
<i>o</i> -cresol	0.44	0.47	0.50	0.55	0.62	0.70	0.75	0.78	0.84
<i>p</i> -cresol	0.28	0.36	0.42	0.47	0.55	0.63	0.69	0.76	0.83
<i>m</i> -cresol	0.39	0.41	0.44	0.58	0.64	0.68	0.72	0.78	0.85
<i>p</i> -hydroxybenzoic acid	0.14	0.19	0.26	0.32	0.40	0.48	0.55	0.64	0.69
<i>o</i> hydroxybenzoic acid	0.04	0.07	0.10	0.18	0.25	0.33	0.46	0.56	0.62
phloroglucinol	0.30	0.35	0.44	0.47	0.53	0.59	0.63	0.64	0.67
pyrogallol	0.34	0.46	0.51	0.53	0.57	0.60	0.63	0.65	0.68
resorcinol	0.35	0.43	0.48	0.52	0.59	0.64	0.69	0.72	0.77
<i>m</i> -nitrophenol	0.15	0.20	0.28	0.33	0.42	0.51	0.62	0.65	0.68
phenol	0.40	0.47	0.51	0.56	0.63	0.68	0.75	0.79	0.83

molarity of acetic acid for the various phenols would be almost parallel straight lines with about the same positive slope. A consequence of this is that the separability of a mixture of the phenols possible with any given solvent cannot be enhanced by changing solvents, as was found with solubilization chromatography in columns. If plots of R_F vs. M had been a group of crossing straight lines with widely varying slopes, changing solvents would probably have been of great aid in achieving separations.

The use of the data of Table I and one simple equation allows the determination of the separations possible at any given concentration of acetic acid. The equation

$$DR_{F_1} = DR_{F_2} + l + \Delta S \quad (2)$$

can be used to calculate the R_F value which a solute must have to be separable from another solute with a value R_{F_1} . In this equation, D is the distance between the point at which the solutes are spotted and the point of farthest advancement of the solvent front; l is the length of the spot formed by the solute with the larger R_F value when the solvent has moved D cm. ΔS is the distance between the back of the spot that moves the farthest and the front of the one which moves less far. With the apparatus used in this study, the effective length of the paper sheets used was only 15 of the overall 22-in. length; therefore, D was taken as 15 in. $\frac{1}{4}$ in. was taken as the required value of ΔS for the separation of two spots to be considered complete.

It can be calculated in this way that many 4-component separations are possible at different concentrations of acetic acid. To check the usefulness of eqn. (2), the following 4-component separations were successfully carried out (10 μ g of each phenol in a total volume of 5 μ l in each case):

(1) Phenol, *p*-cresol, *o*-hydroxybenzoic acid, and *m*-nitrophenol completely separated by development with water.

(2) Phenol, *p*-cresol, *o*-hydroxybenzoic acid, and *p*-hydroxybenzoic acid completely separated by development with 2.0 *M* acetic acid.

(3) Phenol, catechol, *m*-nitrophenol, and *o*-hydroxybenzoic acid completely separated by development with 5.0 *M* acetic acid.

(4) Phenol, *o*-hydroxybenzoic acid, resorcinol, and *m*-nitrophenol completely separated by development with 7.0 *M* acetic acid.

Many other 4-component mixtures could have been separated with equal success. By use of a different apparatus, it would be possible to perform separations not possible on the 15 in. of paper available in the system used here, and a number of 5- and 6-component separations could surely be successfully accomplished. A rearrangement of eqn. (2)

$$D = \frac{l + \Delta S}{(R_{F_1} - R_{F_2})} \quad (3)$$

is useful for calculating the length of paper needed to separate any two components whose R_F values are known. In this equation, D is the length of paper needed for a given separation, R_{F_1} is the R_F value of the solute moving the farthest, and l and ΔS are as defined above. It should be remembered that upon development over distances greater than 15 in., the sizes of the spots may be somewhat greater than those described above.

It was attempted to achieve some 5- and 6-component separations on the 15 in. of paper afforded in the present apparatus by the technique of multiple development, in which the chromatogram is developed, dried, and then redeveloped with the same solvent. These attempts were unsuccessful because the effective length of the paper remaining after the first development is only the original 15 in. minus the distance the solutes have moved. The relatively high R_F values of the compounds studied caused too much of the paper to be used in the first development for a useful amount to be left for subsequent developments.

A study was made to evaluate the results which would be obtained if the resin in the paper was changed from the sodium form to the hydrogen form prior to chromatography. The test chromatogram was developed with 8.0 *M* acetic acid so that the results could be compared with the development on sodium-form paper with 8.0 *M* acetic acid. It would be with this solvent of highest hydrogen-ion concentration that the maximum amount of ion exchange would occur between the sodium-form paper and hydrogen ion of the solvent. It was found for the nine phenols studied that the difference between the R_F value on the hydrogen-form paper and that on the sodium-form paper for a given phenol was usually about 0.05, the value on the hydrogen-form paper being always the higher. Interpretation of these results will be made in a future paper after a more complete study of the effect of the ionic form of the paper is made. The present study proved that the convenient practice of using the ion-exchange papers as supplied in the sodium form in no way lessened the usefulness of the method as a separation tool even though a small amount of ion exchange between the paper and the solvent took place during each development.

The theory governing paper solubilization chromatography is even more compli-

cated than that for solubilization chromatography on columns³. Even at low concentrations of acetic acid the phenols are virtually unionized and are separated by virtue of the differences in their partition between the moving solvent phase and the stationary phase. Interactions possible between the phenol molecules and the stationary phase include those with the resin particles (both ion-dipole and London dispersion forces), with the solvent inside the swollen resin particles, and with the paper itself. That the present process does differ from solubilization chromatography in columns is demonstrated by the fact that the order of elution from a strong-acid cation-exchange resin in the hydrogen form with aqueous acetic acid as eluent is catechol before phenol before *o*-cresol³. This means catechol has the least affinity for the resin, and *o*-cresol the most. On strong-acid, cation-exchange resin-loaded filter paper in the hydrogen form, *o*-cresol and phenol have the same R_F values, and catechol a somewhat lower R_F . This means catechol has the greatest affinity for the ion-exchange paper. Furthermore, a preliminary study of the use of aqueous methanol rather than aqueous acetic acid as the developing solvent has shown that methanol has a displacing power no greater than water on the SA-2 paper used, whereas 1.0 *M* methanol proved to be a considerably better eluent than water in the conventional solubilization chromatography of the ketones². It is hoped that more detailed studies of these and other variables in the future will clarify the mechanisms involved in both processes.

ACKNOWLEDGEMENT

One of the authors (J.S.) would like to thank the Committee on Advanced Study and Research of Lafayette College for financial support of this project.

SUMMARY

The R_F values of a series of eleven phenols have been determined using paper-chromatographic techniques on filter paper loaded with ion-exchange resin. The data have been used to predict the separation of various mixtures of these phenols by development with aqueous solutions of acetic acid.

RÉSUMÉ

Les auteurs ont effectué une série de déterminations de R_F de onze phénols, par chromatographie sur papier, en utilisant un papier filtre, chargé de résine échangeur d'ions.

ZUSAMMENFASSUNG

Es werden die R_F Werte von 11 Phenolen bestimmt unter Verwendung eines Filterpapiers, das mit einem Ionenaustauscherharz beladen ist.

REFERENCES

- ¹ J. SHERMA AND W. RIEMAN, *Anal. Chim. Acta*, 18 (1958) 214.
- ² J. SHERMA AND W. RIEMAN, *Anal. Chim. Acta*, 19 (1958) 134.
- ³ J. SHERMA AND W. RIEMAN, *Anal. Chim. Acta*, 20 (1959) 357.
- ⁴ G. M. BARTON, R. S. EVANS AND J. A. G. GARDNER, *Nature*, 170 (1952) 249.
- ⁵ H. BROUMARD AND J. H. SMITH, *J. Am. Chem. Soc.*, 74 (1953) 1013.

SEMI-MICRO CRYOSCOPIC MOLECULAR
WEIGHT DETERMINATION WITH A THERMISTOR THERMOMETER*

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INTRODUCTION

The determination of molecular weights of small quantities of materials has wide applicability. A technique has been developed for the determination of the molecular weight of compounds with volumes as small as 0.3 ml of solution by the steady state freezing point method. The method can be refined to extend to smaller volumes. The apparatus is simple, inexpensive, and dependable. Accuracies in the order of 2% have been demonstrated (see Table I). The technique is even easier to use than the conventional macro method.

TABLE I
SUMMARY OF MOLECULAR WEIGHT DETERMINATIONS

Compound	Molecular weights		
	calculated	determined	% error
2,2,4,6,6-Pentamethylheptane	170	167	-1.8
Tetraisobutylene	224	226	+0.9
<i>n</i> -Decane	142	146	+2.8
Di- <i>n</i> -butylphthalate	278	275	-1.1
Naphthalene	128	127	-0.8
Phenanthrene	178	178	0.0
Benzil	210	208	-1.0

Thermistors have been employed previously in techniques for the determination of molecular weights. NEUMAYER¹ has reported on the use of a 2-thermistor setup for determining molecular weights on the basis of differences in temperatures of a solution and its solvent in contact with the solvent vapors. DIMBAT AND STROSS² have reported on a thermistor ebulliometer. The technique reported in this article employs a single thermistor to detect the steady state freezing point difference between a solvent and its solution of the material whose molecular weight is to be determined. A Wheatstone bridge circuit is used to detect the change in resistance of the thermistor with temperature. The cooling curve and steady state freezing point are recorded on a strip chart recorder. Benzene, a very satisfactory solvent for determining molecular weights of hydrocarbons in the molecular weight range 200 to 600, was used as the solvent for this work³.

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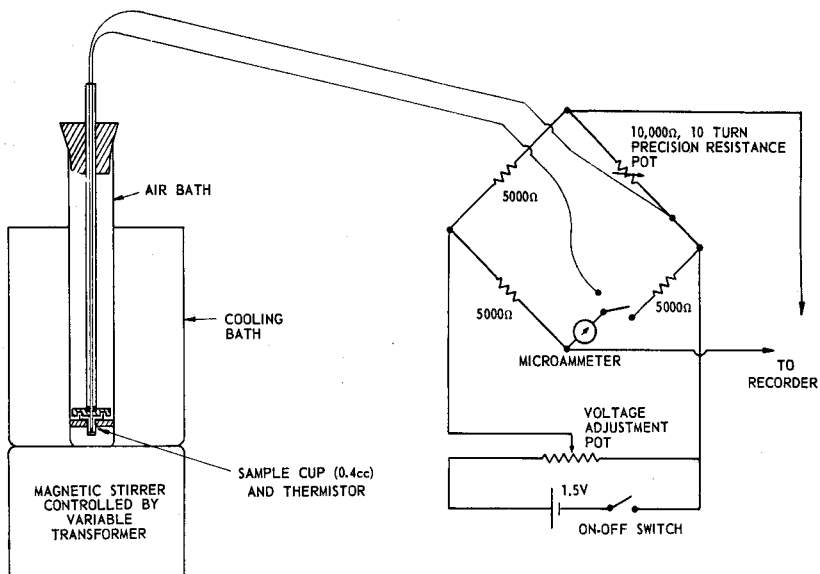


Fig. 1. Apparatus for molecular weight determination, with associated circuitry.

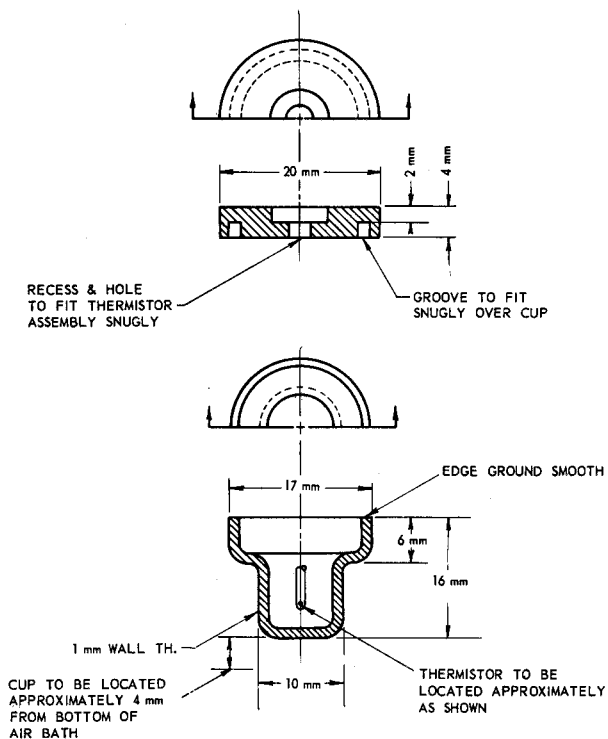


Fig. 2. Sample cell and cover plate.

APPARATUS

The apparatus with the bridge circuitry is shown in Fig. 1. For the studies reported in this paper, a water and ice mixture in a 1000-ml beaker was adequate as a constant temperature bath. The dimensions of the air bath surrounding the sample holder were selected to give the proper cooling rate of the sample. Stirring of the ice bath is necessary to produce a uniform bath temperature. For solvents other than benzene, a regulated bath could be used to provide a temperature several degrees below the freezing point. A high degree of regulation would be required due to the sensitivity of the thermistor. A magnetic stirrer is used to stir the sample by a small nickel-plated stirring bar in the sample holder.

The thermistor element used in this work was a VECO 32A84, manufactured by the Victory Engineering Corporation, Union, New Jersey. At 25° this thermistor has a resistance of 2000 ± 400 ohms and a negative temperature coefficient of resistance ($-3.9\%/^{\circ}\text{C}$). Its resistance at the freezing point of benzene is approximately 5000 ohms. It is necessary that the thermistor be positioned as shown in Fig. 2, which gives details of sample cell and coverplate.

EXPERIMENTAL

Adjustment of the apparatus

The range and the position of the freezing points of the solvent and a solution on the recorder chart may be varied by varying the voltage to the bridge and the setting of the 10-turn precision resistance pot. Additional adjustment is available with a multi-range recorder. The bridge voltage must be low to prevent excessive heating of the thermistor. The apparatus is adjusted for a large recorder deflection in the range of molal concentration being studied. This is accomplished by a series of trial and error experiments. A small amount of experience will allow the rapid selection of a suitable range.

Standardization of the voltage supply

The recorder range is adjusted as described above. A constant resistance is switched in for the thermistor. The readings of the precision resistance pot and an ammeter, which is located in the thermistor arm of the bridge, are noted. The voltage may hereafter be standardized by reproducing the readings of the pot and ammeter.

Calibration and molecular weight determinations

The procedure for determining the steady state freezing point of a solvent or a solution follows. The stirring bar and a small amount of desiccant, such as finely divided magnesium sulfate, are placed in the cell. The cell is then inserted in the air bath and seated in a cork ring. The liquid is then pipetted into the cell to the level of the shoulder. The sample cell coverplate and the thermistor probe assembly are then quickly put in place. The air bath is lowered into the ice water bath so that it touches the bottom of the beaker. Stirring is started immediately and the stirring rate is adjusted to the maximum value not producing a vortex. When the recorder pen comes on scale, the chart is started and the cooling curve is drawn by the recorder. The sample is allowed to continue to cool until freezing occurs. This is indicated by a rapid rise of the recorder pen from the supercooling region to a peak which

corresponds to the steady state freezing point. The peak for pure benzene is a flat plateau with a duration of one and a half minutes. Solutions exhibit a shorter plateau, the length decreasing with increasing concentration. Fig. 3 shows typical cooling curves. In this work, a 5-mV recorder setting was used; part of the supercooling region was off scale.

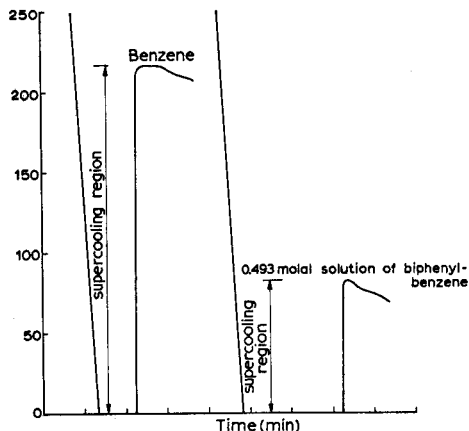


Fig. 3. Typical cooling curves for benzene and benzene solution. Thermistor current: $95 \mu\text{A}$; precision resistance pot setting: 5190Ω ; recorder range 5 mV.

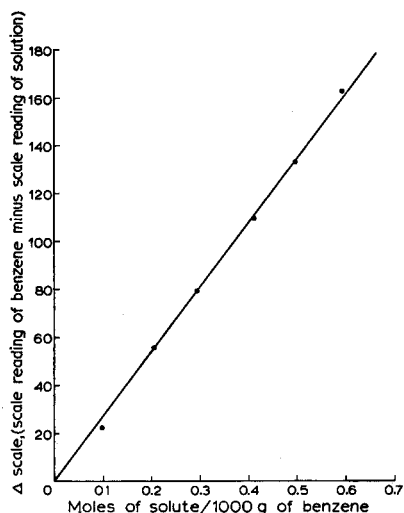


Fig. 4. Typical calibration curve with known solutions of biphenyl in benzene. Thermistor current, $95 \mu\text{A}$; precision resistance pot, 5190Ω ; recorder range, 5 mV.

Since this technique employs the steady state freezing point method, it is necessary to calibrate the apparatus with solutions of benzene and a material of known molecular weight. For this work, biphenyl was chosen as the standard material. The steady state freezing points for benzene and a number of solutions of biphenyl in benzene were determined as described above, and the chart was calibrated directly in molal

concentration units. The calibration curve is shown in Fig. 4. Since the variation of the resistance of the thermistor with temperature is not linear, it might seem that the calibration curve should also be non-linear. However, since the temperature range over which the thermistor operates is small (approximately 0.4°), the calibration curve is linear within experimental accuracy. Calibration can be simply accomplished by determining the cooling curves for benzene and one solution. It is desirable to recalibrate from day to day as characteristics of thermistors may drift slightly. The apparatus should be allowed to warm up. Recalibrations should be performed for changes in batches of solvent or for any change in the precision resistance pot setting.

The procedure for determining molecular weights follows. The difference between the scale readings for freezing points of benzene and a solution of the unknown in benzene is obtained. The molal concentration is read on the calibration curve. The molecular weight is calculated from weights of the solvent and unknown.

The molecular weights of a number of known compounds were determined as described above and the results compared with the calculated values. These results are summarized in Table I.

SUMMARY

An apparatus for extending the steady state freezing point depression method to small volumes, of the order of 0.3 or 0.4 ml, has been developed. A thermistor is used as the temperature sensing element, in one arm of a Wheatstone bridge. The apparatus is simple and dependable. Accuracies in the order of 2% are easily attainable.

RÉSUMÉ

Des semi-microdéterminations cryoscopiques de poids moléculaires ont été effectuées à l'aide d'un "Thermistor", permettant ainsi des mesures sur des volumes de 0.3 à 0.4 ml.

ZUSAMMENFASSUNG

Beschreibung einer kryoskopischen Methode zur Molekulargewichtsbestimmung unter Verwendung von Thermistoren.

REFERENCES

- ¹ J. J. NEUMAYER, *Anal. Chim. Acta*, 20 (1959) 519.
- ² M. DIMBAT AND F. H. STROSS, *Anal. Chem.*, 29 (1957) 1517.
- ³ C. B. WILLINGHAM, P. A. FAETH, L. J. SULLIVAN, R. J. FRIES AND J. V. KENNEDY, *The Determination and Correlation of Physico-Chemical Properties of High Molecular Weight Hydrocarbons*, Report of Petroleum Research Fund-83, Mellon Institute of Industrial Research, Pittsburgh, Penna., 1956.

DIFFERENTIAL PRECIPITATION IONOGRAPHY FOR QUALITATIVE CATION ANALYSIS*

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INTRODUCTION

It is frequently desirable to have a rapid method of detecting the presence of certain metallic ions in a chemical specimen. In various studies of air pollution, industrial hygiene, and metal analysis the necessity of dissolving dusts and small portions of solid samples to perform wet chemical tests can be tedious and time-consuming.

Various investigators have described methods of overcoming these difficulties. Spectrographic methods are capable of detecting or determining numerous metals in the same sample, as exemplified by their use by the National Air Sampling Network of the U.S. Public Health Service¹. However, the cost of a suitable spectrograph limits the use of the procedure. The ring-oven technique of WEISZ² can be used to separate minute quantities of solutions containing many ions. The electrophoretic methods used by KIRK *et al.*³ on cellulose acetate membranes takes advantage of the properties of these membranes to study limited amounts of materials. Precipitation chromatography has been used to detect metals as they diffuse into an agar gel column⁴. This paper describes a method of rapidly identifying certain metal ions in this important microgram range in one or two simple operations.

DEVELOPMENT OF METHOD

Some adaptation of an ion migration technique seemed desirable as a method of cation analysis. In the course of experimentation, a method was discovered which appears to depend not upon relative migration speed, but upon the pH at which precipitation of the metal hydroxide occurs. Gels were investigated as substrates, but were too seriously deformed by heating at the electrodes to be useful. Membrane filters proved to be a desirable substrate in this case (Millipore Filter Corporation, Bedford, Mass.). Heavy gauge platinum wire was chosen for the electrodes as the material least likely to be affected by surface changes.

A dependable method of holding the sample and applying the current was necessary. A device was built on a triangular base which could be leveled by means of three adjustable screws. This base supported the electrode clamps which were variable in separation and were controlled by set screws. The electrodes, of 24-gauge platinum wire or 1/8-in. diameter rods, made contact with the substrate on a microscope slide supported directly below the electrode holder. A small leveling bubble attached to

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the base directly back of the sample area facilitated exact adjustment. Power was obtained from a 0-50 V D.C. power supply. A mA-meter was included in the circuit (Fig. 1).

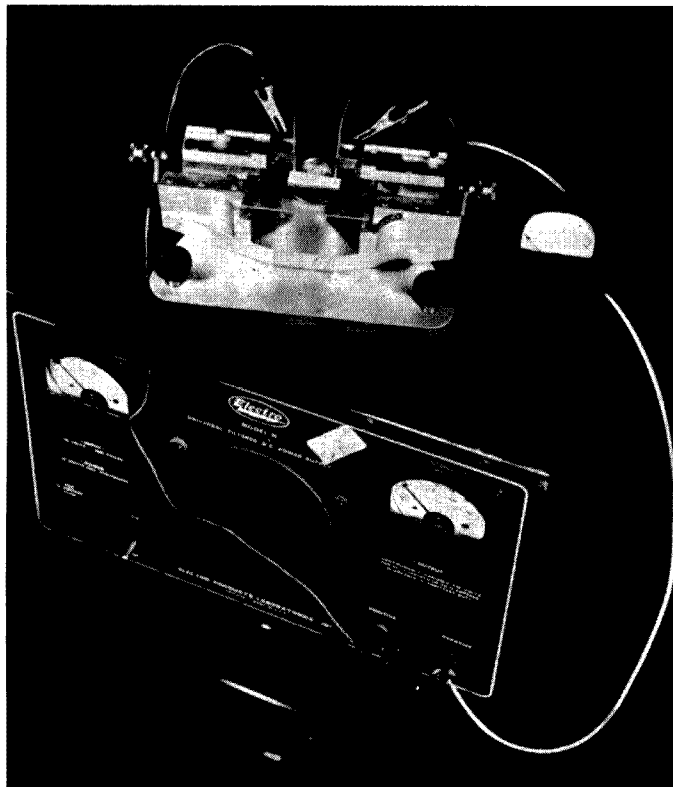


Fig. 1. Instrument as designed for ion migration, showing platinum electrodes in contact with filter strip.

In order to provide electrolyte to conduct the current, a small piece of blotting paper on a microscope slide is soaked with a sodium chloride-hydrochloric acid solution. A small strip of membrane filter (30 mm by 5 mm is a suitable size) is placed on the wet blotter and allowed to take up the electrolyte. The sample is placed on the center of the filter with a needle or the shaped end of a toothpick. If the material is soluble, current is applied. For insoluble dusts pre-treatment in hot acid fumes may be necessary; 1 h at 50° is usually sufficient. Ideally, the potential applied moves the cations toward the negative pole. Simultaneously, electrolysis of sodium chloride liberates sodium hydroxide at the negative pole causing a pH gradient around the electrode. When the cations reach a point which corresponds to their precipitation pH they cease to migrate.

When migration is complete the filter is removed from the electrode holder and placed on a few drops of a suitable reagent (Table II) on a clean slide. It is examined microscopically with transmitted light at low magnification. Colored precipitates in circles or semicircles around the area of the negative pole will indicate the presence of the cations for which the test was made (Fig. 2). The precipitates diffuse rapidly

and as the filter dries, the color may change, so that for best results the sample should be examined at once. Rapid diffusion may be partially prevented by "fixing" the sample with a clear plastic spray, such as Krylon. When the plasticized filter has dried, it may be mounted with immersion oil in the usual fashion. This changes the appearance of colored precipitates somewhat, and care must be used in interpretation.

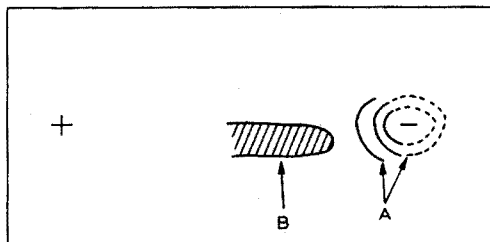


Fig. 2. Diagram showing ion separation after migration. A, Area of clearly separated bands partially or completely circling negative pole. B, Area of poor separation caused by slow moving ions such as iron(III), resulting in indistinct outline.

In the case of extremely refractory metal dusts or solid samples of metals, the sampling method of STEPHEN⁵ was adapted. For the first part of the test the platinum electrodes were replaced with an aluminum electrode at the negative pole and one of stainless steel turned to a point as he describes at the positive pole. The movable electrode holders are adjusted for the size of the sample and the wet filter placed on the sample in such a way that the aluminum electrode touches the sample. If the sample is a dust it is put on a slide in a small pile; the filter and aluminum electrode covers one edge of the pile and the stainless steel electrode is thrust into the remainder of the pile. Current is passed as STEPHEN describes. A small amount of sample is deposited on the filter by anodic dissolution. This method of obtaining a soluble sample is applicable to a number of types of analysis and is particularly amenable to analysis by the migration methods described above. The entire process may be completed in 10 min.

A series of tests was made to determine the best separation of the ion bands (Table I). The amount of electrolyte used was kept constant by using a piece of blotting paper sufficiently large to be saturated, with only a slight excess, by the quantity of electrolyte. The electrolyte is delivered from a calibrated dropper. For these tests, 1 ml was used. As can be seen from Table I, the strength of the electrolyte is not critical over a fairly large range.

TABLE I
EFFECT OF ELECTROLYTE COMPOSITION ON SEPARATION

Electrolyte			Potential gradient			Results after reaction
H ₂ O (ml)	Conc. acid (drops)	NaCl (mg)	V	min	mA	
5	1 drop HCl	6	20	2	20	no migration
5	1 drop HCl	15	20	2	20	diffuse ppt., poor separation
5	1 drop HCl	20	20	2	20	complete migration, good separation
5	1 drop HCl	30	20	2	20	complete migration, good separation
5	2 drop HCl	30	20	2	30	very large "blister" at neg. pole
10	1 drop HCl	30	20	3	20	requires long time for poor separation
5	1 drop HCl	60	20	2	?	chlorine given off
5	1 drop HNO ₃	16 ^a	20	2	50	slow movement
5	1 drop HNO ₃	16 ^a	50	2	80	good separation, much heat and boiling

^a NaNO₃ instead of NaCl.

A series of tests was made to determine the optimum potential gradient. Electrode separations of 12 mm, 15 mm, and 24 mm were used. A separation of 15 mm seems to give the most consistent results. At this electrode separation, 20 V gives an ammeter reading of approximately 18 mA. This is somewhat interdependent with the strength of the electrolyte. At a 15-mm electrode separation and 20 V, 18 mA, migration is fairly complete for all but the slowest ions, *i.e.*, iron(III), after 1.5 to 2 min. Considerable heat is generated at the negative pole which manifests itself in "blistering" of excess electrolyte at the negative pole and violent bubbling. To reduce the heat, a 100-Ohm resistor may be added to the circuit in parallel with the sample substrate. At 20 V the current drops to 4 mA and the bubbling is correspondingly decreased. Migration and separation of ions seems to be unimpaired except for those ions whose migration rate is slow.

The type of reagent used depends on the nature of the sample. A saturated solution of rubeanic acid in 50% aqueous methyl alcohol will determine the presence of iron, copper, nickel and cobalt in a single sample by the formation of yellow, green, blue, and pink precipitates, respectively. Some care is needed in interpretation, as small amounts of nickel give a pinkish-purple color which may be confused with cobalt. Other general reagents such as 10% aqueous potassium ferrocyanide, and benzidine in acetic acid, may be used to determine the presence or absence of groups of cations. In many cases if the first reagent gives a slight precipitate, excess reagent may be blotted away and a second or even a third applied to the same filter. Up to four ions have been identified in a single test. Where an extremely heavy precipitate occurs due to large amounts of one cation, it will be necessary to prepare one or more fresh samples to confirm the presence of trace amounts of other ions. Confirmatory tests may be made by using sensitive spot test reagents, such as are described by FEIGL⁶. A reagent which gives a white or pale yellow precipitate is not satisfactory unless the filter is to be made transparent and viewed with transmitted light.

DISCUSSION

The most probable explanation for the formation of circles or semicircles around the negative pole is the establishment of a pH gradient by the electrolysis of sodium chloride and the diffusion of the resulting base into the substrate. The cations of the sample will migrate under the potential gradient until their characteristic precipitation pH is reached. At this point they will precipitate as the appropriate oxide or hydroxide. Since the migrating ions will follow the lines of force, whether they ultimately precipitate as arcs, semicircles, or complete circles will depend on the initial location of the sample on the filter and on the geometry of the filter and the electrodes.

Other characteristics of the migration which lend support to the theory of the precipitation mechanism are the precipitation of the cations in the order of their precipitation pH and band width independent of time of migration. No matter where the original sample is placed on the filter, as long as it is outside the area of pH gradient, the final band of precipitated material will be in the pH gradient area, in some fraction of a circle, independent of the shape of the original sample. This also suggests that the mechanism is other than ionophoresis, and is in addition an advantage when sampling particulate matter or sampling by anodic dissolution.

The technique has been applied to several different types of samples (Table II). Dusts, collected in bulk and deposited on the filter, or collected on the membrane

TABLE II
RESULTS WITH SAMPLES

Sample	Pretreatment	Reagent	Ions found	Ions known to be present
Dust prepared in lab	—	rubenic acid	iron, nickel	iron, nickel, as chlorides
Dust prepared in lab	—	rubenic acid and sodium rhodizonate	iron, nickel, copper, lead	iron, nickel, copper and lead as soluble salts
Dust prepared in lab	1 h in HCl vapor	rubenic acid	iron, copper	iron, copper, nickel as oxides
Scrapings from iron meteorite	1 h in HCl vapor	rubenic acid	iron, nickel	iron, nickel, cobalt
Scrapings from iron meteorite	anodic dissolution	rubenic acid	iron, nickel, cobalt	iron, nickel, cobalt
Magnetic dust from roof	anodic dissolution	potassium ferrocyanide	iron, copper	unknown
Magnetic fly ash	anodic dissolution	potassium ferrocyanide	none ^a	unknown
Nickel, U.S. coin	anodic dissolution	rubenic acid	copper, nickel	copper, nickel
Dime, U.S. coin ^b	anodic dissolution	rubenic acid	silver, copper	silver, copper
Nichrome wire	anodic dissolution	rubenic acid	nickel, iron	nickel, iron, chromium, manganese ^c
Ore from Tabawus Mine, N.Y.	anodic dissolution	1. potassium ferrocyanide 2. hydrogen peroxyde	iron	iron, titanium

^a In the microscope, a few individual blue areas were seen, indicating iron. No circles.

^b When silver is present with NaCl-HCl electrolyte, it is precipitated as AgCl at the point of contact and separates without migration.

^c No tests were made for chromium and manganese.

filter itself, migrate most easily in soluble form. If anodic dissolution as described above is not possible, it is necessary to treat the filter with acid fumes as previously mentioned. Metals such as coins, foil, alloys, etc., yield readily to treatment. The tests with ores show that the sample must be clamped or held in such a way that a flat face is in firm contact with the electrode. The ore must also have a high percentage of metal on the surface and in sufficiently continuous amounts that both electrodes touch the same area. Earthy or low grade ores do not respond.

Great care must be taken with interpretation. The colors of the reaction precipitates are subject to diffusion and fading as the filter dries. Varying amounts of material may give changes in shades of color. The reagent should always be allowed to soak up through the membrane filter as described above, to avoid washing away the reaction product. Test samples should be made with knowns until the operator is completely familiar with the behavior of the ions. The tests are not quantitative. However, an experienced technician can arrive at a fairly precise estimate of the amounts present by comparing color, amount of precipitate, and general appearance. The technique is primarily designed for rapid qualitative work, as it is not as sensitive as some spot test techniques. It should be emphasized that the amounts of material required are sufficiently small that in many cases the method is essentially non-destructive testing. Estimates can be made well into the 10^{-6} – 10^{-9} g range depending on how the original sample was collected. The method should be readily applicable to qualitative examination of industrial dusts, metals testing and similar areas of interest.

ACKNOWLEDGEMENTS

F. HUNEMULLER, student technician, assisted in preparing samples for these experiments. E. A. NEIL aided in designing the instrument. This assistance is gratefully acknowledged.

SUMMARY

A method — differential precipitation ionography — is described for the separation and detection of cations in mixtures in trace amounts. The ions are caused to migrate by application of current to a supporting membrane. The substrate is kept moist with an electrolyte so chosen that its electrolysis provides a pH gradient. The migrating ions form narrow bands of their oxides or hydroxides at the point of their precipitation pH in this field. After this separation the filter is developed with a suitable reagent and examined microscopically. Several metal ions can be detected in a single sample. Materials in amounts as low as 10^{-9} g may be detected.

RÉSUMÉ

Une méthode rapide, par ionographie à précipitation différentielle, a été mise au point pour la séparation et l'identification de cations à l'état de traces (jusqu'à 10^{-9} g). Après séparation, le filtre est traité par un réactif approprié et examiné au microscope.

ZUSAMMENFASSUNG

Beschreibung einer raschen Methode zur Trennung und zum Nachweis von Kationen in Spuren-mengen durch differentielle Fällung auf einer mit einem geeigneten Elektrolyten getränkten Membran, an die eine Spannung angelegt wird; dies führt zur Bildung eines pH Gefälles. Die an den entsprechenden pH Stellen gebildeten Niederschläge werden mit geeigneten Reagenzien behandelt und die entstandenen Niederschläge mikroskopisch untersucht.

REFERENCES

- ¹ U.S. Public Health Service, *Air Pollution Measurements of the National Air Sampling Network*, PHS Publication No. 637, Govt. Printing Office, Washington, D.C., 1958, 259 pp.
- ² H. WEISZ, *Mikrochim. Acta*, (1956) 667.
- ³ B. W. GRUNBAUM, P. L. KIRK AND W. A. ATCHLEY, *Anal. Chem.*, 32 (1960) 1361.
- ⁴ J. D. SPAIN, *Anal. Chem.*, 32 (1960) 1622.
- ⁵ W. I. STEPHEN, *Mikrochim. Acta*, (1956) 1531.
- ⁶ F. FEIGL, *Spot Tests*, Vol. 1, 4th Ed., Elsevier, Amsterdam, 1954.

ORGANIC COMPOSITION ANALYSIS BY COMBINATION OF GAS CHROMATOGRAPHY WITH INFRARED SPECTROPHOTOMETRY

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As a result of the rapid development and increasing complexity of industrial chemical technology, the demands made on the analytical chemist have increased from the standpoints of time, precision and selectivity. This is particularly true in the petroleum and other organic chemical industries where complicated mixtures of related compounds have become an everyday problem. Lacking the desired selectivity in most cases, the analysis of these complicated organic mixtures becomes a case of separation, identification and determination.

One approach to solving this problem has been through the combination of gas chromatography with infrared spectrophotometry. Barring preparative scale work, the samples charged to the gas chromatographic unit are usually the order of microliters. The separation, trapping, and identification of a component from this size charge becomes a significant problem. SZYMANSKI¹ approached the problem by placing an activated surface material on rock salt and trapping the species by adsorption. An infrared spectrum of the adsorbed species was then obtained. A number of other workers, including DOERING AND BUTTERY², BELLIS AND SLOWINSKI³, and CRAIG *et al.*⁴ have attempted to trap the samples as liquids via cold trap techniques. Another approach, that of trapping as a gas, has been the topic of papers by WHITE *et al.*⁵, STEWART *et al.*⁶, and ANDERSON AND DUNCAN⁷.

In this paper a technique for trapping and obtaining infrared spectra in the gas phase is presented and some of its potentialities are discussed.

EXPERIMENTAL

Apparatus

A Fisher-Gulf Partitioner was used for the gas chromatography work. The outlet for the gas chromatographic effluent was connected to a Republic four-way reversing valve, #310-6. The Perkin-Elmer minimum volume gas cell was connected across the valve using 1/8 in. copper tubing for lines. Two Hoke valves were connected into the system to provide a quick flushing arrangement. The cell and lines were wrapped and heated with thermocouple wire. The spectra were run on a Perkin-Elmer 221 spectrophotometer.

Reagents

(1) The *n*-butanol, *sec*-butanol and *tert*-butanol were obtained from the Eastman Kodak Company.

(2) The hexene-1, heptene-1 and octane-1 were Phillips Petroleum Company pure grade reagents (99 mol % minimum).

Mode of operation

A schematic diagram of the apparatus is given in Fig. 1. The trapping arrangement is best illustrated by tracing the flow of the carrier gas through the system. The carrier gas passes through the reference side of the thermal conductivity cell, picks up the

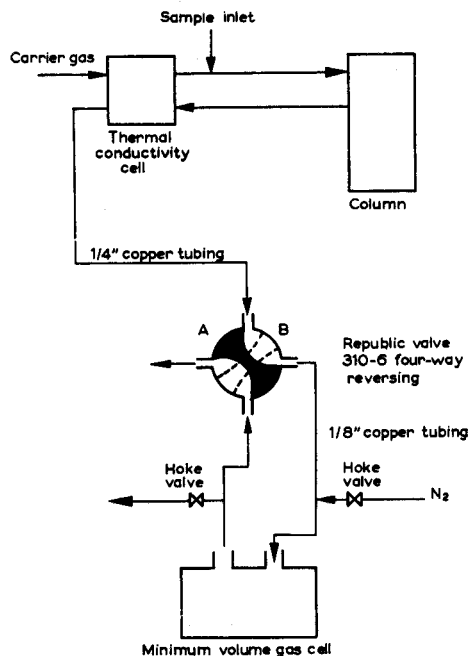


Fig. 1. Schematic diagram of apparatus.

sample and enters the column. The effluent from the column passes back through the thermal conductivity cell and into a Republic four-way reversing valve. When the Republic valve is in position A, the gas flows through the minimum volume gas cell whereas in position B it is vented to the atmosphere and the gas cell sealed off.

In order to trap a sample, the minimum volume gas cell was positioned in the spectrophotometer and the instrument set on a characteristic vibration of the component in question, generally a carbon-hydrogen stretching frequency. The buildup of a component in the gas cell was monitored and the cell sealed off when maximum absorption was reached. The infrared spectrum was then run under the desired conditions. Flushing was accomplished by opening the two Hoke valves and passing a stream of dry nitrogen through the cell. The Hoke valves were then closed and the Republic valve opened to trap another component.

In general, one component was trapped for each charge to the gas chromatograph. However, where fast scans were applicable, *i.e.*, 4 min, it was possible to trap consecutive components if they were separated by 6 min in retention time.

Sensitivity

An important point concerning an apparatus of this type is the amount of sample that must be charged to the gas chromatograph in order to obtain a useful infrared spectrum for the trapped component. This sensitivity is a function of the specific

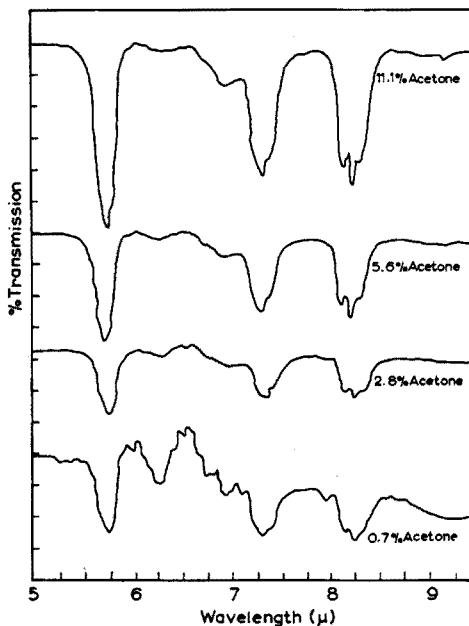


Fig. 2. Infrared spectra of trapped acetone fractions. 20- μ l charges.

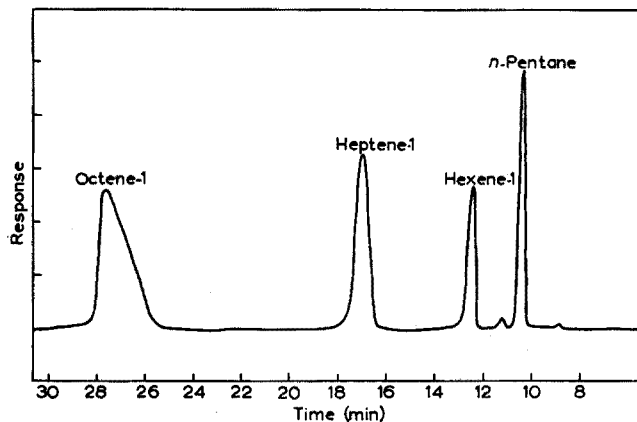


Fig. 3. Gas chromatography trace of alkene blend.

absorptivities of the compound and the maximum concentration that may be attained in the gas cell.

An experimental investigation of the sensitivity aspect was made using acetone as the component to be trapped. Blends of acetone and *n*-butanol were prepared,

separated on the gas chromatograph, the acetone trapped, and its spectrum recorded. A selected portion of the spectra obtained for the various blends is shown in Fig. 2. Based upon these data, acetone can be trapped and identified if it is present as 0.1 to 0.2 μl by volume in the charged sample. A comparison of specific absorptivities with that for acetone will give a rough approximation of the amount of component needed for identification using the same technique. In investigating these acetone blends, 5X scale expansion was used at the 0.7% level. The over-all sensitivity attainable depends upon the scale expansion features available on the spectrophotometer.

Separation of blends

In order to illustrate the potentialities of this technique, we prepared two blends — one an alcohol blend and the other an alkene blend — for separation and determination. The alkene blend consisted of hexene-1, heptene-1, and octene-1 with *n*-pentane added as a retention time standard. The gas chromatographic trace of this alkene blend is shown in Fig. 3. Using 50- μl charges to the gas chromatograph, each

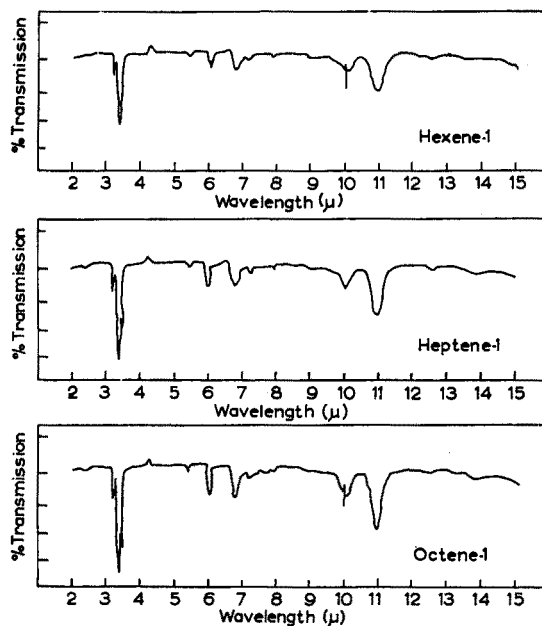


Fig. 4. Infrared spectra of resolved alkene blend.

of the major alkene components was trapped and the infrared spectrum recorded. The spectra are shown in Fig. 4. From these spectra it is easy to ascertain that each compound is an unsaturate; this is evidenced by the ethylenecarbon-hydrogen stretch at 3.25 μ and the C=C stretch at 6.1 μ . Furthermore, it is also evident that each compound has terminal unsaturation as evidenced by the fingerprint structure at 10.1 μ and 11 μ .

As another example, a blend consisting of *t*-butyl alcohol, *sec*-butyl alcohol, and *n*-butyl alcohol was prepared. Using 50- μl charges to the gas chromatograph, the

compounds were separated, trapped, and their spectra recorded. The gas chromatographic trace of the alcohol blend is shown in Fig. 5. The clarity of the spectra obtained (Fig. 6) should be pointed out with respect to the free OH stretching vibration at approximately 2.7μ and the normal alcohol fingerprint region ($8.0-9.5 \mu$) in which differentiation as to types can be very easily seen.

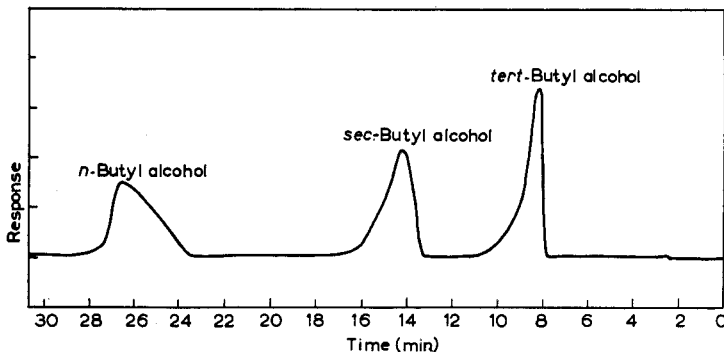


Fig. 5. Gas chromatography trace of alcohol blend.

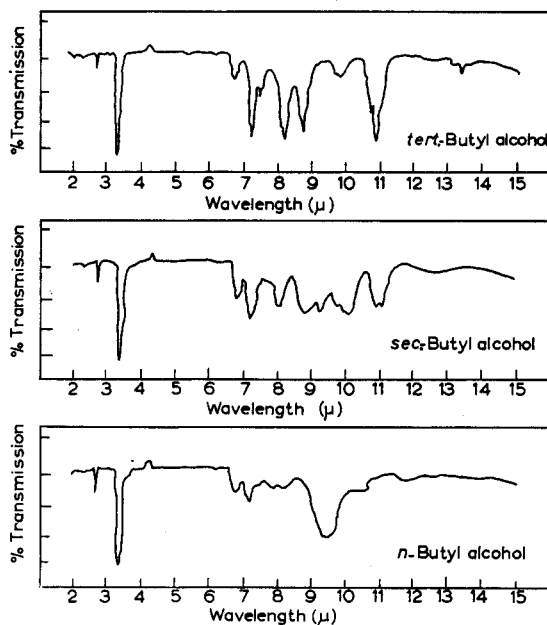


Fig. 6. Infrared spectra of resolved alcohol blend.

These data, in conjunction with the retention times, allow positive identification of the compounds. Once identity has been established, quantitative data may be calculated using the proper calibration curves and the peak area of the component.

The spectra obtained on these blends were run using $1/4$ scale expansion and automatic suppression. Time required per scan was approximately 4 min.

DISCUSSION

The basic data provided by this technique are retention time, infrared spectrum and peak area. The combination of retention time and the infrared spectrum usually suffices to identify the component. From proper calibration curves the peak area can be used to secure quantitative data. Thus, a complicated organic mixture can be analyzed qualitatively and quantitatively in a very short time.

Applications of this technique have been made in three areas to date. First, it has been used to analyze mixtures from exploratory organic reactions. Secondly, it was applied in producing pure compounds in order to obtain reference spectra. Thirdly, it has been used in determining composition in process streams in order to facilitate gas chromatographic calibration procedures. These applications are but a few of the many possible through the use of combination techniques.

ACKNOWLEDGEMENT

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SUMMARY

A technique combining gas chromatography with infrared spectrophotometry for analysis of complex organic mixtures has been described and modes of application discussed. The components are trapped and run as gases. Proper use of the data makes possible qualitative and quantitative analysis.

RÉSUMÉ

Une technique est proposée pour l'analyse de composés organiques, en combinant la chromatographie gazeuse et la spectrophotométrie infra-rouge.

ZUSAMMENFASSUNG

Beschreibung eines Verfahrens zur Analyse von Gemischen organischer Substanzen durch kombinierte Anwendung von Gaschromatographie und IR-Spektrophotometrie.

REFERENCES

- ¹ H. SZYMANSKI, *Anal. Chem.*, **31** (1959) 2110.
- ² W. DOERING AND R. G. BUTTERY, *J. Am. Chem. Soc.*, **78** (1956) 3224.
- ³ H. E. BELLIS AND E. J. SLOWINSKI JR., *J. Chem. Phys.*, **25** (1956) 794.
- ⁴ B. M. CRAIG, T. M. MALLARD AND L. L. HOFFMAN, *Anal. Chem.*, **31** (1959) 319.
- ⁵ J. V. WHITE, N. L. ALPERT, W. M. WARD AND W. S. GALLAWAY, *Anal. Chem.*, **31** (1959) 1267.
- ⁶ J. E. STEWART, R. O. BRACE, T. JOHNS AND W. F. ULRICH, *Nature*, **186** (1960) 628.
- ⁷ D. M. W. ANDERSON AND J. L. DUNCAN, *Chem. and Ind. (London)*, (1958) 1662.

THE ABSORPTIOMETRIC DETERMINATION OF PHOSPHORUS IN IRONS AND STEELS

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INTRODUCTION

Many procedures have been published for the absorptiometric determination of phosphorus in irons and steels, based mainly on reactions producing either molybdenum blue or vanadomolybdiphosphate for final colour measurement. Many of these procedures have been used in this laboratory, but the need was felt for a fuller understanding of the factors affecting reliability and accuracy. A literature search revealed many conflicting and widely different conditions, and it was decided to investigate the reactions to produce a reliable method for routine work. The vanadomolybdiphosphate reaction was chosen without a final solvent extraction procedure, since this would probably lead to a simpler final method even if subject to some limitation due to some alloying elements.

EXPERIMENTAL

Reagents and apparatus

All reagents were of "AnalaR" quality where possible. Optical density measurements were made on a Unicam SP. 600 spectrophotometer for the plotting of absorption spectra, and on a "Spekker" absorptiometer using a tungsten lamp and violet No. 601 filters for all subsequent work. This latter instrument was chosen because it was to be used for routine work.

Principle of method

The sample is dissolved in nitric acid and the phosphorus in solution is then oxidised to the reactive orthophosphate state. Addition of vanadate and molybdate then produces the vanadomolybdiphosphate complex, the optical density of which is related to phosphorus concentration.

Absorption spectra

For absorptiometric measurement of the final complex, several wavelengths have been recommended, mainly in the 400-480 m μ band. It was considered that for routine work, measurements in the ultra-violet region should be avoided, and since simple photo-electric absorptiometers are commonly used in metallurgical analysis, investigations were limited to the near ultra-violet and visible region. By using a combination of methods from the literature, the absorption spectra in Fig. 1 were plotted of iron,

reagents, and phosphorus complex. It was found that all absorptions increased rapidly towards the ultra-violet, but Beer's law was sensibly obeyed at wave-lengths between 385–430 $m\mu$. By using the violet No. 601 filters on the "Spekker" absorptiometer, virtually linear calibrations could be obtained.

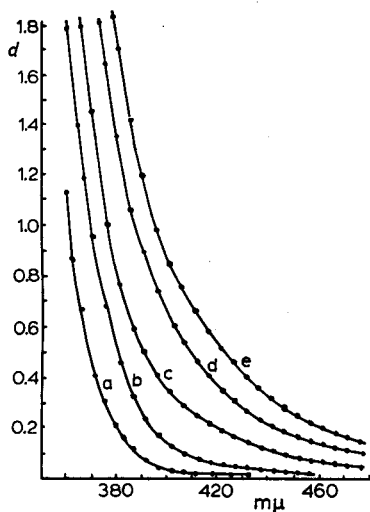


Fig. 1. Absorption spectra. (a) Reagents; (b) Reagents + 200 mg Fe/l; (c) Reagents + 200 mg Fe/l + 3 mg P/l; (d) Reagents + 200 mg Fe/l + 9 mg P/l; (e) Reagents + 200 mg Fe/l + 12 mg P/l.

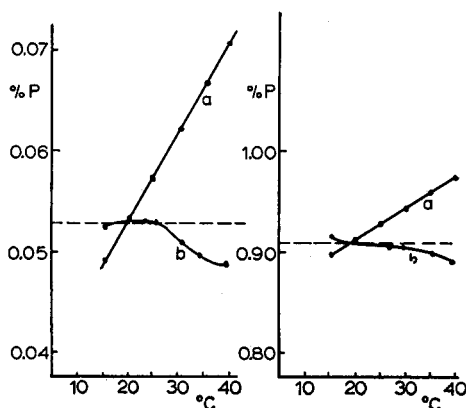


Fig. 2. Temperature compensation. (a) not compensated; (b) compensated.

Reaction conditions

The main factors governing the production of the vanadomolybdiphosphate are the acid, vanadate and molybdate concentrations, and their effects were investigated. Due to the large number of experiments required, a preliminary investigation was made in which acidity and molybdate concentration were varied between 1 and 1.75 *N* nitric acid and 15–62.5 *mM* molybdate. With these limits, the effects of variation in vanadate concentration were next investigated as described below. The optimum amount of vanadate required thus established was used in the subsequent investigation of the effects of acidity and molybdate concentration.

Vanadate concentration

Sodium vanadate has been proposed^{1,2} as reagent in place of the more usual ammonium vanadate because of its greater solubility. However, with the concentrations required for this work, solubility does not present a problem, and ammonium vanadate (available in "AnalaR" quality) was used throughout. Various concentrations of vanadate have been recommended^{3–7} e.g. 0.4–1.2, 1.7, 2–2.6, and 1–4 when expressed as *mM* vanadium(V) in the final test solution. In some cases the addition of too large an excess has led to the production of more intense final colours^{7–9}. This reaction is often carried out in hot or boiling solution, but times of heating are generally not

specified. For these experiments a boiling time of 3 min was used after vanadate addition, although as shown below, reaction in the cold is equally satisfactory.

Varying amounts of ammonium vanadate solution were added to solutions containing both low and high ratios of acid and molybdate. In the test solutions the concentration of phosphorus was 3 mg/l, the phosphorus being omitted from the blank solutions. For both blank and test solutions iron concentrations of 1.5 g and 5 g/l were used. Density readings were taken at timed intervals after the final molybdate addition to observe the rate of development of the final complex.

The total density due to iron, reagents and phosphorus complex increased as the vanadium concentration increased; an increase also occurred in the density of the blank. By using the blank for compensation the density due to the phosphorus complex increased rapidly as the vanadium concentration increased up to 2 mM, then between 2–4 mM vanadate the density was virtually constant. With low acid and molybdenum concentrations an excessively long time was required for full colour development, even with up to 4 mM vanadium(V). However, when the molybdate was increased, a rapid development could be obtained with low vanadium concentration, but the time required further increased as the vanadate increased. With high acid and molybdenum concentrations the most rapid colour development occurred within the range 2–4 mM vanadium(V). From the above results it is apparent that the final solution should contain 2–4 mM vanadium(V) for rapid colour development, constant colour intensity and independence from a relatively large variation in iron concentration. By adding 10 ml of 0.35% w/v ammonium vanadate solution for a final 100 ml volume of test solution, the optimum 3 mM concentration is obtained. This addition is not critical to within ± 2 ml.

In many procedures nitric acid is added to the vanadate reagent, although no specific reasons for this are given. Experiments showed that simple aqueous solutions gave identical results to those obtained using acidified solutions, and subsequent work was carried out using the unacidified reagent.

Acid and molybdate concentrations

Nitric acid is probably the most widely used dissolving acid for this determination, although sulphuric¹⁰, hydrochloric¹⁰ and perchloric^{7,10} acids have been used. For convenience in routine work on low alloy samples, nitric acid was chosen. Control of acidity is important, since too low a concentration may lead to the formation of precipitates^{11,12} or to the formation of yellow vanadomolybdate complexes^{3,10}. Too high an acidity may result in slow colour development^{1,4,5,9-12} and the production of paler⁸ or more intense^{1,11} colours, which are often not reproducible. There is a wide variation in recommended acidities from about 0.2 to about 1.6 *N*.

As molybdenum reagent, ammonium molybdate is generally used, with or without the addition of ammonium hydroxide. In preliminary experiments the addition of ammonium hydroxide produced no difference in results and consequently was omitted in later work. The molybdenum concentrations which have been recommended range from the equivalent of about 6 to about 57 mM molybdenum(VI). Experiments were carried out involving 24 combinations of acid and molybdate and both blank and test solutions were treated with each combination. Iron (0.3 g) was present in the solutions (to cover phosphorus ranges for cast iron) and the effect of an increase

to 0.5 g for steel analysis is described further below. In the test solutions the phosphorus concentration was 3 mg/l and to determine the rate of colour development, absorption readings were made at timed intervals after adding the molybdate.

For any given molybdenum concentration an increase in acidity produced a decrease in density of both the blank and test solutions. This effect of acidity was more pronounced the lower the molybdenum concentration.

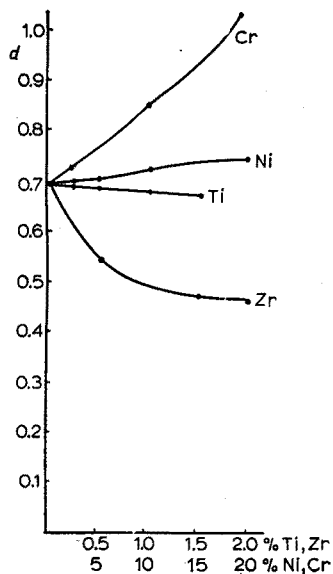


Fig. 3. Effects of Cr, Ni, Ti and Zr. 0.5 g Fe; 0.076% P; 4-cm cells.

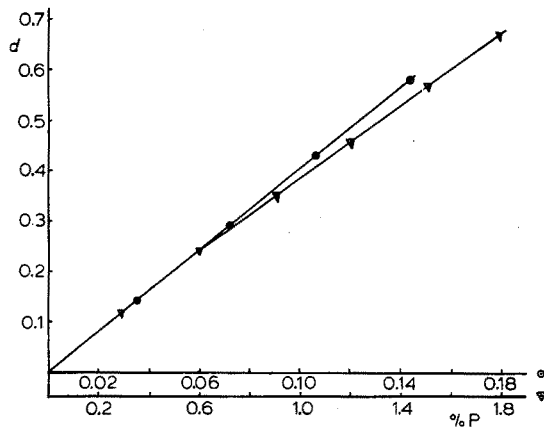


Fig. 4. Calibration curves. \circ 0.5-g sample, 4-cm cells; \triangle 0.3-g sample, 0.5-cm cells.

For any given acidity the blank and test densities increased as molybdate increased, this being more pronounced the higher the acidity. By compensating for the blank absorptions however, the effects of variations in the reagent concentrations upon the colour intensity of the vanadomolybdiphosphoric acid were largely minimised. Thus, the same colour intensity can be reproduced by selection of the correct amounts of acid and molybdate, and it was found that the required molar ratio of nitric acid to molybdate was 2-3 : 1. However, with 1.25 N nitric acid and 60 mM molybdate reproducible colours can be obtained which will tolerate quite an appreciable variation in reagent concentrations, *viz.* ± 0.5 N nitric acid and ± 10 mM molybdate. The rate of colour development was also dependent on the reagent concentrations. For any given acidity, the rate increased as the amount of added molybdate increased and maximum development rate occurred within the above-mentioned reagent ranges. Full colour was developed within 5 min of adding the molybdate reagent. It was thus decided to use final reagent concentrations in the test solution of 1.25 N nitric acid and 60 mM molybdate. This can be achieved by using 25 ml of nitric acid (s.g. 1.16) and 10 ml of 10.5% w/v ammonium molybdate per 100 ml of final test solution. A tolerance of ± 5 ml of acid and ± 2 ml of molybdate can be allowed.

Combined vanado-molybdate reagent

For routine work, a considerable saving in time would be achieved if the vanadate and molybdate reagents could be combined and if the total reaction could be carried out in the cold. Tests were made using separate and combined reagents, in the former case 3-min boiling being employed after the vanadate addition. When the combined reagent was used, it was added direct to the cold test solutions after the orthophosphate oxidation. In all cases no differences were observed in the rate of formation or in the colour intensity of the final complex. Calibration by both techniques yielded exactly the same relationship. No difference in results was obtained when a mixed reagent which had been stored for 2 months was used. As a result the combined reagent was formulated to contain 1.75 g of ammonium vanadate and 53 g of ammonium molybdate per l; 20 ml of this reagent is added to the cold test solution which is then diluted to 100 ml. A tolerance of ± 2 ml can be allowed on this addition.

Effect of iron concentration

From previous experiments it became apparent that for cast iron analysis 0.3-g samples with suitable cell widths would cover phosphorus contents to 2%. For steel analysis, using 4-cm cells, 0.5-g samples would be required, and the effect of this increase in iron concentration was investigated. Mixtures of 0.5 g of pure iron and 3 mg of phosphorus were processed using acidities of 0.75–2.0 *N* nitric acid in the final solution. Final concentrations of vanadate and molybdate were fixed at 3 *mM* and 50 *mM* respectively. The latter is less than the 60 *mM* optimum and was chosen so that any adverse effects due to the increased iron concentration would be more apparent.

As the iron concentration increased, the effect of variation in acidity became more pronounced on both blank and test solutions. When the blank was used for compensation, acidity control was slightly more critical in the presence of the higher iron concentration, but the degree of control required is well within routine tolerances. The rate of colour development was independent of the variation in iron content, and since the presence of 0.5 g of iron had no detrimental effect on the reaction conditions, this sample weight was chosen for steel analysis.

Oxidation of phosphate and combined carbon

After dissolution of irons and steels in nitric acid, most of the phosphorus is present as metaphosphate, and combined carbon is converted to a brown colloid which is probably a nitrated hydrocarbon. The colour of the latter varies with the conditions and shows pronounced absorption in the violet wave-band, hence gross errors will occur if it is not destroyed. The metaphosphate must be oxidised to reactive orthophosphate which process also serves to destroy the combined carbon colour. For nitric acid solutions, potassium permanganate is often used as oxidant, although ammonium persulphate has also been used. After oxidation, excess of permanganate can be reduced by sulphurous acid, hydrogen peroxide, or sodium nitrite; with persulphate, excess is destroyed by boiling.

The persulphate and the permanganate methods were investigated. With the former, a 15-min boiling time was used for oxidation and for destruction of excess oxidant; with the latter, 3-min boiling was used and excess was reduced with 20 vol. hydrogen peroxide. The peroxide excess was removed by a 3-min boil.

A sample of relatively high phosphorus content was used (B.C.S. No. 206/1; 1.38% P) to compare the results of both oxidants. Identical results were observed with between 0.05 and 2.0 g of permanganate, but with the persulphate, a minimum of 1 g was required for full oxidation.

Since permanganate is much more convenient to use and since a much smaller amount is required and conditions are less critical, it was decided to use this as oxidant.

To investigate oxidation of combined carbon a sample of relatively high combined carbon and low phosphorus content was used (B.C.S. No. 215; 0.94% C; 0.038% P), varying amounts of permanganate being used for oxidation. The same lower limit of 0.05 g proved to be sufficient, but the upper limit was reduced to 0.3 g; above this amount higher colour intensities were observed.

In view of these results, 0.1 g potassium permanganate "Analoids" were subsequently used, the time of boiling being fixed at 3 min, since times between 1 and 8 min gave identical results.

Effects of temperature

Temperature variation has been quoted as having little effect within the range 20°–30°, although in some cases the temperature effect has been found to be serious. HILL¹³ has reported that the effect becomes more serious as the iron concentration increases. BAGHURST AND NORMAN¹ have shown that with acidities between 0.8 and 1.2 *N* little variation of colour occurred with temperature change, whereas between 1.2 and 2.0 *N* the temperature effect increased rapidly. To investigate temperature effects on the final colour intensity, readings were made at various temperatures on processed solutions of pure iron, phosphate and iron plus phosphate. In all cases the amounts used corresponded to both low and high phosphorus contents. The relation between density and temperature was linear for all the solutions used. With the low iron, high phosphorus solutions, the iron had no effect on the rate of change of colour. With the higher iron content and cell width used for the low phosphorus solutions, a more pronounced effect was apparent in the presence of the iron.

By measuring blank and sample solutions at corresponding temperatures the temperature effect can be largely eliminated as shown in Fig. 2. Curves (a) were obtained when the blank solutions were measured at 20° and sample solutions at the variable temperature. Curves (b) were obtained when the blank and sample solutions were both measured at the indicated temperatures. Thus, provided that the blank and sample solutions are within $\pm 1^\circ$, measurements can be made within the range 15°–25° and relative errors will be within $\pm 1\%$ of the phosphorus content.

Development and stability

Experiments showed that the full colour of the vanadomolybdiphosphoric acid was developed within 5 min of adding the vanado-molybdate reagent. This colour was then stable for at least 24 h. This applied to samples of both low and high phosphorus contents.

Interfering elements

Graphitic carbon interferes owing to the additive absorption caused by the suspension of graphite in the solution. Appreciable amounts of silicon (about 4%) have been stated to interfere¹¹ owing to the possible formation of silicomolybdate, and

serious interference from arsenic has been reported^{8,14-17} owing to the formation of arsenic complexes. In previous methods^{8,15-17}, arsenic has been removed by volatilisation with brominated hydrochloric acid or with hydrobromic acid. Chromium(III) has been quoted as causing no interference¹⁸, whereas with chromium(VI), serious interference has been reported^{7,10,18}. Tungsten, if present, can be initially oxidised to tungstic oxide and then filtered off and under these conditions no interference has been reported^{14,18}. For routine control work, particularly on low alloy and non-alloyed samples, it was decided to use the straightforward method without solvent extraction. To investigate the effects of interfering elements, solutions of these were added to samples of B.C.S. carbon steel, and the resulting mixtures were processed. The results may be summarised as follows:

Graphitic carbon. When this was separated by filtration before the absorptiometric measurement, sorption of the vanadomolybdiphosphate occurred on the filter paper leading to low results. By filtering the initial acid solution of a sample through pre-wetted Whatman No. 4 filter paper and washing with hot water, accurate results were obtained.

Arsenic. Up to 1% arsenic showed no interference and thus the volatilisation procedure for its removal need not be applied.

Chromium. In this method chromium is present in the final solution in the trivalent state, and this showed serious positive interference above about 1% chromium (Fig. 3).

Zirconium. As seen in Fig. 3, this element seriously suppressed the reaction, but up to 0.05% can be tolerated.

Tungsten. This can be separated as tungstic oxide by acid oxidation followed by filtration. However, even when precautions were taken to avoid coprecipitation of phosphorus and incomplete separation of tungsten, serious interference was encountered. Thus, tungsten-bearing samples cannot be analysed by this method.

Copper, cobalt, nickel. These elements showed positive interference which is due to the additive absorptions of the ions of these elements.

Other elements. The remaining elements which showed no interference are: Mn (up to 10%); Al, Pb, Mo, Si (up to 5%); Mg (up to 2%); Ti (up to 1%); Ce, V (up to 0.5%). Amounts greater than these were not investigated since these limits were sufficient for the requirements of the method.

TABLE I
RESULTS OBTAINED ON STANDARDS

B.S.C. No.	Type	%P		%P found	
239/1	Steel	0.024	0.024	0.025	0.025
215	Steel	0.038	0.037	0.039	0.039
218	Steel	0.045	0.044	0.045	0.045
161/1	Steel	0.044	0.044	0.044	0.045
232	Steel	0.076	0.078	0.072	0.075
170	Hematite	0.026	0.027	0.028	0.028
	Iron				
236/1	Hematite	0.066	0.067	0.067	0.067
	Iron				
234/3	Cast Iron	0.33	0.32	0.34	0.34
171	Cast Iron	1.07	1.04	1.06	1.06
206/1	Cast Iron	1.38	1.36	1.38	1.36

Calibration

Calibration was carried out by addition of known amounts of standard sodium phosphate solution to pure iron. These mixtures were processed by the full procedure, and difference drum readings were plotted against the percentage of phosphorus. Typical calibration curves are shown in Fig. 4. It is seen that a slight deviation occurred from linearity, but the curves obtained were highly reproducible.

Accuracy

To test the accuracy of the method, replicate determinations were made, in random batches, on B.C.S. steels and cast irons, the results being shown in Table I. Subsequent checks on a variety of standards over several years of routine use have shown very good agreement with certified values.

RECOMMENDED PROCEDURE

As a result of the above investigations the following procedure is recommended.

Reagents

(a) Nitric acid. To 900 ml of water add 400 ml of concentrated nitric acid. Cool to about 20° and adjust this mixture to s.g. 1.160 (by hydrometer) by further addition of acid or water.

(b) Potassium permanganate. Analoids No, 4 C (0.1 g KMnO_4) can be conveniently used.

(c) Hydrogen peroxide. 20 vol. solution.

(d) Vanado-molybdate. Dissolve 1.75 g of ammonium vanadate in about 800 ml of hot water. Add 53 g of ammonium molybdate and stir this hot mixture until dissolved. Filter and dilute with water to 1 l.

Absorptiometer

With the Spekker Absorptiometer, the following settings etc. are used, Lamp: Tungsten. Filters: Violet, Ilford No. 601. Setting: Water to water 1.00. Cells: 0.5 cm for up to 2% P (with 0.3 g sample), 4 cm for up to 0.15% P (with 0.5-g sample).

Intermediate ranges can be covered by using other cell widths if desired.

Procedure

A blank determination with the appropriate weight of pure iron should be carried out, using the full procedure, each day of use.

Transfer 0.5 g of sample (P to 0.15%) or 0.3 g of sample (P to 2%) to a 200-ml conical beaker. Add 25 ml of the nitric acid, cover with a clock-glass and boil gently until the sample is dissolved, taking care to avoid excessive evaporation. Add about 30 ml of water and raise to the boil. At this stage filter off graphitic carbon, if present, through a pre-wetted Whatman No. 4 filter paper and wash with hot water. To the solution add 0.1 g of potassium permanganate (1 Analoid No. 4C) and boil for 2–3 min. Add hydrogen peroxide dropwise to the boiling solution until all excess of permanganate is reduced, then boil for 2–3 min to destroy excess peroxide. Cool, add 20 ml of vanado-molybdate, mix and transfer with water washes to a 100-ml graduated

flask, diluting with water. Transfer the solution to the appropriate cell and measure the colour reading on the absorptiometer. Subtract this from the blank and convert the resultant "difference" reading to % phosphorus by reference to the calibration chart.

Calibration

For the above ranges the following phosphate solutions may be used:

(a) Low range (0–0.15% P, 0.5-g sample, 4-cm cell). 0.4583 g of anhydrous disodium hydrogen phosphate per 1 l. 1 ml = 0.02% P on a 0.5-g sample. Transfer 0, 2, 4, 6, 8 ml to beakers containing 0.5 g of pure iron and treat as described in the above procedure.

(b) High range (0–2% P, 0.3-g sample, 0.5-cm cell). 2.7498 g of anhydrous disodium hydrogen phosphate per 1 l. 1 ml = 0.2% P on a 0.3-g sample. Transfer 0, 2, 4, 6, 8, 10 ml to beakers containing 0.3 g of pure iron and treat as described in the above procedure. Plot "difference" readings against % P to obtain the calibration curves.

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SUMMARY

A critical investigation has been made of the vanadomolybdiphosphate method for the absorptiometric determination of phosphorus in irons and steels. The reaction conditions have been standardised to produce a simple, rapid and reliable control method. The effects of interfering elements have also been studied.

RÉSUMÉ

Une étude critique a été effectuée sur le dosage absorptiométrique du phosphore, sous forme de vanadomolybdiphosphate, dans les fers et les aciers.

ZUSAMMENFASSUNG

Beschreibung einer kritischen Untersuchung über die absorptiometrische Bestimmung von Phosphor als Vanadomolybdiphosphat in Eisen und Stahl.

REFERENCES

- 1 H. C. BAGHURST AND V. J. NORMAN, *Anal. Chem.*, 27 (1955) 1070.
- 2 H. C. BAGHURST AND V. J. NORMAN, *Anal. Chem.*, 29 (1957) 778.
- 3 A. GEE AND V. R. DIETZ, *Anal. Chem.*, 25 (1953) 1320.
- 4 B. ANDERSON AND W. B. WRIGHT JR., *U.S. Atomic Energy Commission*, Y-900 (August 1952).
- 5 F. W. HAYWOOD AND A. A. R. WOOD, *Metallurgical Analysis by Means of the Spekker Photoelectric Absorptiometer*, Hilger and Watts, London, 1957, p. 192.
- 6 C. J. BARTON, *Anal. Chem.*, 20 (1948) 1068.
- 7 K. P. QUINLAN AND M. A. DE SESA, *Anal. Chem.*, 27 (1955) 1626.
- 8 T. S. HARRISON AND W. FISHER, *J. Soc. Chem. Ind. (London)*, 62 (1943) 219.
- 9 D. D. SNELL AND C. T. SNELL, *Colorimetric Methods of Analysis, Part 2, Inorganic*, Van Nostrand, New York, 1951, p. 672.
- 10 R. E. KITSON AND M. G. MELLOR, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 379.
- 11 W. M. MURRAY JR. AND S. E. Q. ASHLEY, *Ind. Eng. Chem., Anal. Ed.*, 10 (1938) 1.
- 12 H. H. WILLARD AND E. J. CENTER, *Ind. Eng. Chem., Anal. Ed.*, 13 (1941) 81.
- 13 U. T. HILL, *Anal. Chem.*, 19 (1947) 319.
- 14 T. S. HARRISON, *Analyst*, 70 (1945) 362.
- 15 G. BOGATZKI, *Arch. Eisenhüttenw.*, 12 (1938) 539.
- 16 V. D. KONKIN, *Zavodskaya Lab.*, 8 (1939) 322.
- 17 M. G. MELLON, *Am. Soc. Testing Materials, Proc.*, 44 (1944) 772.
- 18 W. T. ELWELL AND H. N. WILSON, *Analyst*, 81 (1956) 136.

OXIMIDOBENZOTETRONIC ACID

A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF IRON(II)

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WENGER AND DUCKERT¹ have made a critical study of various organic reagents recommended for the colorimetric determination of iron. In the past few years, a large number of compounds have been suggested for the colorimetric and spectrophotometric determination of iron. Some of these are: 4-hydroxybiphenyl-3-carboxylic acid², ethyl α -isonitrosoacetoacetate³, nitroso R-salt⁴, 5,6-benzoquinolinaldic acid⁵, α -picolinic acid and quinaldic acid^{6,7}, *m*-methoxy-*o*-nitrosophenol⁸, iodoxine⁹, 4,7-dihydroxy-1,10-phenanthroline¹⁰, 2-fluorobenzoic acid¹¹, 2-acetyl-pyridine oxime¹², 4,7-diphenyl-1,10-phenanthroline¹³, 3-hydroxy-2-naphthoic acid¹⁴, quinolinic acid¹⁵, picolinedioxime¹⁶ and *o*-dianisidine¹⁷. But all these reagents suffer from the disadvantage that a strict pH control is necessary, and in many cases organic solvents are needed either to keep the complex in solution or to extract the coloured complex; also in many cases foreign ions interfere in the colorimetric determination. SANDELL¹⁸ has described and recommended various reagents for the colorimetric determination of iron. *o*-Phenanthroline¹⁸ is good, but has certain disadvantages: silver and bismuth give precipitates with the reagent, and the method cannot give accurate results when large amounts of metal ions like zinc, tungstate, nickel, cobalt and tin are present with iron. Although the thiocyanate method¹⁹ is extensively used, the method suffers from the following drawbacks: a large excess of the reagent is necessary for complete colour development, the method can be used only within a narrow pH range, fluoride, phosphate, oxalate, vanadate, molybdenum and tungsten interfere and the colour fades rapidly with time.

During the course of our studies of certain derivatives of benzotetronic acid as analytical reagents²⁰⁻²², it has been observed that oximidobenzotetronic acid (or α -isonitrosobenzotetronic acid) can be successfully employed for the spectrophotometric determination of iron(II). ANSCHÜTZ²³ first prepared this compound and after analysis of its silver salt gave $C_9H_4O_4NAg$ as the molecular formula for the salt. This author also reported the formation of a blue colour when an aqueous suspension or alcoholic solution of the reagent was treated with an aqueous solution of iron chloride. We have now observed that when a freshly prepared alcoholic solution of this reagent is treated with an aqueous solution of iron(II), a deep blue water-soluble complex is instantaneously produced. Although a similar reaction is seen with iron(III), we have studied only the former reaction, as it is more sensitive and the colour development is instantaneous. The iron(II)-complex is quite stable

and the intensity of the colour remains unchanged between the wide pH range of 2.5 and 10.0. The complex obeys Lambert-Beer's law between the concentration range of 0.54–5.4 p.p.m. of iron and the optical density is unaffected within the temperature range of 10–50°. The reagent is quite selective for iron; only cobalt, nickel, cerium(IV) and zirconium give coloured complexes but they interfere only when present in quantities more than fifty times that of iron.

EXPERIMENTAL

Preparation of oximidobenzotetronic acid

4-Hydroxycoumarin, an easily available substance was prepared by the method of STAHPAN *et al.*²⁴, and was readily converted into oximidobenzotetronic acid by the action of nitrous acid as described by ANSCHÜTZ²³. The strength of the solution of oximidobenzotetronic acid in alcohol employed was $1.0 \cdot 10^{-3} M$.

Reagents

Ferrous ammonium sulphate (*pro analysi*) was used. Hydroxylamine hydrochloride was used as the reducing agent to ensure that all iron was in the divalent state. All other reagents were of B.D.H. (A.R.) or Merck *pro analysi* quality.

Apparatus and instruments

A Hilger U.V. Spectrophotometer was employed for the absorption spectrum of oximidobenzotetronic acid. All other spectrophotometric measurements in the wavelength range of 370 $m\mu$ –750 $m\mu$ were made with the Unicam Spectrophotometer Model SP 600; 1-cm absorption cells were used.

All pH measurements were made with the help of a Beckmann pH Meter Model H 2.

Absorption spectra

The absorption spectrum of oximidobenzotetronic acid was ascertained in the ultraviolet as well as in the visible region. Maximum absorption was observed at

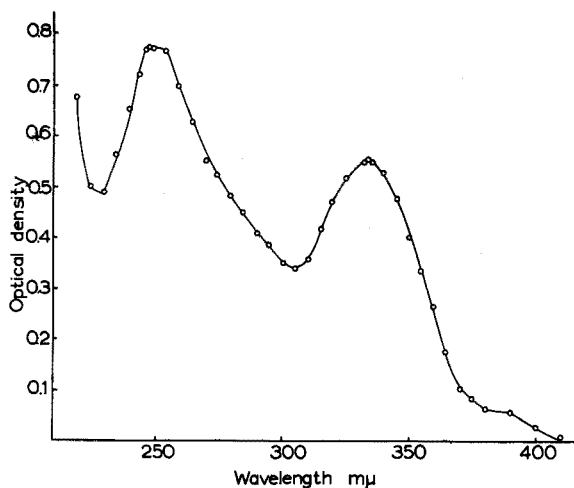


Fig. 1. U.V. spectrum of oximidobenzotetronic acid.

249 $m\mu$ and 334 $m\mu$, the former being more pronounced than the latter (Fig. 1), and no absorption maximum was observed in the visible region. The absorption spectra of the iron(II)-oximidobenzotetronic acid complex was determined at various pH values between 2.0 and 10.0, pH adjustments being made with dilute solutions of hydrochloric acid and sodium hydroxide. The complex exhibited maximum absorption at 625 $m\mu$ in every case (Fig. 2), which indicated that only one type of complex was produced under these conditions of pH. The complex after partial extraction with chloroform exhibited the same absorption maximum. A 50% (v/v) ethanolic solution of the complex also had the absorption maximum at 625 $m\mu$; the absorption due to the reagent

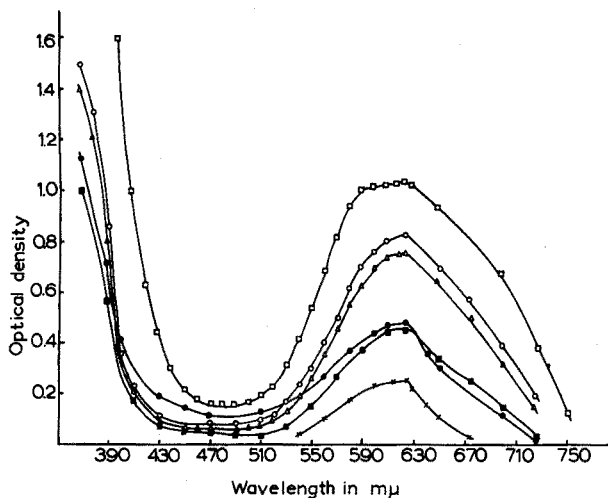


Fig. 2. Absorption spectrum of iron(II)-oximidobenzotetronic acid complex. $\lambda_{\max} = 625 m\mu$
 ● at pH 10.0; ■ at pH 8.0 and 6.0; ○ at pH 4.0; △ at pH 2.0; □ in chloroform; × in 50% (v/v) ethanol.

at this wavelength was found to be negligible. The wavelength 625 $m\mu$ was, therefore, chosen in the subsequent investigations.

Minimum amount of oximidobenzotetronic acid necessary for the determination of iron (II)

The optical densities at 625 $m\mu$ of a series of solutions containing oximidobenzotetronic acid and iron(II) in the molar ratio of 0.5 : 1 to 9 : 1 were determined. A plot of the results showed that maximum density was reached at the molar ratio of 4 and remained constant thereafter. For the determination of iron, however, the molar ratio of the reagent to iron was maintained at 10 in the subsequent studies.

Effect of pH on the optical density of iron(II)-oximidobenzotetronic acid complex

The stock solution of the complex was $6.6 \cdot 10^{-5} M$ with respect to iron; 10 ml of this solution was taken in a 25-ml measuring flask and the volume made up to the mark using dilute solutions of hydrochloric acid and sodium hydroxide to bring the resultant solution to a pH value within the range of 2.5–10. It was found that the

absorption of the complex is at a maximum and remains unchanged over this wide pH range. The pH of each of the solutions was determined using a suitable glass electrode.

Stability of the colour of the complex

The colour of the complex was found to be stable and no change in the optical density could be observed even after keeping the complex for 36 h. The effect of temperature on the optical density of the complex was also studied using a thermostat for temperatures above 25° and a refrigerator for lower temperatures. No change in the optical density of the complex was observed between 10° and 50°. The colour of the complex is, however, destroyed on continuous heating at 100°.

The complex was found to obey Lambert-Beer's law in the concentration range of 0.54–5.4 p.p.m. of iron and in the pH range of 2.5 and 10.0.

TABLE I
INTERFERENCES

<i>Ion</i>	<i>Taken as</i>	<i>p.p.m. tolerated</i>	<i>Ion</i>	<i>Taken as</i>	<i>p.p.m. tolerated</i>
Acetate	Ammonium salt	600	Cobalt	Sulphate	400
Bromide	Potassium salt	1500	Copper	Sulphate	720
Borate	Sodium salt	600	Lanthanum	Nitrate	13200
Chloride	Sodium salt	2000	Lead	Nitrate	200
Citrate	Sodium salt	800	Manganese	Sulphate	400
Fluoride	Sodium salt	400	Mercury(II)	Chloride	1200
Iodide	Potassium salt	800	Molybdenum	Ammonium molybdate	920
Oxalate	Potassium tetroxalate	400	Nickel	Sulphate	200
Phosphate	Sodium hydrogen salt	720	Silver	Nitrate	1440
Salicylate	Sodium salt	500	Thorium	Nitrate	400
Tartrate	Sodium salt	600	Titanium	Pot. titanyl oxalate	200
Thiocyanate	Potassium salt	1500	Wolfram	Sodium tungstate	1200
Aluminium	Sulphate	200	Uranium(VI)	Uranyl nitrate	300
Beryllium	Nitrate	400	Yttrium	Nitrate	3600
Cadmium	Chloride	1020	Zirconium	Oxychloride	120
Cerium(III)	Nitrate	400	Zinc	Sulphate	1110
Cerium(IV)	Ammonium nitrate	100			
Chromium	Sulphate	160			

Interference due to foreign ions

The stock solution of the complex was $1 \cdot 10^{-4} M$ with respect to iron, and the mole ratio of the reagent to iron was 10. 10 ml of this solution was transferred to a 25-ml standard flask and mixed with a known amount of a solution of a foreign salt, and the volume was made up to 25 ml with water. The optical density was determined within 10 min of mixing. The concentration of the foreign salt in the complex solution was progressively increased till the optical density changed by 2% from the theoretical values. The concentrations of the ions tested which caused no interference are given in Table I.

No interference was caused by tin(II) or sulphite. Hydroquinone was used as the reducing agent when the interference of silver was studied.

Recommended procedure

The given iron(II) solution at pH 2.5–10.0 containing 0.54–5.4 p.p.m. of iron is treated with a fresh solution containing a ten-fold amount of the reagent in the minimum amount of alcohol within the temperature range 10–50°. The optical density at 625 m μ of the ferrous complex so produced is measured and the concentration of iron deduced from a standard calibration curve obtained under similar conditions.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. T. R. SESHADRI, F.R.S., Head of the Chemistry Department, for his kind interest and helpful discussions, and to the Department of Atomic Energy, Govt. of India, for financial assistance.

SUMMARY

Oximidobenzotetronic acid is proposed for the spectrophotometric estimation of iron. A freshly prepared alcoholic solution of the reagent produces a deep blue water-soluble complex with an aqueous solution of iron(II). The complex is stable and its optical density is constant at pH 2.5–10. Lambert-Beer's law is followed from 0.54–5.4 p.p.m. of iron at 625 m μ ; temperature has no effect between 10° and 50°. The reagent is highly selective for iron.

RÉSUMÉ

Un nouveau réactif, l'acide oximidobenzotétronique, est proposé pour le dosage spectrophotométrique du fer(II). Ce réactif est très sélectif et donne un complexe bleu très stable.

ZUSAMMENFASSUNG

Zur spektrophotometrischen Bestimmung von Fe-(II) wird Oximidobenzotetrone Säure als Reagenz vorgeschlagen, das mit Fe-(II) einen stabilen, blau gefärbten Komplex bildet.

REFERENCES

- 1 P. WENGER AND R. DUCKERT, *Helv. Chim. Acta*, 27 (1944) 757.
- 2 J. H. YOE AND A. E. HARVEY, *J. Am. Chem. Soc.*, 70 (1948) 648.
- 3 A. BOUCHERLE, *Ann. pharm. franç.*, 11 (7-8) (1953) 540.
- 4 J. A. DEAN AND HAROLD LADY JR., *Anal. Chem.*, 25 (1953) 947.
- 5 A. K. MAJUMDAR AND B. SEN, *Anal. Chim. Acta*, 9 (1953) 529.
- 6 A. K. MAJUMDAR AND B. SEN, *Anal. Chim. Acta*, 9 (1953) 536.
- 7 K. SHINRA, Y. YOSHIKAWA, T. KATO AND Y. NOMIZO, *J. Chem. Soc. Japan*, 75 (1954) 44.
- 8 TETSUYA TORII, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 76 (1955) 333.
- 9 A. K. MUKHERJEE AND B. BANERJEE, *Naturwiss.*, 42 (1955) 416.
- 10 A. A. SCHILT, G. F. SMITH AND A. HEIMBUCH, *Anal. Chem.*, 28 (1956) 809.
- 11 E. B. BUCHANAN JR. AND W. WAGNER, *Anal. Chem.*, 29 (1957) 745.
- 12 K. K. TRIPATHI AND D. BANERJEE, *Sci. and Culture (Calcutta)*, 23 (1958) 611.
- 13 H. DIEHL AND E. B. BUCHANAN JR., *Talanta*, 1 (1958) 76.
- 14 A. K. MAJUMDAR AND C. P. SAVARIAR, *Anal. Chim. Acta*, 21 (1959) 47.
- 15 A. K. MAJUMDAR AND S. P. BAG, *Anal. Chim. Acta*, 21 (1959) 324.
- 16 H. HARTKAMP, *Z. anal. Chem.*, 170 (1959) 399.
- 17 C. VASSILIADIS AND G. MANOUSSAKIS, *Bull. soc. chim. France*, 2 (1960) 390.
- 18 E. B. SANDELL, *Colorimetric Determination of Traces of Metals*, 2nd Ed., Interscience, New York, 1950, p. 364.
- 19 F. D. SNELL AND C. T. SNELL, *Colorimetric Methods of Analysis*, Vol. II, 3rd Ed., Van Nostrand, New York, 1954, p. 307.
- 20 A. N. BHAT AND B. D. JAIN, *Talanta*, 4 (1960) 13.
- 21 A. N. BHAT AND B. D. JAIN, *Talanta*, 5 (1960) 271.
- 22 A. N. BHAT AND B. D. JAIN, *Proc. Indian Acad. Sci.*, 53A (1961) 147.
- 23 R. ANSCHÜTZ, *Ann. Chem., Liebigs*, 367 (1909) 169.
- 24 M. A. STAHPMAN, I. WOLFF AND K. P. LINK, *J. Am. Chem. Soc.*, 65 (1943) 2285.

SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC
DETERMINATION OF METALS WITH
1-(2-PYRIDYLAZO)-2-NAPHTHOL

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INTRODUCTION

Although dithizone and oxine have been widely accepted as important chromogenic agents for metals, many other heavy metal ions interfere in determinations with these reagents. The aim of this investigation was to develop rapid direct and sensitive methods with 1-(2-pyridylazo)-2-naphthol¹⁻³ in which possible interferences would be minimized or eliminated.

The determination of cadmium at the low concentration which may be of nuclear chemical significance requires a highly sensitive and selective method. The dithizone method⁴ has the requisite sensitivity; however, nearly a score of other metals react with dithizone to produce intense colours, most of which resemble that of cadmium. The growing importance of yttrium in the fields of metallurgy and nuclear chemistry has necessitated the development of a method for the rapid determination of yttrium. A sensitive colorimetric method for the determination of yttrium with arsenazo⁵ has been described. But, in this method many heavy metals, alkali metals and rare earth interfere. Recently, a pyrocatechol violet method⁶ has been reported, but, as in the case of arsenazo, it is not particularly selective. Although several colorimetric methods have been described for the determination of manganese (especially the permanganate method) and mercury, the colour reactions are not very sensitive or selective. In the establishment of methods for the separation and the spectrophotometric determination of metals by solvent extraction as 1-(2-pyridylazo)-2-naphtholates, procedures have already been proposed for uranium⁷⁻⁹, indium¹⁰, and for the simultaneous determination of indium and iron¹⁰. In a previous paper³, the author has indicated that cadmium, manganese, mercury, gallium, iron, and yttrium react with 1-(2-pyridylazo)-2-naphthol (PAN) to form stable chelates. Recently, HNILÍŤKOVÁ AND SOMMER¹¹ reported that the sensitivity of reaction with metals of PAN analogues decreased as follows. PAN > PAR (4-(2-pyridylazo)-resorcinol) > Pyridine-2-azo-1-dihydroxynaphthalene-2,3-sulfonic acid-6 > PAO (4-(2-pyridylazo)-orcinol) > Pyridine-2-azo-2-chromotropic acid > Pyridine-2-azo-2-amino-1-hydroxy-8-naphthalene-3,6-disulfonic acid, hence the present study was confined to PAN. The reaction with PAN is extremely sensitive and quite selective so that many commonly associated ions do not interfere and the reaction can be applied to the solvent extraction and spectrophotometric determination of these metals.

From dilute acid or alkaline solutions of the above metals a red or dull red precipi-

tate is obtained when a methanolic solution of PAN is added; this precipitate is readily extracted by a suitable organic solvent to give red or dull red colour. PAN chelates are sensitive to changes in hydrogen ion and the reagent is therefore comparatively selective in its action. In the present paper, the detailed conditions for the spectrophotometric determinations of these metals by solvent extraction are described. The various recommendations are summarized in Table I.

The method has been applied to (1) determination of iron in clay and anorthosite, (2) separation of manganese from nickel, and (3) separation of yttrium from lanthanum and cerium.

TABLE I
DATA ON THE ANALYTICAL WORK

Metal	Colour of chelate	pH conditions solvent	Wave length (m μ)	Range of detn. (p.p.m.)
Mn ⁺²	wine red	9 ~ 10 ether	560	0 ~ 1
Cd ⁺²	red	8.7 ~ 10 chloroform	555	~ 2.5
Hg ⁺²	red	6 ~ 7.5 chloroform	560	~ 2
Ga ⁺³	red	3.6 ~ 5 chloroform	560	~ 3
		aqueous soln.	515, 530	~ 5
Fe ⁺³	dull red	4 ~ 8 benzene	775	~ 4
Y ⁺³	red	8.5 ~ 11 ether*	560	~ 1

* In a previous article³, Table I on p. 368, column 5, line 15, yellow should read red.

EXPERIMENTAL

Apparatus

All measurements were made with a Model EPV-2 Hitachi spectrophotometer, with 1-cm cells. A Horiba M-3 type pH meter was used.

Standard solution of metals

Cadmium: This solution was prepared by dissolving 0.5903 g of pure metal (99.9%) in nitric acid and diluting to 500 ml with redistilled water.

Gallium: This solution was prepared by dissolving 0.500 g of pure metal (Yokozawa Chem. Co., 99.99%) in hydrochloric acid and diluting to 500 ml with redistilled water.

Manganese: This solution was prepared by dissolving pure manganese sulfate in redistilled water.

Mercury: A solution was prepared containing 1.00 mg of mercury per ml by dissolving pure mercuric nitrate in redistilled water.

Iron: This solution was prepared by dissolving 0.517 g of electrolytic iron in 10 ml of concentrated nitric acid and diluting to 500 ml with redistilled water.

Yttrium: A solution was prepared by dissolving 0.200 g of pure yttrium nitrate hexahydrate (British Drug Houses Ltd.) in 200 ml of slightly acidic solution.

Gallium, cadmium and yttrium solutions were standardized gravimetrically as oxinate, and the manganese solution was standardized gravimetrically as Mn₃O₄.

Other reagents

1-(2-Pyridylazo)-2-naphthol(PAN) solution: A 0.1% solution was prepared by dissolving 100 mg of PAN (Tokyo Kasei Chem. Co.) in pure methanol, filtering through

glass wool, and diluting to 100 ml with methanol. This solution is stable for several weeks if stored in an amber bottle.

Buffer solution: Sodium acetate-acetic acid and ammonium chloride-ammonia mixed solutions were used for the pH adjustment.

0.2 N KCN, 0.2 N NaF, 10% sodium citrate, and 0.1 N EDTA (disodium salt) solutions were used. Organic solvents were purified by the normal methods.

All other reagents used in this work were made from analytical grade chemicals or from purified materials and all solutions were prepared with redistilled water.

General procedure

Transfer an aliquot of the slightly acid solution containing appropriate amounts of the required metals to a separatory funnel, and dilute to approximately 20 ml. Add 1 ml of 0.1% PAN solution and 5 ml of the buffer solution and allow to stand for several minutes. Then add exactly 10.0 ml of organic solvent to the mixture and shake vigorously for 1-2 min. Centrifuge the extract or aqueous phase and measure the absorbance at a definite wavelength against a reagent blank or water (see Table I for the correct conditions for each metal).

Solvent for extraction

The complex of manganese was most efficiently extracted with ether or chloroform, the iron complex with benzene or chloroform, the yttrium complex with ether, the gallium complex with chloroform, the cadmium complex with chloroform, ether, benzene or carbon tetrachloride, and the mercury complex with chloroform or benzene.

Absorption spectra

The absorption spectra of the chelates formed with cadmium, manganese, gallium, yttrium, iron, and mercury are shown in Figs. 1-6 respectively. The maximum absorption of the yttrium chelate in ether appears at 530 and 560 $m\mu$. The absorption maxima of the manganese chelate in ether and of gallium and cadmium in chloroform

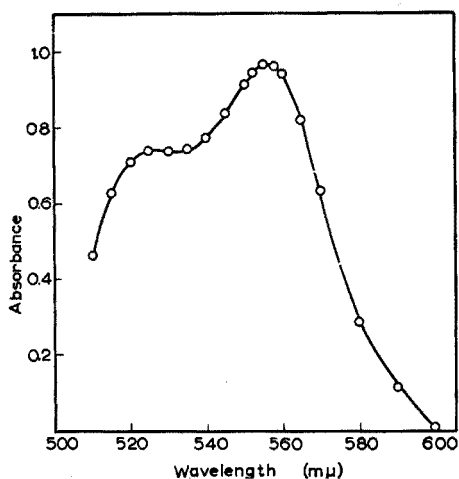


Fig. 1. Absorption spectra of cadmium-PAN chelate in chloroform, 2.3 μg Cd/ml.

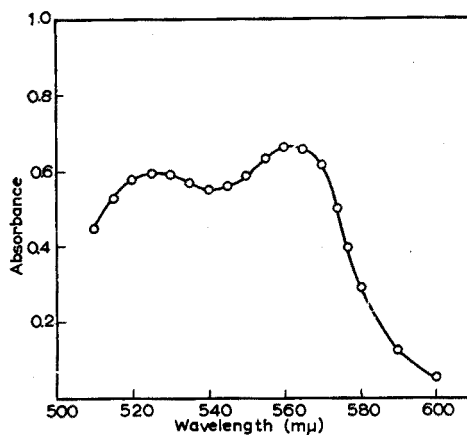


Fig. 2. Absorption spectra of manganese-PAN chelate in ether. 6.3 μg /10 ml manganese.

appear at 560, 555, and 560 $m\mu$ respectively. In benzene solution the iron chelate has an absorption maximum at 775 $m\mu$. Although gallium chelate cannot be extracted by ether, the excess of reagent can be easily extracted into the organic layer, the gallium chelate remaining in the aqueous layer as a true solution. In this aqueous solution the gallium chelate has absorbance maxima at 515 and 530 $m\mu$.

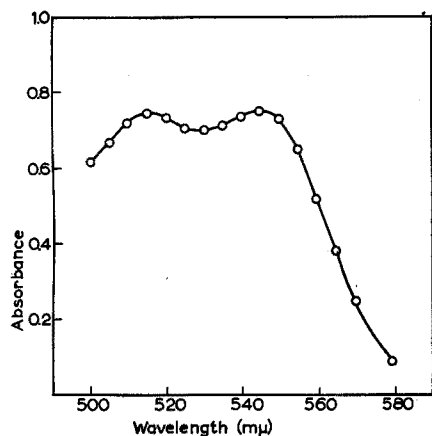


Fig. 3. Absorption spectra of gallium-PAN chelate in aqueous solution, against water.

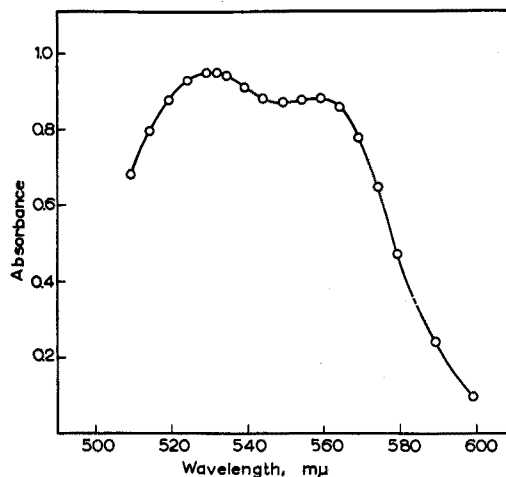


Fig. 4. Absorption spectra of yttrium-PAN chelate in ether extract.

Effect of pH

A series of solutions containing definite amounts of the required metal and 1 ml of 0.1% PAN solution was prepared. Sodium acetate-acetic acid and ammonium chloride-ammonia were used for the pH adjustment.

The results obtained show that the optimum pH range of manganese, cadmium,

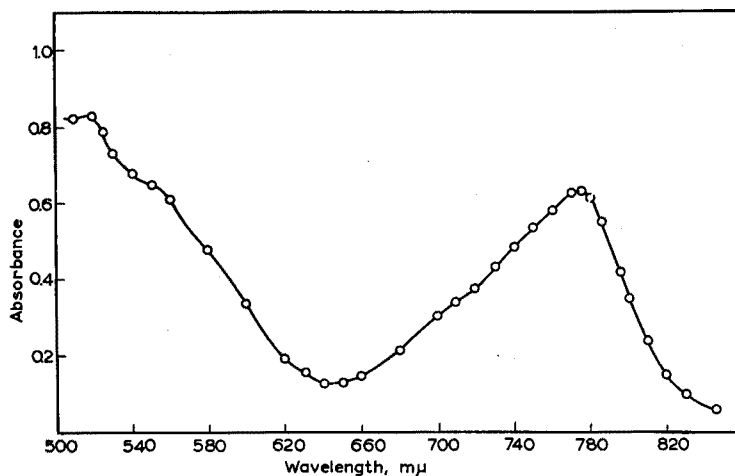


Fig. 5. Absorption spectra of iron-PAN chelate in benzene. 2.1 μg Fe/ml, against reagent.

mercury, gallium, iron, and yttrium were from 5 to 9, from 8.7 to 10, from 6 to 7.5, from 3.6 to 5, from 4 to 8, and from 8.5 to 11 respectively. At higher pH (above 7) no significant complex between gallium and PAN was formed. Above pH 11, the complexes of manganese and cadmium could not be extracted completely by chloroform, and below pH 7, no significant complexes of manganese, yttrium and cadmium were formed. Also, below pH 3 and above pH 10, the iron chelate could not be extracted completely with benzene.

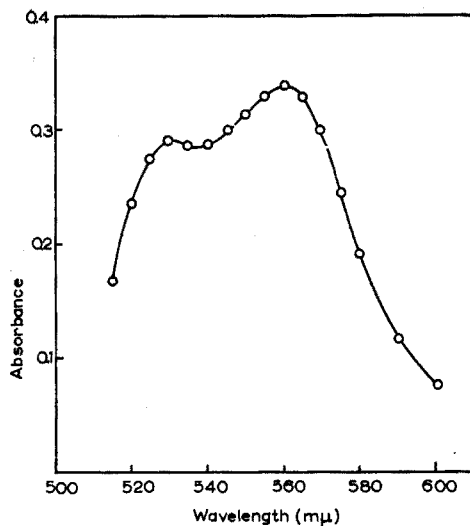


Fig. 6. Absorption spectra of mercury-PAN chelate in chloroform. 1.6 $\mu\text{g/ml}$ Hg.

Beer's law

The absorbances of the metal chelates in organic solvents or aqueous solution were found to be linearly related to the concentration of metals. The results show that the manganese, cadmium, mercury, gallium, iron, and yttrium complexes followed Beer's law, at least in the range up to 10 μg , 50 μg , 20 μg , 30 μg , 50 μg , and 10 μg resp.

Effect of reagent concentration

The PAN concentration was varied from 0.2 to 1 ml, keeping other variables constant (Table II). 1 ml of 0.1% PAN solution suffices to complex 10 μg of manganese, 25 μg of cadmium, 15 μg of mercury, 30 μg of gallium, 40 μg of iron and 10 μg of yttrium. With higher concentrations the absorbance is essentially constant.

TABLE II
EFFECT OF CONCENTRATION OF PAN

0.1% PAN soln. added ml	Mn abs. at 560 $m\mu$	Cd abs. at 555 $m\mu$	Fe abs. at 775 $m\mu$	Ga abs. at 560 $m\mu$	Y abs. at 560 $m\mu$
0.2	0.592	0.400	0.350	0.473	0.821
0.4	0.620	0.730	0.610	0.805	0.820
0.6	0.690	0.940	0.628	1.130	0.820
0.8	0.680	0.950	0.628	1.142	0.822
1.0	0.690	0.950	0.628	1.140	0.822

Time of standing and colour stability

The time required for the complete colour development of PAN with manganese, cadmium, mercury, gallium, iron, and yttrium were 5, 5, 10, 30, 5, and 2 min resp. (Table III).

TABLE III
TIME OF STANDING

<i>Time min</i>	<i>Mn abs. at 560 mμ</i>	<i>Cd abs. at 555 mμ</i>	<i>Fe abs. at 775 mμ</i>	<i>Ga abs. at 560 mμ</i>	<i>Y abs. at 560 mμ</i>
2	0.700	1.04	—	0.615	0.780
5	0.695	1.06	0.940	0.795	0.780
10	—	1.07	0.940	0.785	0.785
15	0.695	1.07	—	1.087	0.800
30	0.696	1.08	0.942	1.140	0.775
60	0.698	1.07	0.950	1.140	0.780

TABLE IV
COLOUR STABILITY OF YTTRIUM CHELATE IN ETHER

<i>Time min</i>	<i>Absorbance at 560 mμ</i>
5	0.820
10	0.818
15	0.785
30	0.758
60	0.724

After this time, the colour of the extract was very stable, except in the case of yttrium, and suitable for quantitative work. Although the colour of the ether extract of the yttrium chelate was not very stable when compared with those of other metals its stability was sufficient for spectrophotometric determination. The results obtained are given in Table V.

Composition of the coloured complex

The empirical formula of the coloured complexes of the metals was determined by adopting the continuous variation and the mole ratio methods. The results obtained are given in Table V.

TABLE V
COMPOSITION OF THE COLOURED COMPLEX

[MePy ₂ *] ⁰	Mn ⁺² , Cd ⁺² , Ni ⁺² (UO ₂ ⁺²)
[MePy ₂] ⁺	Fe ⁺³ , Y ⁺³ , (In ⁺³ , Co ⁺³) ^a
[MePy] ⁺²	Ga ⁺³ , (Tl ⁺³) ^b
[MePy] ⁰	(VO ₂ ⁺) ^c
[MePy] ⁺	(Pd ⁺² , Cu ⁺²) ^d

^a see ref. 12

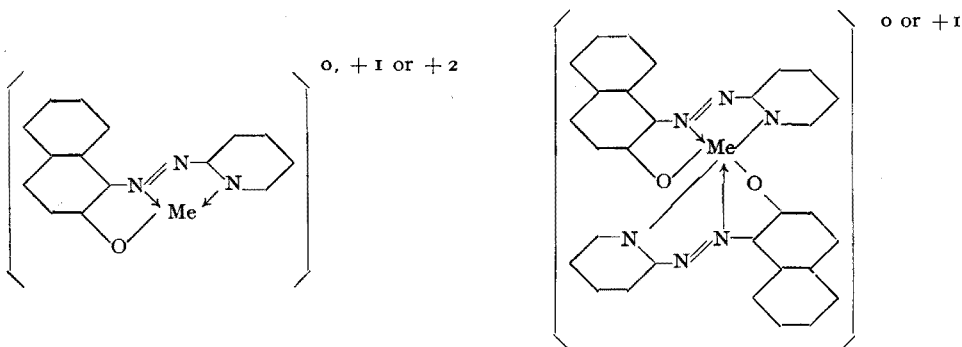
^b see ref. 13

^c see refs. 14, 15

^d see refs. 16-19

* Py ~ basic form of PAN

Metals presumably form a complex similar to the structure below:



Interfering ions

To study the effect of various metals on this determination of these metals, a series of solutions containing the metal concerned and the other metals was treated according to the procedure. The results obtained are given in Table VI.

Chloride, bromide, sulfate, nitrate, and acetate as their sodium, potassium, or ammonium salts did not interfere. The strong interference of iron can be avoided by means of a simultaneous determination or masking with citrate. Interferences of several other metals could be removed by the use of suitable masking agents or by back-extraction.

Back-extraction

The selectivity of extraction and determination of metals could be increased by back-washing or back-extraction. Table VII shows the possibility of the back-extraction of some metal-PAN chelates from the organic layer.

Effect of complexing agents

Citrate, cyanide, fluoride, and EDTA were examined as sequestering agents for the masking of various metals.

In Table VIII, the effects of these masking agents on the chelate formation are given and, in Table IX, the effects of cyanide and citrate on the determination of manganese are given. PAN forms many insoluble chelates, but in the presence of EDTA, only uranium precipitated. Interference from cadmium, mercury, iron, nickel, zinc, cobalt, gallium, and bismuth can be obviated by masking with potassium cyanide. The complexing of metals with cyanide, followed by the selective demasking of zinc and cadmium cyanide complexes with formalin has been used for the determination of these metals with PAN in the presence of nickel²⁰.

APPLICATIONS

I. Determination of iron in clay and anorthosite. In order to test the reliability of the proposed procedure, the determination of iron in clay and anorthosite was carried out. The method should also be useful for the determination of very small amounts of iron in a wide variety of samples.

0.500 g of sample powder was weighed into a platinum crucible, dissolved in the

TABLE VI
 EFFECT OF FOREIGN IONS

Ion added	Amount added μg	Added as	Found*					
			Cd	Mn	Fe	Ga	Y	Hg
Al ⁺³	10000	Al(NO ₃) ₃	20.5	—	—	—	—	—
	5000		20.0	—	20.0	46.3	—	—
	2500		20.0	—	—	—	—	—
	1000		20.0	5.0	—	—	7.1	—
	500		—	—	—	—	7.5	9.2
Be ⁺²	400	BeCl ₂	—	—	—	46.0	7.5	—
	200		20.0	—	—	—	—	—
Bi ⁺³	500	Bi(NO ₃) ₃	20.0	5.1	—	—	—	—
	250		—	—	—	48.2	—	12.4
	50		—	—	19.7	—	—	—
Cr ⁺³	200	CrCl ₃	20.5	5.4	20.0	—	—	—
	100		—	—	—	—	7.8	—
Co ⁺²	5	CoSO ₄	—	—	20.0	—	—	—
Cu ⁺²	100	CuSO ₄	—	—	19.4	—	—	—
Cd ⁺²	100	Cd(NO ₃) ₂	—	—	20.0	47.5	—	20.0
Ti ⁺⁴	200	Ti(SO ₄) ₂	19.5	—	19.7	62.6	—	—
Mn ⁺²	300	MnSO ₄	—	—	—	60.0	—	12.5
	100		—	—	19.7	—	—	—
Mo ⁺⁶	50	(NH ₄) ₆ Mo ₇ O ₂₄	—	—	20.0	—	7.3	—
Ni ⁺²	150	NiSO ₄	—	—	19.9	—	7.4	—
	100		—	—	—	—	7.4	—
Pb ⁺²	1000	Pb(NO ₃) ₂	23.5	—	19.2	—	—	10.5
	500		23.2	5.5	—	48.5	—	—
Zn ⁺²	100	ZnSO ₄	—	—	19.8	—	7.3	—
Mg ⁺²	500	MgCl ₂	20.9	5.2	—	50.6	7.3	11.6
Ca ⁺²	100	CaCl ₂	—	—	—	—	7.8	—
As ⁺³	250	K ₃ AsO ₃	20.7	5.4	—	47.0	—	—
Sb ⁺⁴	250	SbCl ₄	19.0	4.9	—	50.6	—	—
Sn ⁺⁴	200	SnCl ₄	—	—	—	—	7.5	—
In ⁺³	200	InCl ₃	19.8	—	—	—	—	—
Th ⁺⁴	200	Th(NO ₃) ₄	21.4	5.1	—	—	6.0	—
Zr ⁺⁴	100	Zr(SO ₄) ₂	—	—	19.0	—	—	—
Tl ⁺	200	TlNO ₃	—	—	—	47.0	—	12.0
WO ₄ ⁻²	200	Na ₂ WO ₄	20.0	5.0	—	41.0	—	—
VO ₄ ⁻³	200	Na ₃ VO ₄	19.7	4.8	—	—	7.3	—
F ⁻	200	NaF	20.7	5.2	—	45.0	—	12.0
	100		—	—	—	—	6.8	—
CN ⁻	5 ml 0.2 N	KCN	—	—	—	—	7.5	—
PO ₄ ⁻³	1000	KH ₂ PO ₄	19.3	—	—	—	—	10.0
SO ₂ ⁻²	500	NaSO ₄	—	—	—	—	7.7	—
NO ₃ ⁻	500	KNO ₃	—	—	—	—	7.0	—
citrate	10% 1 ml	—	19.0	—	—	—	—	11.0

* Cd 20.0, Mn 5.0, Fe 20.0, Ga 47.0, Y 7.4 and Hg 12.0 μg taken respectively.

usual way and then diluted appropriately in a volumetric flask. Iron was determined by the procedure mentioned above. The results obtained are given in Table X.

II. Simultaneous determination of iron and other metals. The ferric chelate of PAN in organic solvents has its absorbance maximum at 765–775 $m\mu$ approximately. On

TABLE VII
 BACK-EXTRACTION

<i>Metals</i>	<i>with 0.2 N KCN soln.</i>	<i>with pH 4.5 buffer soln.</i>
Cd ⁺²	possible	possible
Mn ⁺²	impossible	possible
Zn ⁺²	possible	impossible
Ni ⁺²	impossible	impossible
Cu ⁺²	possible	impossible
Hg ⁺²	possible	possible
Co ⁺³	impossible	impossible
Fe ⁺³	impossible	impossible
In ⁺³	possible	impossible
Ga ⁺³	possible	impossible
Pb ⁺²	possible	possible

 TABLE VIII
 REACTIVITY OF METALS WITH PAN IN THE PRESENCE OF MASKING AGENTS

<i>Metals</i>	<i>KCN</i>	<i>Citrate</i>	<i>Fluoride</i>	<i>EDTA</i>
Mn ⁺²	+	+	+	—
Cd ⁺²	—	+	+	—
Hg ⁺²	—	+	+	—
Ni ⁺²	—	+	+	—
Co ⁺³	—	+	+	—
UO ₂ ⁺²	+	—	+	+
Ga ⁺³	—	—	—	—
Fe ⁺³	—	—	—	—
Y ⁺³	+	+	+	—
In ⁺³	+	+	+	—
Zn ⁺²	—	+	+	—
Bi ⁺³	—	—	—	—
La ⁺³	+	—	—	—
Ce ⁺³	+	—	—	—

+ reaction, — no reaction; 0.2 N KCN, 10% sodium citrate, 0.2 N NaF, and 0.1 N EDTA solution (5 ml/25 ml) respectively.

 TABLE IX
 * EFFECT OF MASKING AGENTS ON ABSORBANCE OF MANGANESE

<i>0.2 N KCN soln. added (ml)</i>	<i>Absorbance at 560 mμ</i>	<i>10% citrate soln. (ml)</i>	<i>Absorbance at 560 mμ</i>
—	0.510	—	0.510
0.5	0.520	0.25	0.500
1.0	0.499	0.5	0.500
2.0	0.495	1.0	0.495
3.0	0.374	2.0	0.490

 TABLE X
 DETERMINATION OF IRON IN CLAY AND ANORTHOSITE

<i>Sample</i>	<i>PAN method %</i>	<i>Thiocyanate method %</i>
clay	0.14	0.18
anorthosite	0.17	0.16
	0.08	0.08

the other hand, most other metal chelates have no absorption at this wavelength. Therefore, some metals and iron can both be determined simultaneously by the treatment mentioned above. In a previous paper¹⁰, the author already reported a simultaneous determination of indium and iron.

III. Separation of manganese from nickel. A simultaneous extraction and determination of microgram amounts of nickel and manganese was carried out. The nickel and manganese could be separated quantitatively by means of back-extraction with potassium cyanide solution or by pH control.

An aliquot of the slightly acidic mixed solution of nickel and manganese was transferred to a separatory funnel, and diluted to approximately 25 ml. 2 ml of 0.1% PAN solution and 5 ml of pH 9.5 buffer solution was added, and the mixture was allowed to stand for 5 min. Exactly 10.0 ml of chloroform was added to the mixture which was then shaken vigorously for 1-2 min and the absorbance was measured at 575 m μ against a reagent blank (Ni + Mn). When a chloroform extract of the nickel and manganese chelates was shaken with 10 ml of 0.2 N KCN solution, the manganese chelate was destroyed and the manganese reverted to the aqueous layer. Thus, the absorbance of the chloroform solution measured again at 575 m μ allowed the determination of nickel. The amount of manganese could then be calculated from the difference of these two absorbance values. Typical results are shown in Fig. 7.

IV. Extraction of yttrium. Yttrium can be extracted with organic solvents after the formation of chelates with thenoyltrifluoroacetone²¹ and dibutylphosphoric acid²².

In the method described below, the solvent extraction of yttrium-PAN chelate was performed with ether and, the separation of yttrium from lanthanum and cerium was examined.

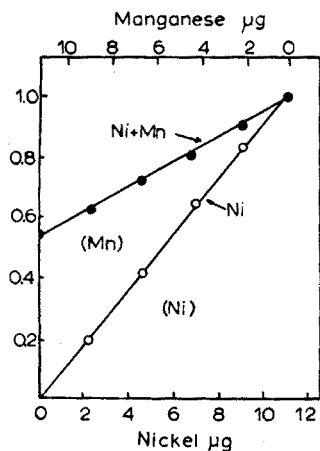


Fig. 7. Determination of manganese and nickel, $\lambda = 575 \text{ m}\mu$.

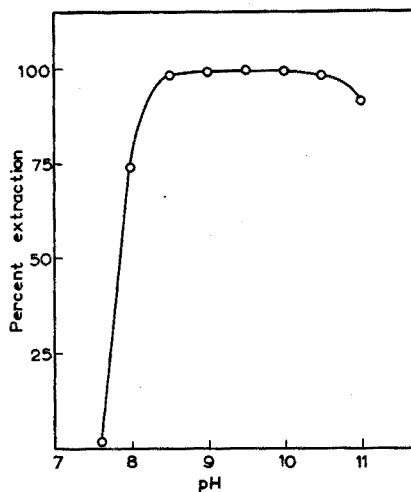


Fig. 8. Effect of pH on percentage extraction.

In order to ascertain the chemical recovery, yttrium was determined colorimetrically by the neothoron (arsenazo) method⁵.

Effect of reagent concentration: 1 ml of 0.1% PAN solution sufficed for the extraction of 15 μg of yttrium. The most important fact is that yttrium chelate was found

to be hardly soluble in ether, in the absence of excess reagent. Thus it was confirmed that the presence of excess reagent is a very important factor.

Effect of pH: The effect of the pH value on the extraction yield was investigated using 1 ml of 0.1% PAN solution. The experimental results are presented in Fig. 8. Almost 100% of yttrium was recovered when the extraction was made at pH values between 9 and 10.

Effect of potassium cyanide: For the separation of yttrium from many other metals, the use of potassium cyanide as a masking agent was tested. The results indicated that 2 or 5 ml of 0.2 *N* potassium cyanide solution gave no trouble as regards the extraction yield.

Procedure for the separation of yttrium: From the experimental results, the procedure for the separation of yttrium was designed as follows.

Transfer an aliquot of the sample solution, which contains up to 20 μg of yttrium, to a separatory funnel and dilute to approximately 20 ml (if necessary, add 5 ml of 0.2 *N* potassium cyanide solution). 1 ml of 0.1% PAN solution and 5 ml of the buffer solution of pH 9–10 were added and the mixture was allowed to stand for several minutes. Exactly 10.0 ml of ether was added to the mixture which was then shaken vigorously for 1–2 min.

Separation of yttrium from lanthanum and cerium. In order to test the reliability of the proposed procedure, the separation of yttrium from lanthanum and cerium was carried out. The solutions containing 20 μg of lanthanum and cerium were treated according to the above procedure. The lanthanum and cerium extracted were determined colorimetrically by the neothoron method^{23,24}. The extraction yield of lanthanum and cerium was about 0.1 and 33% respectively. These results indicate that the procedure is successfully applied to the separation of yttrium from lanthanum.

CONCLUSIONS

PAN is an extremely sensitive and comparatively selective reagent and can be used for the determination of microgram amounts of manganese, cadmium, yttrium, iron, gallium and mercury. The extraction and determination of these metals with PAN

TABLE XI
DATA ON OTHER APPLICATIONS

Metals	Colour of chelates	pH condition	Solvent	Wave-length μm	Range of det. p.p.m.
Ni ⁺²	red	5.5 ~ 10	benzene chloroform	575	~1.5
Pd ⁺²	green	3 ~ 4	chloroform	678	~16
Zn ⁺²	red	6 ~ 8 ²⁰	chloroform	560	~1.2
UO ₂ ⁺²	red	10	chloroform	560	~10
V ⁺⁵	blue	3.5 ~ 4.5	chloroform	615	~3
		3 ~ 4	acetone	560	~6
In ⁺³	red	5.3 ~ 6.7	chloroform	560	~5
Co ⁺³	green	3 ~ 6	chloroform	640	0.01 ~ 2.4
Cu ⁺²	red	3 ~ 4	20% dioxane	550	—
		8 ~ 10	chloroform	560	—

offers the definite advantage of increased selectivity by (1) control of pH, (2) selection of solvent, (3) using of masking agents or back-extraction. Further studies with this reagent, particularly with regard to its applications to various samples, should be quite fruitful. For reference purposes data on the analytical work done for other metals with PAN are summarized in Table XI. Bismuth, cerium, lanthanum and thorium have very sensitive colour reactions but a suitable organic solvent has not yet been found in which the stabilities of the chelates are great enough. Further work on the structure and stability of these metal chelates is now in progress.

SUMMARY

PAN(1-(2-pyridylazo)-2-naphthol) is proposed for the solvent extraction and spectrophotometric determination of manganese, iron, cadmium, mercury, gallium, and yttrium. The reagent, which is highly specific for iron, has been applied to the determination of iron in clay and anorthosite. The separation of yttrium from lanthanum and the separation of manganese from nickel were successful.

RÉSUMÉ

Le 1-(2-pyridylazo)-2-naphtol est proposé pour l'extraction dans solvant et le dosage spectrophotométrique du manganèse, du fer, du cadmium, du mercure, du gallium et de l'yttrium. Les séparations yttrium-lanthane et manganèse-nickel sont décrites.

ZUSAMMENFASSUNG

Für die Extraktion durch Lösungsmittel und zur spektrophotometrischen Bestimmung von Mn, Fe, Cd, Hg, Ga und Y wird PAN (1-(2-Pyridylazo)-2-naphthol) als Reagenz vorgeschlagen. Es werden die Trennungen des Yttriums von Lanthan und des Mangans von Nickel beschrieben.

REFERENCES

- ¹ K. L. CHENG AND R. H. BRAY, *Anal. Chem.*, 27 (1959) 782.
- ² W. BERGER AND H. ELVERS, *Z. anal. Chem.*, 171 (1959) 186.
- ³ S. SHIBATA, *Anal. Chim. Acta*, 23 (1960) 367.
- ⁴ B. E. SALTZMAN, *Anal. Chem.*, 25 (1953) 495.
- ⁵ J. S. FRITZ, M. J. RICHARD AND W. J. LANE, *Anal. Chem.*, 30 (1958) 1776.
- ⁶ J. C. WHITE AND R. G. BALL, *Anal. Chem.*, 32 (1960) 929.
- ⁷ S. SHIBATA, *Anal. Chim. Acta*, 22 (1960) 479.
- ⁸ H. H. GILL, R. F. ROLF AND G. W. ARMSTRONG, *Anal. Chem.*, 30 (1958) 1778.
- ⁹ K. L. CHENG, *Anal. Chem.*, 30 (1958) 1027.
- ¹⁰ S. SHIBATA, *Anal. Chim. Acta*, 23 (1960) 434.
- ¹¹ M. HNILÍŤKOVÁ AND L. SOMMER, *Z. anal. Chem.*, 177 (1960) 425.
- ¹² G. GOLDSTEIN, D. L. MANNING AND O. MENIS, *Anal. Chem.*, 31 (1959) 192.
- ¹³ A. I. BUSEV AND V. G. TIPTSOVA, *Zhur. Anal. Khim.*, 15 (1960) 573.
- ¹⁴ F. W. STATEN AND E. W. D. HUFFMAN, *Anal. Chem.*, 31 (1959) 2503.
- ¹⁵ S. WAKAMATSU, *Japan Analyst*, 9 (1960) 284.
- ¹⁶ A. I. BUSEV AND L. V. KISSELEVA, *Vestnik Moskov. Univ.*, 4 (1958) 179.
- ¹⁷ T. DONO, G. NAKAGAWA AND M. HAYASHI, *Nippon Kagaku Zasshi*, 81 (1960) 1703.
- ¹⁸ M. MIYAMOTO, *Japan Analyst*, 9 (1960) 925.
- ¹⁹ B. F. PEASE AND M. B. WILLIAMS, *Anal. Chem.*, 31 (1959) 1044.
- ²⁰ W. BERGER AND H. ELVERS, *Z. anal. Chem.*, 171 (1959) 256.
- ²¹ R. A. BOLOMEY AND L. WISH, *J. Am. Chem. Soc.*, 72 (1950) 4483.
- ²² E. M. SCADDEN AND N. E. BALLOU, *Anal. Chem.*, 25 (1953) 1602.
- ²³ S. SHIBATA AND T. MATSUMAE, *Repts. Govt. Ind. Research Inst., Nagoya*, 8 (1959) 408.
- ²⁴ S. SHIBATA, F. TAKEUCHI AND T. MATSUMAE, *Anal. Chim. Acta*, 21 (1959) 177.

STUDIES ON THE EXTRACTION OF ZIRCONIUM WITH ORGANOPHOSPHORUS COMPOUNDS

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INTRODUCTION

Zirconium is one of the elements which are readily extracted with organophosphorus solvents, and solvent extraction with tri-*n*-butyl phosphate, TBP, has been successfully employed for the fractional isolation of zirconium from hafnium¹. Although the solvent extraction technique is already in plant scale use for the isolation of zirconium, only a few papers have dealt with the fundamental aspects of zirconium extraction²⁻⁵. The present study was initiated in an attempt to obtain a pattern of zirconium behaviour during extraction with organophosphorus compounds including alkyl phosphates, phosphonate, phosphinate and phosphine oxide, so that a better selection of reagent could be made for analytical purposes.

EXPERIMENTAL

Chemicals

Zirconium. The radioisotope ⁹⁵Zr was supplied by Oak Ridge National Laboratory in the oxalate form, which was converted to nitrate by boiling with nitric acid, and a reagent grade ZrO(NO₃)₂ was supplied by Yokozawa Chemical Co., Tokyo. Throughout the work ⁹⁵Zr was separated from its daughter ⁹⁵Nb immediately before use^{5,6}. For the macroscale experiment, the zirconium solution was prepared as follows: after the tracer ⁹⁵Zr was added to the solution of zirconyl nitrate, the zirconium was precipitated as the hydroxide, then dissolved in nitric acid. The above process was repeated three times in order to mix the ⁹⁵Zr tracer thoroughly with the non-radioactive zirconium carrier.

Organophosphorus solvents. These were: Phosphates — triethyl, tri-*n*-propyl, tri-*n*-butyl, tri-*iso*-butyl, tri-*sec*-butyl, and tricyclohexyl phosphates; phosphonate — diethyl butyl phosphonate; phosphinate — tri-*n*-butyl phosphinate, and phosphine oxide — tri-*n*-butyl phosphine oxide. All the organophosphorus solvents were synthesized by Tama Chemical Co., Tokyo, and purified by vacuum distillation. The tri-*n*-butyl phosphine oxide was purified by recrystallization from benzene. The stock solutions of these solvents were kept in a refrigerator to avoid decomposition.

Other chemicals. Nitric acid and carbon tetrachloride were of reagent grade, the latter being distilled before use.

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Procedure

The extraction was carried out in nitric acid media. The solvent was diluted with carbon tetrachloride. The zirconium solution and the solvent were mixed in equal volumes in a measuring flask, and shaken in a thermostat. After equilibrium had been reached, suitable volumes of both the aqueous and organic phases were taken, and the radioactivity and aqueous nitric acid concentration were determined. The solvent was pre-equilibrated with nitric acid before the extraction.

The radioactivity of ^{95}Zr was measured with a gamma scintillation counter, and the nitric acid concentration in the aqueous phase was determined by ordinary titration.

The extraction ability of the solvent is expressed in terms of the distribution coefficient between aqueous and organic phases.

An "Infracord" spectrometer with silver chloride cells was used to measure the infrared spectra.

RESULTS AND DISCUSSION

Distribution coefficient, K_d

Extraction curves of typical phosphates, phosphonate, phosphinate and phosphine oxide are shown in Fig. 1. In the extraction with normal alkyl phosphates and tri-*iso*-butyl phosphate, the K_d values increase steeply as the nitric acid concentration increases, whereas in the extraction with tri-*sec*-butyl phosphate, tricyclohexyl phosphate, phosphonate, phosphinate and phosphine oxide the K_d values decrease after slowly reaching a maximum at about 5-7 *M* nitric acid. The extraction ability

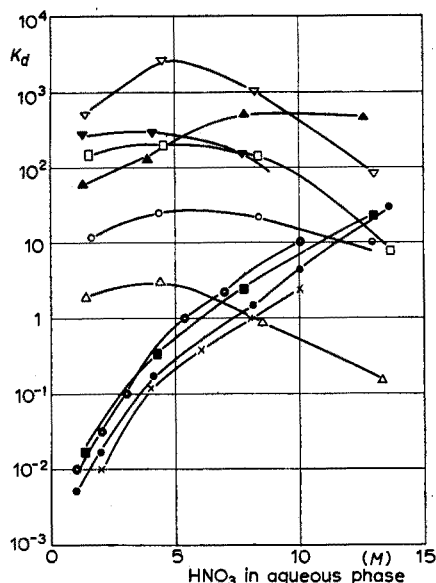


Fig. 1. Variation of K_d values with aqueous nitric acid concentration. \square Tri-*n*-butyl phosphine oxide, 0.00732 *M*; ∇ Tri-*n*-butyl phosphinate, 0.00732 *M*; \circ Tri-*sec*-butyl phosphinate, 0.00732 *M*; Δ Diethyl butyl phosphonate, 0.00732 *M*; ∇ Tri-*sec*-butyl phosphate, 0.732 *M*; \blacktriangle Tricyclohexyl phosphate, 0.732 *M*; \blacksquare Tri-*iso*-butyl phosphate, 0.732 *M*; \bullet Tri-*n*-butyl phosphate, 0.732 *M*; \times Triethyl phosphate, 0.732 *M*; \odot Tripropyl phosphate, 0.92 *M*.

is affected by the substituents in the phosphoryl group as well as by the structure of the solvent. As for the phosphates with normal alkyl groups, it was observed that the extraction ability increases slightly as the carbon number of the alkyl group increases. The extraction abilities of normal alkyl phosphates are in the following order: tri-*n*-butyl phosphate > tri-*n*-propyl phosphate > triethyl phosphate.

The effect of branching in the alkyl group was examined with tri-iso-butyl phosphate, tri-*sec*-butyl phosphate and tricyclohexyl phosphate. The results indicate that branching causes a definite increase in the distribution coefficient compared to that of normal alkyl phosphates. Moreover, the existence of branching near the alkoxy oxygen enhances the extraction ability to a remarkable extent. Tri-*sec*-butyl phosphate clearly shows a different extraction behaviour from that of tri-*n*-butyl phosphate, although tri-iso-butyl phosphate gives a curve somewhat similar to the latter. The highly branched tricyclohexyl phosphate also has a high extraction ability which is similar to that of phosphinate or phosphine oxide.

The removal of the alkoxy oxygen definitely results in an increase in the extraction ability. But the change in the extraction ability does not follow a regular pattern, and the K_d values for the phosphorus compounds tested decrease in the following order: tri-*n*-butyl phosphinate > tri-*n*-butyl phosphine oxide > tricyclohexyl phosphate and tri-*sec*-butyl phosphate > diethyl butyl phosphonate > phosphates with normal alkyl groups.

Determination of the reaction mechanism and the equilibrium constant

The extraction mechanism was examined on the normal alkyl phosphates. To determine the equation of extraction, both the solvent and acid dependences were studied. The variation of K_d values with TBP concentrations, the solvent dependence, was determined over the TBP concentration range of 6–90% and nitric acid range of 2–10 *M*, and in all cases a plot of K_d values vs. TBP concentrations gave a second power dependence. The acid dependence of the extraction is of the fourth power, and is determined by plotting the values of $K_d/[\text{TBP}]^2$ against the activities of nitric acid. With other normal alkyl phosphates the same results were obtained.

To test the effect of hydrogen ion concentration, the nitric acid concentration was varied to 1, 3 and 5 *M*, while the total nitrate ion concentration was maintained at 5 *M* by addition of sodium nitrate. Zirconium was then extracted with tri-*n*-butyl phosphate. The results tabulated in Table I show no proton dependence in the extraction, hence it may be concluded that the hydrogen ion does not take part in the extraction reaction.

TABLE I

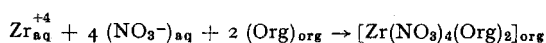
EFFECT OF HYDROGEN ION CONCENTRATION ON K_d VALUES AT CONSTANT NITRATE CONCENTRATION

Total NO_3^- concentration: 5 *M*, TBP concentration: 0.732 *M*

<i>H conc.</i> (<i>M</i>)	1.12	1.12	3.13	3.15	5.19	5.19
K_d	0.35	0.34	0.37	0.38	0.49	0.47

The K_d values for 10^{-5} *M* zirconium solution and tracer zirconium solution were found to be the same, thus there was no dependence on the zirconium concentration.

These results indicate that the reaction mechanism may be written as follows:



The evidence that two molecules of organic solvent and four molecules of nitrate ions combine with one zirconium atom suggests the charge of zirconium to be +4 over the range of 2–10 *M* nitric acid media. For the extraction of zirconium with tri-*n*-butyl phosphate, ALCOCK *et al.*⁵ reported a second power solvent dependence, and MURBACH AND McVEY² demonstrated that three molecules of tri-*n*-butyl phosphate combine with one atom of zirconium.

The equilibrium constant for the above extraction reaction was determined only in one case, *i.e.* with tri-*n*-butyl phosphate. This constant was calculated at various nitric acid concentrations according to the above extraction reaction, the acid concentrations being corrected by using the appropriate activity coefficients. Table II shows the values obtained, the average of which is taken as the equilibrium constant. This was determined to be $1.6 \cdot 10^{-2}$ at 23°. MURBACH AND McVEY² gave a value of $5 \cdot 10^{-3}$ at 25° for the extraction of zirconium with tri-*n*-butyl phosphate, but the value was determined on the basis that three solvent molecules combined with one atom of zirconium.

TABLE II
EQUILIBRIUM CONSTANT FOR TBP EXTRACTION AT VARIOUS NITRIC ACID CONCENTRATION AT 23°

1. Zirconium concentration: Tracer amount							
<i>HNO</i> ₃ (<i>M</i>)	1.0	1.4	1.8	2.0	3.0	4.0	5.2
<i>K</i> ($\cdot 10^{-2}$)	2.3	0.85	0.88	1.4	1.1	1.4	1.9
Mean <i>K</i> ($\cdot 10^{-2}$)	1.4						
2. Zirconium concentration: $5 \cdot 10^{-5}$ <i>M</i>							
<i>HNO</i> ₃ (<i>M</i>)	1.0	1.5	2.0	3.1	3.9	5.2	7.0
<i>K</i> ($\cdot 10^{-2}$)	3.8	1.5	1.3	1.2	1.1	1.8	1.3
Mean <i>K</i> ($\cdot 10^{-2}$)	1.7						

Effect of temperature

The effect of temperature was examined for the extraction with tri-*n*-butyl phosphate. The results indicate that the temperature dependence is affected by the nitric acid concentration in the aqueous phase as illustrated in Fig. 2. At low acid concentration, the *K_d* values increase as the temperature rises, whereas an entirely opposite relationship is observed at high acid concentrations. In the intermediate range of nitric acid concentration, no appreciable temperature dependence is observed.

Infrared spectra

The infrared spectra of zirconium extracted from 10 *M* nitric acid solution with tri-*n*-butyl phosphate, diethyl butyl phosphonate, tri-*n*-butyl phosphinate and tri-*n*-butyl phosphine oxide were measured. The infrared spectrum of the extracted complex was compared to that of corresponding solvent, and changes between these two spectra were analysed.

The changes observed are not characteristic only for the zirconium complexes: the same changes are commonly observed in infrared spectra of other metal organophosphorus complexes. Although the analysis and the interpretation of the changes observed in the infrared spectra of metal organophosphorus complexes will be published as a separate paper, the following major changes are referred to here: (1) the shift in the P=O stretching frequency by complexing with zirconium, (2) the split of the ionic nitrate degenerate stretching vibration, which is attributed to the covalent

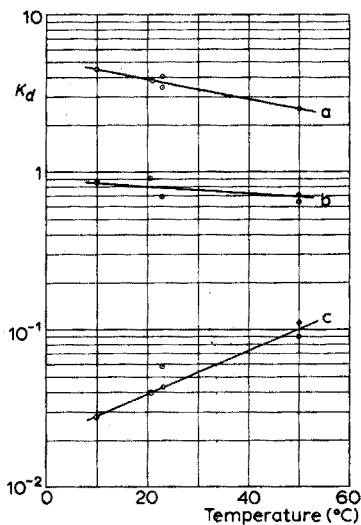


Fig. 2. Temperature dependence of K_d values. a, 10 M HNO_3 in aqueous phase; b, 5 M HNO_3 in aqueous phase; c, 1 M HNO_3 in aqueous phase.

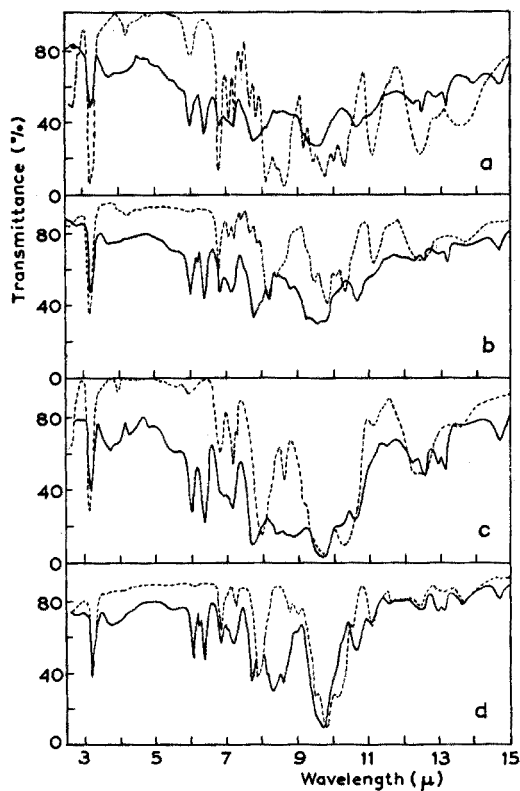


Fig. 3. Infrared spectra of the extracted complexes. a, — Zr + tri- n -butyl phosphine oxide, ---- tri- n -butyl phosphine oxide; b, — Zr + tri- n -butyl phosphinate, ---- tri- n -butyl phosphinate; c, — Zr + diethyl butyl phosphonate, ---- diethyl butyl phosphonate; d, — Zr + tri- n -butyl phosphate, ---- tri- n -butyl phosphate.

nature of the complexes, and (3) the change in P—O—C stretching bond, the nature of which is not clearly understood as yet. Some of the typical spectra are shown in Fig. 3.

The observation of the infrared spectra supports the evidence of covalent complex formation between zirconium and organophosphorus solvents.

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SUMMARY

The extraction of zirconium from nitric acid media with alkyl phosphates, phosphonate, phosphinate and phosphine oxide was studied. The extraction ability is affected by alkyl substituents attached to the phosphoryl group as well as by the solvent structure, the order of efficiency being: tri-*n*-butyl phosphinate > tri-*n*-butyl phosphine oxide > tricyclohexyl phosphate and tri-*sec*-butyl phosphate > diethyl butyl phosphate > normal alkyl phosphates. In the extraction with normal alkyl phosphates, two solvent molecules and four nitrate ions combine with one atom of zirconium. The equilibrium constant and the effect of temperature were studied in the extraction with tri-*n*-butyl phosphate. The infrared spectra of zirconium extracted from 10 *M* nitric acid solution with the organophosphorus solvents were measured; it was confirmed that a covalent complex was formed.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'extraction du zirconium, au moyen de solvants organophosphorés, en milieu nitrique. Ils ont examiné en particulier l'extraction à l'aide de tributylphosphate.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Extraktion von Zirkonium mit organischen Phosphorverbindungen, besonders Tributylphosphat.

REFERENCES

- ¹ M. J. HURE AND R. SAINT JAMES, *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva*, 8 (1956) 551.
- ² E. W. MURBACH AND W. H. McVEY, *IRL-115* (1954).
- ³ A. E. LEVITT AND H. FREUND, *J. Am. Chem. Soc.*, 78 (1956) 1545.
- ⁴ D. F. PEPPARD, G. W. MASON AND J. L. MAIER, *J. Inorg. & Nuclear Chem.*, 3 (1956) 215.
- ⁵ K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK AND H. A. C. MCKAY, *J. Inorg. & Nuclear Chem.*, 4 (1957) 100.
- ⁶ H. UMEZAWA AND R. HARA, *Anal. Chim. Acta*, 23 (1960) 267.

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SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM WITH STANNOUS IODIDE REAGENT

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AYRES *et al.*¹ and others² have reported on the use of a tin(II) chloride reagent for the spectrophotometric determination of rhodium. The method is simple and reproducible but lacks sensitivity. BERMAN AND IRONSIDE³ have reported on the use of tin(II) bromide in hydrobromic acid as the color developing agent for rhodium analysis. Recently, PANTANI AND PICCARDI⁴ have studied the behavior of Rh, Pt, Pd and Au ions with tin(II) bromide both in aqueous solutions and in isoamyl alcohol extracts. The tin(II) bromide method for rhodium is more sensitive than the tin(II) chloride method but it requires a redistillation of hydrobromic acid and the use of perchloric acid as a color stabilizing agent. Each method has serious interferences from other transition metals which necessitates the separation of rhodium from these elements before an analysis.

This study was undertaken to explore the possibility that a tin(II) iodide reagent might be more sensitive to rhodium than either the tin(II) chloride or bromide reagent. The development of such a method is described below.

EXPERIMENTAL

Apparatus and reagents

The spectra were recorded with a Beckman DK-1 spectrophotometer. Individual absorbancy measurements were made with a Beckman DU spectrophotometer using 1-cm quartz cells.

Rhodium(III) solutions were prepared by dissolving the trichloride in 0.3 *N* hydrochloric acid and standardizing by the method of GILCHRIST⁵.

Tin(II) chloride solutions were prepared by dissolving 2 parts by weight of $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ in 1 part by volume of concentrated hydrochloric acid and diluting with 5 parts by volume of distilled water. For acidity calculations this solution was considered 2 *N* in hydrochloric acid. Tin metal was placed in the stock solution.

All other reagents were of analytical grade and were used as indicated.

Recommended procedure

Transfer the rhodium(III) sample to a 25-ml volumetric flask. Add sufficient hydrochloric acid so that the final solution will be 1 *N* in hydrochloric acid. Add 5 ml of 20% (w/v) potassium iodide solution, mix, and heat for 15 min in a boiling waterbath.

Cool to room temperature. Pipet 5 ml of the stannous chloride solution into the flask and dilute to volume with distilled water. Mix and heat the unstoppered flasks for 2 min in a boiling waterbath. Cool immediately to room temperature in an ice bath. Measure the absorbancy of the solution at 460 m μ vs. a blank prepared identically to the sample except for the omission of rhodium. Determine the rhodium concentration from a standard curve.

Effect of temperature on solution absorbancy

Time studies indicated that the sample must be heated with potassium iodide in a boiling waterbath for at least 8–10 min to convert the rhodium chloride complex to a reproducible iodide complex; 15 min heating was accepted as routine to insure a complete conversion with each sample. Upon the addition of tin(II) chloride to the sample containing the rhodium iodide complex a rose colored solution is formed which rapidly changes to a golden brown. At room temperature the absorbancy increases continuously for 18 h and then decreases. A 2 min heating period, however, produces a solution whose color is stable for at least 24 h and which exhibits an absorption maximum at 460 m μ . The time of heating is not critical; heating periods up to 5 min do not alter the results. The spectral curve is shown in Fig. 1.

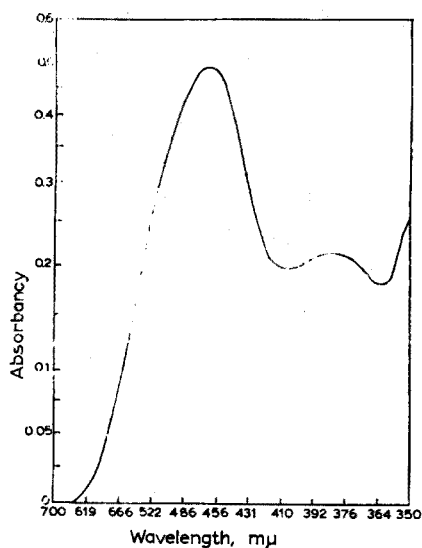


Fig. 1. Absorption spectra of rhodium-tin(II) iodide complex.

Effect of hydrochloric acid concentration on solution absorbancy

The molar absorptivity of the rhodium complex increases with a decrease in acid concentration as shown in Fig. 2. The lowest practical acidity is about 1 *N* due to the precipitation of SnI₂ in solutions below this acidity. The acid concentration of the final solution is somewhat critical since the absorbancy changes 0.01 units for each 0.1 *N* increment in solution acidity for a solution with an absorbancy of about 0.5. The precision of the method indicates, however, that acidity control is easily effected.

Effect of potassium iodide concentration on solution absorbancy

The absorbancy increases as the volume of iodide solution added approaches 5 ml but remains constant for greater volumes of reagent. Large excesses of iodide reagent must be avoided to prevent the precipitation of SnI_2 . A precipitate forms if as much as 11 ml of reagent are added.

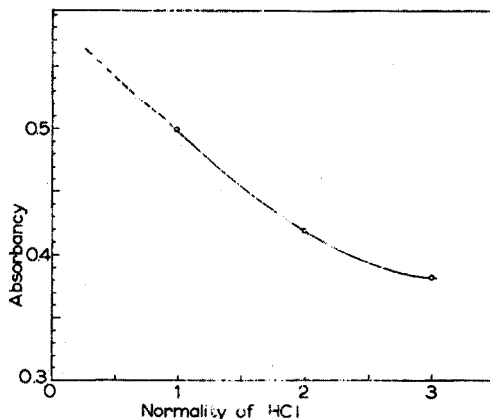


Fig. 2. Variation of absorbancy of rhodium-tin(II) iodide complex at 460 μ with changes in hydrochloric acid concentration.

Effect of tin(II) chloride concentration on solution absorbancy

Variations from 40 to 200% of the prescribed amount of tin(II) chloride produce only a small increase (10%) in absorbancy if the hydrochloric acid content is maintained constant. 5 ml of reagent were chosen as a practical upper limit.

TABLE I

CONCENTRATION OF INTERFERENCES NECESSARY TO GIVE A 1% VARIATION IN SAMPLE ABSORBANCY FOR A 2 p.p.m. Rh(III) SOLUTION

Interfering ion	Concentration in p.p.m.	Direction of change
Co as CoCl_2	7	+
Sb as SbCl_3	1	+
Ti as TiCl_4	8	-
Cu as CuCl_2	5	+
Fe as FeCl_3	10	+
Ni as NiCl_2	20	+
Cr as CrCl_3	10	+
Ir as IrCl_3	0.08	+
Pd as PdCl_2	3	ppt. forms
Pt as PtCl_2	0.1	+
I_2	280	+
Na_2SO_4	11,000	+
NaCl	3,300	-
H_2SO_4	50,000	-

Effect of diverse ions, salts and sulfuric acid on solution absorbancy

The more common interferences and the amounts that can be tolerated by the procedure are listed in Table I. Note that other platinum group metals and transition metals interfere seriously.

The positive effect of sodium sulfate is probably due to a decrease in hydrochloric acid concentration by the metathetical formation of unionized HSO₄⁻.

Small amounts of iodine are formed during the first heating period, presumably due to dissolved oxygen in the distilled water and reagents. This does not affect the reproducibility of the method as can be seen from the following. The absorbancy of the blank is increased by only 0.006 units if 50 mg (2000 p.p.m.) of free iodine are added but the effect on the sample is more pronounced. 280 p.p.m. of iodine can be tolerated without causing an error in the absorbancy measurement greater than 1%. Consequently the solutions must be free of oxidizing agents in amounts sufficient to produce an iodine concentration of 280 p.p.m.

Optimum working range

The Ringbom plot (Fig. 3) shows the reliable working range to be from 0.4 to 3 p.p.m. Rh. The system obeys Beer's law and has a molar absorptivity of $3.9 \cdot 10^4$ at 460 m μ .

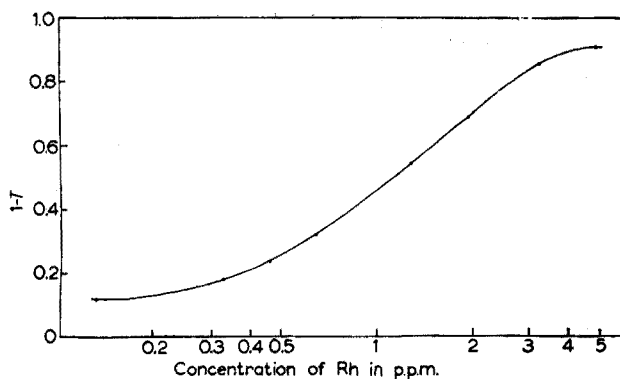


Fig. 3. Ringbom plot of rhodium-tin(II) iodide complex determined at 460 m μ .

Precision of method

6 samples containing 2 p.p.m. of Rh(III) were analyzed on three different days giving an average deviation of 0.3% and a standard deviation of 0.4%.

DISCUSSION

A choice among the tin(II) halide reagents for the determination of rhodium may rest upon the sensitivity desired, the iridium and nickel content of the sample, the analyst's aversion to the use of perchloric acid, the cost and redistillation of hydrobromic acid, the greater stability of SnCl₂ in hydrochloric acid than in hydrobromic acid, and knowledge of the acid content of the sample. All three reagents produce stable and

reproducible colors with rhodium and the analytical procedures are simple and not very different.

The molar absorptivities of the rhodium-tin(II) chloride¹, rhodium-tin(II) bromide³, and rhodium-tin(II) iodide complexes are $3.9 \cdot 10^3$, $2.9 \cdot 10^4$ and $3.9 \cdot 10^4$ respectively.

Except for the lower sensitivity which often may be satisfactorily increased simply by using absorption cells of longer path length, the stannous chloride reagent appears to be superior to both the bromide and iodide reagent. The tin(II) chloride method has the greatest tolerance for iridium (45%) and nickel ions.

For samples requiring a greater sensitivity the choice of methods lies between the use of the bromide or iodide reagents. The bromide method appears to tolerate more iridium than the iodide method although different tolerances are reported^{3,4}. The iodide method appears to be slightly more sensitive to changes in acid concentration than the bromide method.

All three halide methods are subject to serious interferences from other platinum group metals and numerous other transition metals. The difficulty can be eliminated only by the prior separation of rhodium from the sample.

The chief advantages of the tin(II) iodide method are its sensitivity, lack of dependence on perchloric acid for stability, and its use of cheaper and more easily prepared reagents.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support given this program by Celanese Corporation of America.

SUMMARY

The tin(II) iodide reagent reacts with rhodium to form a stable colored complex with an absorption maximum at 460 m μ . The system obeys Beer's law and exhibits a molar absorptivity of $3.9 \cdot 10^4$ at 460 m μ . Rhodium concentrations between 0.4 and 3.0 p.p.m. can be determined with an average deviation of only 0.3%. The method compares favorably with the tin(II) chloride and bromide methods for rhodium and is considerably more sensitive. Ir, Pd, Pt, Sb, Ti, Cu, Co, Ni and Fe interfere with the method. Consequently, just as is the case with the chloride and bromide reagent, Rh must be separated from most samples prior to an analysis.

RÉSUMÉ

L'iodure d'étain(II) est proposé comme réactif pour le dosage spectrophotométrique du rhodium. La sensibilité est beaucoup meilleure que celle obtenue avec les chlorure et bromure d'étain(II). Les éléments Ir, Pd, Pt, Sb, Ti, Cu, Co, Ni et Fe gênent également.

ZUSAMMENFASSUNG

Zur spektrophotometrischen Bestimmung von Rhodium ist als Komplexbildner das Zinn-(II)-jodid besser geeignet als Zinn-(II)-chlorid oder -bromid. Die störenden Elemente Ir, Pd, Pt, Sb, Ti, Cu, Co, Ni und Fe müssen vorher entfernt werden.

REFERENCES

- 1 G. H. AYRES, B. L. TUFFLY AND J. S. FORRESTER, *Anal. Chem.*, 27 (1955) 1742.
- 2 A. D. MAYNES AND W. A. E. MCBRYDE, *Analyst*, 79 (1954) 230.
- 3 S. S. BERMAN AND R. IRONSIDE, *Can. J. Chem.*, 36 (1958) 1151.
- 4 F. PANTANI AND G. PICCARDI, *Anal. Chim. Acta*, 22 (1960) 231.
- 5 R. GILCHRIST, *Bur. Standards J. Research*, 12 (1934) 294.

REFERENCE ELECTRODES FOR VOLTAMMETRY IN ACETONITRILE

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Over the past few years interest in acetonitrile as a polarographic solvent has produced some extremely fruitful results. These studies have developed some ambiguities with regard to reference electrodes for acetonitrile polarography. Recently when one of the authors attempted to convert the data of several workers to a common reference electrode (aqueous saturated calomel), it became apparent that it was not clear how the individual reference electrodes had been used.

In general, reference electrodes for acetonitrile have been either the ordinary aqueous saturated calomel or the silver ion-silver system used by PLESKOV¹ in potentiometric measurements. PLESKOV measured potentials of various metal-metal ion couples in acetonitrile using a half-cell of $\text{AgNO}_3(0.01 M)$, $\text{CH}_3\text{CN}/\text{Ag}$ as the reference. KOLTHOFF AND COEJZE² preferred the aqueous saturated calomel electrode but compared their data to PLESKOV's reference apparently by measuring the system $\text{AgNO}_3(0.01 M)$, $\text{Ag} \parallel \text{S.C.E. aq.}$ They reported the silver ion-silver electrode to be $+0.29 \text{ V vs. S.C.E. aq.}$ However, if it is assumed that their polarographic $E_{1/2}$ for silver ion reduction in $0.1 M$ sodium perchlorate medium ($0.32 \text{ V vs. S.C.E.}$) can be identified as usual with E° for silver ion-silver, then $E_{\text{Ag}^+(0.01 M), \text{Ag vs. S.C.E. aq.}}$ would be $+0.20 \text{ V}$. This appears inconsistent with the value $+0.29 \text{ V}$. On the other hand, the $E_{1/2}$ for silver ion reduction in $0.1 M$ tetraethylammonium perchlorate reported by LARSON AND IWAMOTO³ ($+0.42 \text{ V vs. S.C.E.}$), when converted to $E_{\text{Ag}^+(0.01 M), \text{Ag}}$ gives $+0.30 \text{ V vs. S.C.E. aq.}$

POPOV AND GESKE⁴ developed a silver-silver chloride electrode where the solubility of silver chloride in acetonitrile was controlled by a fixed concentration of tetramethylammonium chloride. Again the data were converted to PLESKOV's $\text{Ag}^+(0.01 M)/\text{Ag}$ reference using the value $+0.29 \text{ V}$. In more recent acetonitrile work, GESKE^{5,6} has used the aqueous saturated calomel as the actual reference electrode.

LARSON AND IWAMOTO, in fundamental studies of solvent effects on metal ion reductions, used the aqueous saturated calomel electrode but did not make conversions to the silver ion-silver system³. Similarly KUWANA⁷, as well as VOORHIES AND FURMAN⁸, studied anodic oxidations in acetonitrile using the aqueous saturated calomel.

LUND⁹, in pioneering studies of the oxidation of hydrocarbons in acetonitrile, used as a reference electrode what has been tacitly assumed to be the silver ion-silver system of PLESKOV. His reference actually was $\text{AgClO}_4(0.1 M)$, $\text{NaClO}_4(0.5 M)$, Ag .

Since the aqueous saturated calomel does function satisfactorily in acetonitrile

polarography (the effect of leakage through the usual salt bridge is easily minimized by working with an H-type cell where any drainage is kept from contact with the actual polarographic medium), it would seem very desirable to convert all existing $E_{1/2}$ values in acetonitrile to the aqueous saturated calomel reference. This is in keeping with polarographic practice where, in aqueous media, it is rare indeed that any reference other than saturated calomel is used today. Due to the uncertainties in the nature of the silver ion-silver reference systems, a series of such reference electrodes have been measured vs. an aqueous saturated calomel electrode. The data indicate that care must be exercised in converting from one reference to the other.

EXPERIMENTAL

Potential measurements were made with an H-type cell separated by a porous frit. One compartment (side A) was filled with an acetonitrile silver salt system and the other (side B) with an acetonitrile solution of either lithium, sodium, or tetraethylammonium perchlorate. An aqueous S.C.E. was immersed in side B and a heavy silver foil in side A. Several different calomel and silver foil electrodes were used. Potential measurements were made with a Rubicon Model 2730 potentiometer. Table I summarizes the data obtained with the various cells. Each observed voltage is the

TABLE I
VARIOUS Ag^+/Ag REFERENCE ELECTRODES IN ACETONITRILE vs. S.C.E. aq.

Cell No.	Side "A"	Side "B"	E(V)
	<i>LiClO₄</i>		
1	0.1 M AgNO ₃	0.1 M LiClO ₄	0.305
2	0.1 M AgNO ₃ , 0.1 M LiClO ₄	0.1 M LiClO ₄	0.320
3	0.1 M AgNO ₃ , 0.5 M LiClO ₄	0.5 M LiClO ₄	0.308
4	0.01 M AgNO ₃	0.1 M LiClO ₄	0.259
5	0.01 M AgNO ₃ , 0.1 M LiClO ₄	0.1 M LiClO ₄	0.267
	<i>NaClO₄</i>		
6	0.1 M AgNO ₃	0.1 M NaClO ₄	0.301
7	0.01 M AgNO ₃	0.1 M NaClO ₄	0.253
8	0.1 M AgClO ₄ , 0.5 M NaClO ₄	0.5 M NaClO ₄	0.301
	<i>Et₄NClO₄</i>		
9	0.1 M AgNO ₃	0.1 M Et ₄ NClO ₄	0.336
10	0.1 M AgNO ₃ , 0.1 M Et ₄ NClO ₄	0.1 M Et ₄ NClO ₄	0.337
11	0.01 M AgNO ₃	0.1 M Et ₄ NClO ₄	0.291
12	0.01 M AgNO ₃ , 0.1 M Et ₄ NClO ₄	0.1 M Et ₄ NClO ₄	0.291
	<i>No supporting electrolyte</i>		
13	0.1 M AgNO ₃	0.1 M AgNO ₃	0.337
14	0.01 M AgNO ₃	0.01 M AgNO ₃	0.300

average of at least two measurements with different silver foils. The differences between these measurements were never greater than 2 mV. Especially in the case where the aqueous saturated calomel dipped into the 0.5 M sodium perchlorate medium, some precipitation occurred on the outside of the salt bridge tip and it is felt that the accuracy of these measurements is about ± 2 mV. For convenience of discussion, the various cells are numbered in Table I as indicated.

DISCUSSION

Unless the aqueous saturated calomel reference electrode is immersed directly in a 0.01 *M* acetonitrile solution of silver ion, it does not appear possible to determine definitively the value of PLESKOV's reference electrode, $\text{AgNO}_3(0.01)$, Ag , CH_3CN , *vs.* S.C.E. aq. As the data in Table I show, the potential difference between PLESKOV's reference electrode and an aqueous saturated calomel electrode is affected quite markedly by the nature of the electrolyte solution in which the aqueous saturated calomel electrode is immersed (See cells No. 4, 7, 11 and 14). With 0.1 *M* acetonitrile solutions of sodium perchlorate and lithium perchlorate as the electrolyte solution, $E_{\text{PLESKOV's electrode vs. the aqueous saturated calomel}}$ is close to +0.26 V. With 0.1 *M* acetonitrile solution of tetraethylammonium perchlorate, $E_{\text{PLESKOV's electrode vs. aqueous saturated calomel}}$ is +0.291 V, a value which agrees closely with that reported by KOLTHOFF AND COETZEE². This potentiometric value of +0.291 V *vs.* S.C.E. aq. agrees closely with the value +0.30 V *vs.* S.C.E. aq. derived from polarographic data. The potentiometric value of +0.26 V *vs.* S.C.E. where sodium perchlorate and lithium perchlorate were involved, however, is not consistent with the polarographic data for silver ion reduction in sodium perchlorate. The interesting effect of sodium perchlorate and lithium perchlorate, on one hand, and tetraethylammonium perchlorate, on the other, has been observed by LARSON AND IWAMOTO³. They observed shifts in $E_{1/2}$ values for the reduction of metal ions when the concentration of lithium perchlorate, the supporting electrolyte, was varied, whereas variation of the concentration of tetraethylammonium perchlorate, however, had no effect on the $E_{1/2}$ values¹⁰. This difference in behavior between the two alkali perchlorates and tetraethylammonium perchlorate is probably due to a difference in the nature of the "solvated" cations. Lithium and sodium ions probably are appreciably solvated and to about the same extent, while the tetraethylammonium ion is not. The potential measurements with tetraethylammonium perchlorate and of cells 13 and 14, which contain no supporting electrolyte, appear to bear out such an interpretation. Thus the value of PLESKOV's reference electrode is +0.30 V *vs.* S.C.E. aq.

Since LUND carried out his electrochemical studies in 0.5 *M* acetonitrile solution of sodium perchlorate, *i.e.*, a cell identical with No. 8 in Table I, conversion of his $E_{1/2}$ values to the aqueous saturated calomel reference does not present any problem.

It is interesting to note that a tenfold change in silver ion concentration does not give quite the theoretical 0.059 change in $E_{\text{Ag}^+, \text{Ag}}$. The values fall between 0.045 and 0.053.

ACKNOWLEDGEMENT

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SUMMARY

The saturated calomel electrode is the reference electrode in aqueous polarographic studies. Such is not the case, however, with nonaqueous polarographic studies. In particular acetonitrile has been used as the solvent for many polarographic studies with just as many reference electrodes. An attempt has been made to correct this unfortunate situation. Appropriate measurements have been made to evaluate the potential of the various reference electrode systems used in acetonitrile with respect to the aqueous saturated calomel electrode.

RÉSUMÉ

Au cours de leurs recherches de polarographie en milieux nonaqueux (en particulier dans l'acétonitrile), les auteurs ont effectué des mesures appropriées pour déterminer le potentiel de divers systèmes de référence, par rapport à l'électrode aqueuse à calomel saturée.

ZUSAMMENFASSUNG

Beschreibung von Untersuchungen über die Polarographie in nicht-wässrigem Medium, besonders Acetonitril. Es wurden die Potentiale verschiedener Referenz-elektrodensysteme in Acetonitril bestimmt und mit der Kalomelelektrode verglichen.

REFERENCES

- ¹ V. A. PLESKOV, *Zhur. Fiz. Khim.*, 22 (1948) 351.
- ² I. M. KOLTHOFF AND J. F. COETZEE, *J. Am. Chem. Soc.*, 79 (1957) 870, 1852.
- ³ R. C. LARSON AND R. T. IWAMOTO, *J. Am. Chem. Soc.*, 82 (1960) 3239, 3526.
- ⁴ A. I. POPOV AND D. H. GESKE, *J. Am. Chem. Soc.*, 79 (1957) 2047.
- ⁵ D. H. GESKE, *J. Phys. Chem.*, 63 (1959) 1062; *J. Am. Chem. Soc.*, 81 (1959) 4145.
- ⁶ D. H. GESKE AND A. H. MAKI, *J. Am. Chem. Soc.*, 82 (1960) 2671.
- ⁷ T. KUWANA, *Ph.D. Thesis*, University of Kansas.
- ⁸ J. D. VOORHIES AND N. H. FURMAN, *Anal. Chem.*, 31 (1959) 381.
- ⁹ H. LUND, *Acta Chem. Scand.*, 11 (1957) 491, 1323.
- ¹⁰ R. C. LARSON AND R. T. IWAMOTO, Unpublished results.

Anal. Chim. Acta, 25 (1961) 371-374

APPLICATION OF CONTROLLED-POTENTIAL ELECTROLYSIS TO THE ANALYSIS OF LEAD- AND TIN-BASE ALLOYS

II. TIN-BASE ALLOYS

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Solders

Besides lead and tin, solders may also contain antimony (1-2%) and several impurities like copper, arsenic, etc. Even when tin is the base metal, the analytical methods for antimony, lead and tin are the same as those described in Part I for the lead-base alloys¹. Copper may be determined by the methods described in an earlier paper².

Bearing alloys

(a) *Separate analysis of antimony and subsequent determination of copper and lead.* In tin-base bearing alloys, while antimony and copper are present in quantities that may be determined with accuracy on a 1-g sample, lead is quite frequently present in small percentages which do not allow an exact determination by cathodic deposition from a 1-g alloy sample. For this reason, a separate controlled potential electrolytic

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method was described by which the determination of copper and lead is made on a 5-g weighed sample². In such a case, antimony must be assessed on another sample of the alloy and the method already described¹ for lead-base alloys may be followed.

(b) *Successive determination of antimony, copper and lead.* When lead is not less than 1%, the 1-g sample is sufficient for an accurate determination and successive deposition of antimony, copper and lead may be done. Antimony is titrated with bromate according to the method already described for lead-base alloys¹; then 5 g of tartaric acid, 2 g of succinic acid, 1 g of hydrazine dihydrochloride are added to the solution and the pH is brought to 5-5.2 with ammonia. Any adjustments of the pH, if required, may be done with 1:1 hydrochloric acid and ammonia. Copper is deposited between -0.30 and -0.40 V vs. S.C.E. and, after weighing the copper, lead is deposited on the copper-plated cathode between -0.60 and -0.65 V vs. S.C.E.

In this case, bismuth and silver, which are almost always present in very small percentages, are determined together with the copper. Table I gives the results of the successive determination of antimony, copper and lead on standard sample 54c (N.B.S.). The values found agree quite well with the certified percentages.

With slight modifications to the method, the synthetic solutions indicated in Table II were analyzed. Since the dissolution of copper together with the other metals by sulfuric acid proved quite difficult, these solutions were prepared by dissolving copper and lead in 1:1 nitric acid and evaporating twice to white fumes with sulfuric acid; after cooling, antimony, tin and 2 g of potassium pyrosulfate were added followed by the usual attack already described¹ in Part I.

TABLE I
DETERMINATIONS ON SAMPLE 54c (N.B.S.) — TIN-BASE BEARING METAL

Composition			Weighed g	Found g		
				Sb(+As)	Cu	Pb
Cu = 4.30	Sb = 7.28	As = 0.049	1	7.35	4.31	1.98
Bi = 0.028	Pb = 1.99	Fe = 0.033	1	7.36	4.30	1.99
Ag = 0.02	Sn = 86.29	Ni = 0.012	1	7.34	4.31	2.02
			1	7.33	4.32	2.00

TABLE II
DETERMINATION ON SYNTHETIC SOLUTIONS

No.	Sb (g)		Cu (g)		Pb (g)		Sn (g)
	Weighed	Found	Weighed	Found	Weighed	Found	Weighed
1	0.1497	0.1494	0.0233	0.0235	0.1085	0.1088	0.7518
2	0.1490	0.1494	0.0208	0.0211	0.1138	0.1132	0.7700
3	0.1566	0.1569	0.0248	0.0250	0.2029	0.2027	0.6606
4	0.1531	0.1527	0.0244	0.0244	0.2001	0.1999	0.6783

In the analyses of solutions 1 and 2, 8 g of tartaric acid were used instead of 5 g, but otherwise the procedure was unchanged; for solutions 3 and 4 the tartaric acid used also amounted to 8 g but this time, owing to the difficulty of dissolving all the lead sulfate present at pH 5, the pH value was brought to 7.2 before the copper was

deposited at -0.45 to -0.50 V vs. S.C.E.; this was followed by the deposition of lead on the copper-plated cathode at -0.60 to -0.65 V vs. S.C.E. with an initial pH of 7.2 for 15–20 min; subsequently the pH was corrected to about 5 at which value the deposition ended; in accordance with the method described for lead-base alloys¹.

(c) *Determination of tin.* Some tests have been run on the electrolytic deposition of tin from the solution resulting after titration of antimony and after electrolysis of copper and lead following the procedure outlined in Part I for tin in lead-base alloys. Tin deposits completely but a partial co-deposition of antimony is unavoidable. This co-deposition starts when most of the tin is already deposited. The following results were obtained, for instance, with sample 54c whose composition is given in Table I: Sn% = 86.63, 86.46, 86.70, 86.94, 86.56.

Other tests performed to obtain a satisfactory successive electrodeposition of tin also gave more or less unfavorable results. In alloys which contain tin as the base metal, tin may be computed by difference, but quite often a direct determination is desirable. Since a rapid successive deposition method could not be developed, the following separate procedure was devised; this is also applicable to lead-base alloys.

METHOD

In a 400-ml tall-form beaker, dissolve 1 g of alloy with 15 ml of sulfuric acid and 2 g of potassium pyrosulfate as described in Part I. Slowly and cautiously, add 20 ml of 1:1 hydrochloric acid, dilute to 100 ml with distilled water and boil for 1–2 min while stirring with a glass rod. Dissolve the lead sulfate while heating by adding a slight excess of 1:1 hydrochloric acid so that during the subsequent cooling, the precipitate will either be absent or negligible; if lead is present in very low percentages hydrochloric acid need not be added at all, while 50 ml of the acid are required for about 0.2 g of lead and 70 ml for about 0.8 g of lead. To the hot solution ($85-95^{\circ}$) then add 0.3 g of hydrazine dihydrochloride; dilute as much as required to keep the electrodes submerged and electrolyze at -0.30 V vs. S.C.E., starting at a more negative cathode potential so as not to exceed, initially, a current intensity of 0.6–0.8 A. During electrolysis, while the solution cools, some lead sulfate may deposit on the gauze but this does not interfere. This preliminary electrolysis serves to separate antimony and part of the copper present; when it is ended, wash the electrodes and the deposited lead sulfate, if any, well with distilled water. Oxidize the solution with potassium permanganate powder up to pink or yellow and then decolorize with some hydrazine dihydrochloride. Add 8 g of tartaric acid and then concentrated ammonia to give pH 7–7.2: a small residue may remain undissolved (apparently due to the presence of manganese) but it does not interfere since it re-dissolves during electrolysis. Then add 2 g of succinic acid and 1 g of hydrazine dihydrochloride, adjust the pH with ammonia and 1:1 hydrochloric acid to about 5 and deposit lead at a final cathode potential of -0.65 V vs. S.C.E. If lead is greater than 0.2 g, adjust the pH to 7–7.2, deposit lead at a final cathode potential of -0.65 V vs. S.C.E. and then correct the pH to about 5 as described in Part I.

To check the pH narrow range test papers will do. Neutralization with ammonia heats the solution but it may be electrolyzed even if warm.

After electrolysis of lead, acidify the solution with 40 ml of concentrated hydrochloric acid, add 0.3 g of hydrazine dihydrochloride and deposit tin at -0.65 V vs. S.C.E. according to the procedure outlined previously¹.

RESULTS

The method described was first tested on sample No. 54c (N.B.S.), the composition of which is given in Table I, and the percentages found, indicated in Table III, are mostly within $\pm 0.05\%$, the maximum deviation being $\pm 0.1\%$.

Some synthetic solutions were then prepared with the addition of lead and antimony — as metals — to the No. 54c sample, as shown in Table IV. In this case results were again excellent.

TABLE III
SAMPLE NO. 54C — TIN-BASE BEARING METAL

Sn %				
86.35	86.20	86.24	86.33	86.20
86.32	86.29	86.24	86.26	86.34
86.22	86.24	86.25	86.25	86.31
86.33	86.29	86.36	86.38	

TABLE IV
DETERMINATION OF TIN IN SYNTHETIC SOLUTION

No.	Sb	Pb	54c	Sn	Sn
	Weighed g	Weighed g	Weighed g	Calculated g	Found g
1	0.0980	0.2031	0.8177	0.7056	0.7052
2	0.1012	0.2068	0.8230	0.7102	0.7108
3	0.0993	0.3039	0.8302	0.7164	0.7159
4	0.1028	0.2067	0.8225	0.7097	0.7086
5	0.1015	0.1970	0.8238	0.7108	0.7108
6	0.1017	0.2168	0.8047	0.6943	0.6946
7	0.1048	0.1108	0.8010	0.6911	0.6911
8	0.1026	0.2345	0.8048	0.6945	0.6944
9	0.1040	0.1041	0.8223	0.7096	0.7097
10	0.1036	0.1031	0.8057	0.6952	0.6952

TABLE V
MIXED SAMPLES, DETERMINATION OF TIN

No.	53d	54c	Sb	Cu	Sn	Sn
	Weighed g	Weighed g	Weighed g	Added g	Calculated g	Found g
1	1.000	—	—	—	0.0494	0.0489
2	1.000	—	0.0503	—	0.0494	0.0490
3	1.000	—	0.1049	—	0.0494	0.0491
4	1.000	—	0.0508	0.0500	0.0494	0.0487
5	0.1951	0.6994	0.0977	—	0.6127	0.6133
6	0.5040	0.5025	0.1040	—	0.4585	0.4586
7	0.5004	0.5031	0.1004	—	0.4589	0.4581
8	0.7549	0.2482	0.1042	—	0.2515	0.2510
9	0.7031	0.2392	0.1006	—	0.2406	0.2505
10	0.9002	0.1003	0.1033	—	0.1310	0.1309
11	0.8979	0.1016	0.0769	—	0.1319	0.1318

To test the method on lead-base alloys, recourse was had to mixtures of samples No. 54c and 53d to which were also added antimony as metal before sample dissolution, and copper as copper sulfate pentahydrate after dissolution and dilution. In all cases, as shown by Table V, the results were satisfactory. The composition of sample No. 53d is as follows: Sb 9.92%, Sn 4.94%, Cu 0.268%, Bi 0.135%, As 0.045%, Ni 0.02%, Pb (by difference) 84.69%.

The method described offers remarkable investigation possibilities for lead- and tin-base alloys. According to SCHOCH AND BROWN³ antimony may be separated from copper, in a hydrochloric acid solution, by electrolyzing at 70° at a cathode potential of -0.40 V vs. S.C.E. On the other hand, at 70°-80° and in the presence of hydrochloric acid, a lot of lead sulfate may be kept in the solution. It is therefore probable that further investigations might lead to a new procedure for the successive and quantitative electrolytic separation of antimony, copper, lead and tin.

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SUMMARY

Electrodeposition methods are described for the determination of antimony, copper and lead in tin-base alloys and a method for the determination of tin by controlled-potential electrolysis is discussed.

RÉSUMÉ

Une méthode est décrite pour le dosage de l'étain par électrolyse à potentiel contrôlé. L'auteur a examiné également le dosage de l'antimoine, du cuivre et du plomb dans des alliages à base d'étain.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Zinn, Antimon, Kupfer und Blei in Zinnlegierungen durch Elektrolyse mit kontrolliertem Potential.

REFERENCES

- ¹ B. ALFONSI, *Anal. Chim. Acta*, 25 (1961) 274.
- ² B. ALFONSI, *Anal. Chim. Acta*, 22 (1960) 431.
- ³ E. P. SCHOCH AND D. G. BROWN, *J. Am. Chem. Soc.*, 38 (1916) 1660.

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POLAROMETRIC DETERMINATION OF AROMATIC ALDEHYDES
WITH 2,4-DINITROPHENYLHYDRAZINE

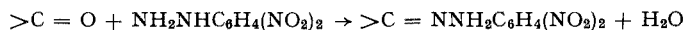
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Several indirect analytical methods are available for the determination of carbonyl compounds, most of which utilize additive or condensation properties of these compounds. Direct volumetric determinations are less common, because carbonyl compounds are mostly neutral substances, which eliminates the possibility of acid-base titrations, and oxidation-reduction reactions with common agents occur too slowly to be useful for direct titrations. We have already reviewed the possibilities for the titration of carbonyl compounds¹. An evaluation of analytical methods from a unified theoretical point of view has recently been given by BUDĚŠŇSKÝ².

2,4-Dinitrophenylhydrazine (DNPH) is most frequently used for the determination of carbonyl compounds. Its solutions in 2 *N* hydrochloric acid are stable, and with a number of carbonyl compounds it forms readily crystallising 2,4-dinitrophenylhydrazones:



In an indirect determination, in which the sample was treated with an excess of this reagent, which was then determined oxidimetrically³ with chloramine-T we observed that some aromatic aldehydes reacted with DNPH so rapidly that this reaction could be used for a direct titration.

ZOBOV, LIALIKOV *et al.*^{4,5} have studied this problem and titrated certain carbonyl compounds with DNPH solution using a polarometric end-point. The results of the individual determinations were, however, subject to large errors, and the smooth course of titration was disturbed by current variations, which the authors think are due to fine particles of the 2,4-dinitrophenylhydrazones influencing the mercury dropping electrode. To eliminate interfering effects these authors used an ultrasonic system in their later work⁶. In the present paper we explain the causes of the unfavourable course of polarometric titrations encountered previously and we describe the conditions under which the direct polarometric titration of aromatic aldehydes by DNPH solution is successful.

EXPERIMENTAL PART

Reagents

A 0.01 *M* 2,4-dinitrophenylhydrazine solution (A.R. grade, Lachema) was prepared by dissolving 1.98 g of the substance in 1 l of 2 *N* hydrochloric acid. After two days

the undissolved residue was filtered off and the factor was determined by titration with chloramine-T in the presence of potassium bromide⁷.

96% Ethanol extract of carbonyls was obtained by distillation from a mixture of 10 parts of pure ethanol and 1 part of 0.01 *M* DNPH solution in 2 *N* hydrochloric acid after boiling for 4 h.

Hydrochloric acid, thymol, gelatine (A.R. grade, Merck or Lachema), testosterone propionate (Spofa), and progesterone (Ciba) were used. Other investigated carbonyl compounds were of the highest available purity*, and their purity was checked gravimetrically⁸ or by titration^{8,9}.

Apparatus

Polarometric titrations were carried out with the conventional apparatus, using a mercury dropping electrode and a saturated calomel electrode with a cellophane diaphragm. The current was recorded by a microammeter having a range of 0 to 20 μ A. Titrations were carried out in a conical vessel and oxygen was removed from the solution before as well as during the titration by bubbling with nitrogen. A 5-ml burette calibrated at 0.01 ml intervals was used.

Polarographic measurements were carried out on a type PO-4 Polariter instrument, manufactured by Radiometer, Denmark.

RESULTS

For the fundamental experiments we chose vanillin, which is easily obtainable in a pure state and is readily soluble in water. Preliminary experiments showed that the reproducibility of the polarometric titration as well as the accuracy and precision of the determination were influenced by a number of factors, especially the potential used (EMF) and the sorption of the reagent on the precipitate.

(i) Influence of the potential used

This was studied by the titration of 3 mg of vanillin in a volume of 15 ml of 2 *N* hydrochloric acid. In the polarometric titration the reduction of the aldehydic group cannot be used, as it follows the hydrogen wave. On the other hand in this medium the reduction of DNPH caused the appearance of a well developed polarographic

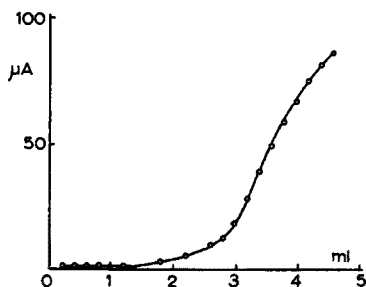


Fig. 1. Titration of 3.010 mg of vanillin in 15 ml 2 *N* HCl with 0.01 *M* DNPH solution in 2 *N* HCl.

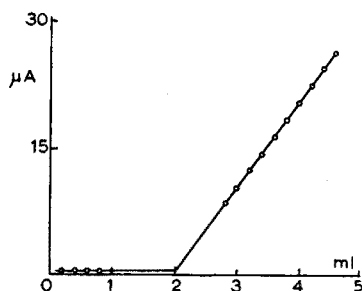


Fig. 2. Titration of 3.010 mg of vanillin in 15 ml 2 *N* HCl with 0.01 *M* DNPH solution in 2 *N* HCl, in the presence of thymol.

* We thank Mr. J. DOLNÍK of the National Enterprise Aroma Prague, for letting us have a number of carbonyl compounds.

wave (i_e from -0.3 V to -0.9 V *vs.* S.C.E.). When the titration was carried out at a potential of -0.7 V (*vs.* S.C.E.) large current variations were observed. Polarographic investigation showed that the precipitate of vanillin 2,4-dinitrophenylhydrazone formed was reduced on the mercury drop electrode at potentials of -0.65 V to -1.0 V (*vs.* S.C.E.). Thus it was possible to explain the current variations in titrations with a potential in this range. In further titrations we therefore used a potential of -0.4 to -0.6 V (*vs.* S.C.E.). Under these conditions it was possible to record reliably the value of the limiting current, but this value did not increase, after reaching the point of equivalence, linearly with increasing DNPH concentration — the straight line became curved (Fig. 1).

(ii) *Investigation of the sorption of the reagent*

That the curvature of the course of the limiting current may be ascribed to sorption of DNPH on the precipitate was proved by a simple experiment:

A. To 15 ml of 2 *N* hydrochloric acid a 0.01-*M* DNPH solution in this 2 *N* acid was added in 0.2-ml portions. Current values were recorded each time after 3 min of bubbling nitrogen through the solution. With increasing reagent concentration the current increased linearly.

B. When this experiment was carried out under the same conditions in the presence of a precipitate corresponding to 3 mg of vanillin the current did not increase linearly, just as in the titration proper.

Indirect proof of the sorption was provided by the fact that addition of some surfactants or a change in the medium eliminated the curvature of the line. When the titration was carried out in the presence of gelatine (0.01%–0.05%) then the current increased linearly with increasing reagent concentration. The obtained results, however, possessed a large negative error (Table I), which we have not been able to explain.

TABLE I

INFLUENCE OF GELATINE CONCENTRATION ON THE TITRATION OF VANILLIN

3.051 mg of vanillin titrated with a 0.01-*M* DNPH solution in 2 *N* HCl; potential -0.5 V *vs.* S.C.E.
Initial volume 15 ml 2 *N* HCl

Gelatine concentration at the beginning of the titration %	Vanillin found mg	Deviation %
0.050	2.932	-3.9
0.030	2.919	-4.4
0.015	3.005	-1.5
0.010	2.902	-4.9

Very good and reproducible results were obtained on adding thymol to the titrated solution in a minimum concentration of 0.002% provided that a potential of -0.4 V to -0.6 V (*vs.* S.C.E.) was used. At more negative potentials difficulties were again found owing to reduction of the precipitate. These difficulties could be eliminated by increasing the thymol concentration (0.02%).

In studying the influence of the ethanol concentration on the titration it was found that when its concentration was about 20% neither sorption of the reagent nor

reduction of the precipitate (in a potential range of -0.4 V to -0.9 V vs. S.C.E.) occurred.

These results were proved by polarographic investigation.

(iii) *Influence of the conditions of the titration*

Since reactions of carbonyl compounds with DNPH take place rapidly in acid medium, and since the reagent itself is very stable in 2 N hydrochloric acid, we first studied the influence of the acid concentration on the rate and stoichiometry of the titration of vanillin. The initial concentration in the titrated solution was 0 to 5 N hydrochloric acid, and the thymol concentration was always 0.02%. Throughout the concentration range the titration was quantitative (Table II). In a medium of 0.5 to

TABLE II

INFLUENCE OF THE CONCENTRATION OF HYDROCHLORIC ACID ON THE TITRATION OF VANILLIN
3.159 mg of the substance titrated with 0.01 M DNPH solution in 2 N HCl; potential -0.5 V vs. S.C.E., thymol concentration 0.02% v/v

Initial HCl concentration N	Vanillin found (mg)	Deviation %	Notes
0.00	3.044	-3.7	slow stabilisation of the current at first
0.25	3.108	-1.7	
0.50	3.219	+1.8	
1.00	3.124	-1.2	
2.00	3.170	+0.3	slow stabilisation of the current at first
3.00	3.170	+0.3	
4.00	3.091	-2.2	
5.00	3.140	-0.7	

TABLE III

INFLUENCE OF ETHANOL CONCENTRATION ON THE TITRATION OF VANILLIN
3.063 mg of vanillin titrated with 0.01 M DNPH solution in 2 N HCl, potential -0.5 V vs. S.C.E., initial volume 15 ml 2 N HCl

Initial ethanol concentration %	Vanillin found mg	Deviation %
60	3.035	-0.9
40	3.018	-1.4
30	3.048	-0.5
20	3.032	-1.0
15	2.989	-2.4
10	2.959	-3.4

3 N hydrochloric acid it was possible to record current values after 3 min bubbling with nitrogen, whereas above or below this range it was necessary to wait for 7 to 10 min (especially at the beginning of the titration).

Because most carbonyl compounds are insoluble in water the influence of ethanol on the course of the titration of vanillin was further studied. It was concluded (see

Table III) that at an initial concentration of 20 to 60% ethanol (the titrated solution did not contain thymol nor gelatine) the titration was rapid and quantitative. The current value could be recorded after only 3 min agitation of the solution. If the initial ethanol concentration was less than 20%, results were erratic because of sorption of the reagent on the precipitate. The quantitative course of the titration was proved by titration of 1 to 5 mg of vanillin in 15 ml of solution.

Three modifications of the procedure for the determination of aromatic aldehydes have been worked out, the choice of which depends partly on the solubility of the aldehyde and partly on the solubility in ethanol of the 2,4-dinitrophenylhydrazone formed.

PROCEDURE

(A) To an amount of the substance corresponding to about 1 to 3 ml of 0.01 *M* aqueous solution of the aldehyde 2.5 ml of concentrated hydrochloric acid and 6 to 7 ml of 0.05% aqueous thymol solution are added. The solution is diluted to 15 ml with distilled water, nitrogen is bubbled through for 5 min and the solution is then titrated with a 0.01-*M* DNPH solution in 2 *N* hydrochloric acid. After each addition of the reagent (0.2 ml) the solution and the precipitate formed are agitated for about 3 min by bubbling nitrogen (until stabilisation of the current value). The titration is carried out at a potential of -0.4 V to -0.8 V (vs. S.C.E.). The recorded current values are corrected for the volume of the titrated solution.

(B) An amount of the substance corresponding to 1 to 3 ml of 0.01 *M* solution is dissolved in at least 5 ml of ethanol, 2.5 ml of concentrated hydrochloric acid are added, the solution is diluted to 15 ml and the procedure is continued as described under A.

(C) An amount corresponding to 1 to 3 ml of 0.01 *M* solution is dissolved in the least possible amount of ethanol, 6 to 7 ml of 0.05% thymol solution and 2.5 ml of concentrated hydrochloric acid are added, the solution is diluted to 15 ml and the procedure is continued as described under A.

Fig. 2 shows an example of the graph of the titration of vanillin according to procedure A.

DISCUSSION OF RESULTS

From the results mentioned above, the main problem in the polarometric determination of carbonyl groups obviously consists of the "irregularities" appearing in the diffusion current of the titrant — DNPH. Another question is the non-linear increase in the current in titrations carried out in a medium of 2 *N* hydrochloric acid.

The polarographic investigation showed that in titrating with an incorrectly chosen potential, the diffusion current not only of the titrant, but also of the 2,4-dinitrophenylhydrazone precipitate formed, may exert an influence. The potential at which the reduction of the precipitate on the mercury drop electrode makes itself felt is influenced not only by the kind of substance which is subjected to condensation, but also by the composition of the solution in which the reaction takes place; this has been observed in similar cases¹⁰. The reduction current of the suspension is far higher when the suspension is agitated, e.g. by electromagnetic stirring, than when the suspension is motionless, when the reduction is conditioned by chance impacts of the particles on the electrode. In our case the precipitate settles rather slowly, so that its reduction

would stop a long time after the suspension had ceased to move. A comparison of the half-wave potentials of DNPH and vanillin with the potential of the maximum of the corresponding hydrazone shows that in the reduction of the suspension the nitro groups are reduced. The so-called variation of the current observed by ZOBOV AND LIALIKOV⁴⁻⁶ is thus explained. A polarographic investigation of the most suitable potential is therefore one of the conditions for obtaining quantitative results in further studies of these condensation reactions.

A second but no less important factor in the correct course of the titration is an elimination of the irregular increase in the current after the equivalence point has been reached. From a number of direct and indirect experiments, it seems that this effect may be explained by sorption of the titrant on the precipitate of the 2,4-dinitrophenylhydrazone, owing to intersurface forces, given by the character and composition of the phases touching each other. This sorption may be eliminated by the addition of gelatine (lower results), thymol or ethanol to the sample solution. These substances in sufficient concentration also eliminate the reduction of the 2,4-dinitrophenylhydrazone precipitate on the mercury dropping electrode.

The proposed polarometric determination of carbonyl groups will not, of course, be as universally applicable as the indirect methods in which a small excess of the reagent may be used, possibly at higher temperatures. The rapidity of the reaction, which is a condition of the direct titration, is influenced not only by the structure of the substance itself^{3,9,11} but also by the medium in which the reaction occurs. From the

TABLE IV
REVIEW OF COMPOUNDS DETERMINED

Compound ^a	Amounts determined	Standard deviation, calculated from 10 determinations %	Procedure
vanillin (1.521)	1.532-4.667	0.85	A
	1.532-4.667	0.89	B
	1.532-4.667	0.61	C
benzaldehyde (1.061)	1.103-3.161	0.84	
3-ethoxy-4-hydroxybenzaldehyde (1.661)	1.743-4.722	0.50	A
<i>o</i> -nitrobenzaldehyde (1.511)	1.487-4.512	0.75	B ^b
<i>p</i> -nitrobenzaldehyde (1.511)	1.509-4.571	0.66	B ^b
cuminaldehyde (1.482)	1.533-4.375	1.08	B
piperonal (1.501)	1.482-4.522	1.45	B
protocatechuic aldehyde (1.381)	1.352-4.115	0.91	C
cinnamic aldehyde (1.321)	1.277-4.089	0.70	B ^b
salicylaldehyde (1.221)	1.270-3.582	0.86	B

^a Figures in brackets denote how many mg of the compound correspond to 1 ml 0.01 M DNPH.

^b Under the conditions specified the compound to be determined is also polarographically reduced and thus the V-shaped curve of the titration is obtained (reduction of nitro-group or double bond respectively).

results it is clear that a 2-N hydrochloric acid medium is well suited to the direct titration, particularly since the titrant is stable in this solution. Therefore substances soluble in water are best determined according to procedure A.

Ethanol must be used to dissolve certain compounds, but the hydrazones formed may then be partly soluble, which unfavourably influences the course of the titration. In such a case the substance is dissolved in the least possible amount of ethanol, and the determination is carried out according to procedure C. If the concentration of ethanol necessary to hold the substance in solution is sufficient to prevent sorption of the reagent on the precipitate, the analysis is carried out according to procedure B. Examples of determinations of aromatic aldehydes according to the different procedures are given in Table IV.

As can be seen from this table, the proposed method is particularly suitable for the determination of aromatic aldehydes, which react easily with DNPH. The reactivity of aromatic aldehydes is of course influenced by the substituents on the aromatic ring, so that the method is not universal even for aromatic compounds. For instance we have not succeeded in determining *p*-aminobenzaldehyde.

In experiments on the determination of ketones (*o*-chloroacetophenone, benzoin, testosterone, testosterone propionate, progesterone) and aliphatic aldehydes (7-hydroxycitronellal, citral, undecylaldehyde, formaldehyde and acetaldehyde) we have not obtained satisfactory results, partly because of the low reaction rate, and partly owing to the large solubility of the 2,4-dinitrophenylhydrazones formed.

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SUMMARY

In the polarometric titration of aromatic aldehydes with a 2,4-dinitrophenylhydrazine solution, the sorption of the reagent on the hydrazone precipitate and the reduction of this precipitate at the mercury dropping electrode have been proved. These effects may be eliminated by the addition of thymol or ethanol to the sample solution, so that most aromatic aldehydes can be determined.

RÉSUMÉ

Une méthode est proposée pour le titrage polarométrique des aldéhydes aromatiques, au moyen de dinitro-2,4-phénylhydrazine.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von aromatischen Aldehyden durch polarometrische Titration mit 2,4-Dinitrophenylhydrazinlösung.

REFERENCES

- 1 A. BERKA, *Chemie (Prague)*, 9 (1957) 528.
- 2 B. BUDĚŠÍNSKÝ, *Chem. listy*, 54 (1960) 916.
- 3 A. BERKA AND J. ZÝKA, *Chem. listy*, 50 (1956) 831.
- 4 E. V. ZOBOV AND J. C. LIALIKOV, *Zhur. Anal. Khim.*, 11 (1956) 459.
- 5 E. V. ZOBOV AND J. C. LIALIKOV, *Izvest. Akad. Nauk Turkmen. S.S.R.*, 1 (1958) 28.
- 6 E. V. ZOBOV, J. C. LIALIKOV AND O. M. MUCHAMMEDNAZAROVA, *Izvest. Akad. Nauk Turkmen. S.S.R.*, 4 (1959) 45.
- 7 A. BERKA AND J. ZÝKA, *Českoslov. farm.*, 5 (1956) 335.
- 8 M. A. IDDLES AND C. E. JACKSON, *Ind. Eng. Chem., Anal. Ed.*, 6 (1934) 454.
- 9 W. SCHÖNIGER, H. LIEB AND R. GASSNER, *Mikrochim. Acta*, (1953) 435.
- 10 K. MICKA, *Chem. listy*, 49 (1955) 1144; *Collection Czechoslov. Chem. Commun.*, 21 (1956) 647.
- 11 J. B. CONANT AND P. D. BARTLETT, *J. Am. Chem. Soc.*, 54 (1932) 2881.

RAPID DETERMINATION OF ALUMINIUM IN BERYLLIUM METAL BY CATHODE RAY POLAROGRAPHY

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INTRODUCTION

Despite the rapidly increasing use of beryllium in the atomic energy field, no completely satisfactory procedure has been published for the determination of aluminium in beryllium metal although it is one of the impurities most frequently analysed for. The principal methods in use appear to be the 8-hydroxyquinoline gravimetric procedure^{1,2}, a spectrographic procedure³, and a polarographic procedure using Solochrome Violet RS (5-sulpho-2-hydroxybenzene-azo-2-naphthol)⁴. The gravimetric method suffers from the disadvantage of requiring an inconveniently large sample, whilst the polarographic method as described by PERKINS AND REYNOLDS⁴ is too lengthy for routine use. PERKINS AND REYNOLDS found that beryllium tended to precipitate at the pH normally used for the determination of aluminium with Solochrome Violet RS, but even when precipitation was avoided, a considerable depression of the aluminium-dye reduction step occurred. To overcome this effect these workers carried out a preliminary separation of aluminium from the bulk of the beryllium by a 8-hydroxyquinoline extraction.

The dye Superchrome Garnet Y (5-sulpho-2',4',2-trihydroxyazobenzene, C.I. 168) is known to react with aluminium at a lower pH than Solochrome Violet RS⁵, and when used in conjunction with a highly sensitive cathode ray polarograph, the depressing effect of beryllium is minimized and the necessity of separating aluminium is obviated. A direct method is described for the determination of aluminium in beryllium metal after a rapid mercury cathode electrolysis to remove iron and other impurities. The sample weight required is only 100 mg, and a single determination may be completed in little over an hour.

The reaction of aluminium with Superchrome Garnet Y in the presence of beryllium

Superchrome Garnet Y, at concentrations below $2 \cdot 10^{-5}$ M, exhibits sharp, well-defined "adsorption-reduction" peaks on the cathode ray polarograph⁶ (Fig. 1). In the presence of aluminium in acetate buffers, the dye peak is reduced in height, and a new peak appears at a more negative potential, its height being proportional to the aluminium concentration (Fig. 2). At pH 3.40 the sensitivity is $6.33 \mu\text{A}/\mu\text{g Al/ml}$. Although beryllium does not produce a discrete reduction peak, relatively high concentrations cause a depression of the aluminium-dye peak (Fig. 3). However, it was found that at a constant beryllium concentration and a favourable pH, a linear relationship was still obtained between peak height and aluminium concentration. A pH range of 3.4-3.5 is optimum for the determination, since the sensitivity decreases

rapidly at lower pH values, whilst at higher values the peak height is not proportional to the aluminium concentration.

It may be seen from Fig. 3 that for an error of less than 2% in the aluminium determination the sample weight of beryllium metal should be controlled so that the final beryllium concentration is within $\pm 3\%$ of that used in the calibration curve. If a sample weight outside this range is inadvertently taken, an approximate result may be obtained by reference to a depression factor (ratio of peak height in the presence of beryllium to peak height in the absence of beryllium) curve such as Fig. 3.

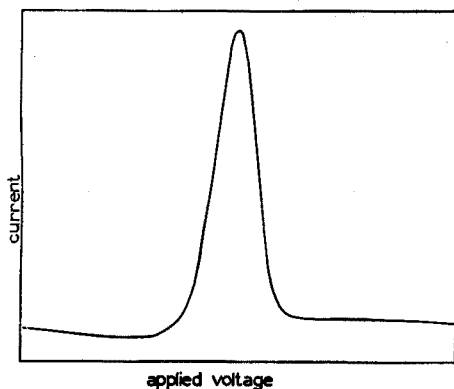


Fig. 1. Oscillogram of Superchrome Garnet Y in an acetate buffer of pH 3.40. Dye concentration = $1 \cdot 10^{-5} M$; peak height = $5.1 \mu A$; peak potential = $-0.30 V$ vs. Hg pool.

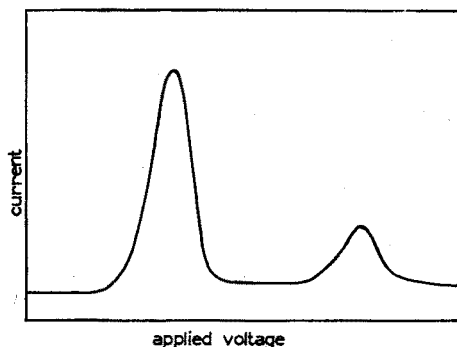


Fig. 2. Oscillogram of Superchrome Garnet Y, plus aluminium in an acetate buffer of pH 3.40. Dye concentration = $1 \cdot 10^{-5} M$; aluminium concentration = $6 \cdot 10^{-6} M$; 1st peak height = $3.8 \mu A$, 1st peak potential = $-0.30 V$ vs. Hg pool; 2nd peak height = $1.0 \mu A$, 2nd peak potential = $-0.51 V$ vs. Hg pool.

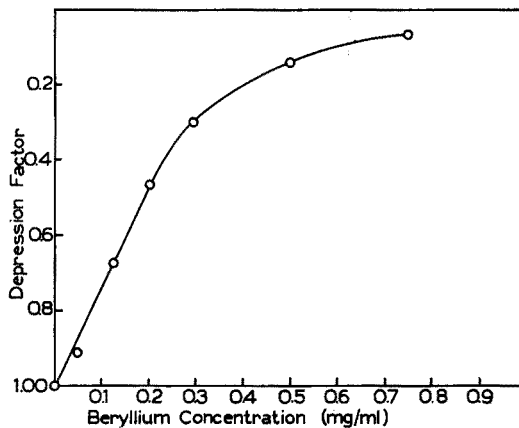


Fig. 3. Depression by beryllium of the aluminium-dye reduction peak.

EXPERIMENTAL

Apparatus

Polarograph: The linear-sweep cathode ray polarograph was supplied by Southern Instruments Computer Division, Surrey, England. This instrument has a sweep rate

of 0.25 V/sec and a delay period of 5 sec. The dropping mercury capillary characteristics were $m = 1.14$ mg/sec, $t = 6.5$ sec (-0.5 V vs. pool). All measurements were made in a thermostated bath at $25.0 \pm 0.2^\circ$.

Mercury cathode cell: The small "constant-current" mercury cathode cell has been described previously⁷.

Reagents

Superchrome Garnet Y: The crude dye was prepared as described by COONEY AND SAYLOR⁵, then purified by a double recrystallization from water. The purity of the final product was not determined.

Acetate buffer: This was prepared by mixing 500 ml of 1 *M* ammonium acetate (from reagent grade ammonia and acetic acid) with 470 ml of 1 *M* hydrochloric acid, and adjusting to pH 3.40 ± 0.05 on a pH meter. The buffer should be stored in a polythene container.

Beryllium metal standard: "Spec-pure" beryllium from Johnson, Matthey and Co. Ltd., London, was used for calibration purposes, and was found to contain 120 p.p.m. of aluminium. The water used throughout was demineralised, then distilled from quartz and collected and stored in a polythene container.

Recommended procedure

Weigh accurately 100 ± 3 mg of fine beryllium metal filings. Dissolve by warming with 16 ± 1 ml of 1 *N* sulphuric acid. Dilute to 25 ml in a volumetric flask. Transfer about 10 ml of the sample solution to the dry mercury cathode cell and electrolyse at 9 V (0.5 A) for 15–20 min. Remove the air condenser and, with current still flowing, withdraw about 5 ml of the solution. Cool to room temperature, take a 2-ml aliquot and neutralize to pH 3–4 with 1 *N* ammonium hydroxide, using indicator paper. Transfer to a 25-ml volumetric flask, add 5 ml of acetate buffer (pH 3.40), 5 ml of a $5 \cdot 10^{-5}$ *M* dye solution, and dilute to volume. Heat at 70° in a water bath for 10–15 min, cool, and transfer a portion to the polarographic cell. After deaeration, measure the peak height of the wave at -0.51 V vs. Hg pool, using a starting potential of -0.32 V. A blank must be carefully carried through the procedure, and the measured peak height multiplied by the depression factor to obtain a true blank peak height.

Construction of calibration curve

A calibration curve was obtained by "spiking" 100-mg portions of "spec-pure" beryllium metal filings with known amounts of aluminium, and carrying through the procedure described above, but omitting the mercury cathode electrolysis step. The relevant depression factor was determined by comparing the slope of this line with that obtained in the absence of beryllium. The minimum concentration of aluminium measurable is governed mainly by the magnitude of the blank, and, using the recommended procedure, is equivalent to about 20 p.p.m. of aluminium in beryllium.

Study of interferences

The concentration of aluminium in nuclear-grade beryllium metal is usually in the range 100–2,000 p.p.m. Other impurities commonly found are¹ Ag, B, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb and Zn. With the exception of iron, these impurities are normally present at a lower concentration than aluminium, but even small amounts

of nickel, lead and molybdenum interfere with the direct determination of aluminium using Superchrome Garnet Y. A mercury cathode electrolysis employing the cell described was found to rapidly remove all interfering elements from a 0.2 *N* sulphuric acid electrolyte.

TABLE I
RECOVERY OF ALUMINIUM FROM BERYLLIUM USING SUGGESTED PROCEDURE

<i>Al added</i> (μg)	<i>Al found</i> (μg)	% recovery
nil	12	—
10	20	91
20	31	97
50	59	94
75	85	97
100	117	105
150	162	100
200	208	98

Each solution contained 0.100 ± 0.001 g of "spec-pure" beryllium metal, plus 500 μg of each of the following elements: Ag, B, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb and Zn.

Analysis of synthetic samples

A series of solutions containing 100 mg of "spec-pure" beryllium metal was "spiked" with known amounts of aluminium, and 500 μg of each of the 14 impurities mentioned above. These solutions were then analysed for aluminium by the recommended procedure; the results are tabulated in Table I.

SUMMARY

A rapid method is presented for the determination of aluminium in beryllium metal by cathode ray polarography using the dye Superchrome Garnet Y. A mercury cathode electrolysis is used to remove heavy metal impurities, but the need for a separation of aluminium from beryllium is avoided. A single determination requiring a 100-mg sample may be completed in little over an hour, with normal polarographic precision.

RÉSUMÉ

Une méthode rapide est proposée pour le dosage de l'aluminium dans le béryllium, par polarographie à rayons cathodiques, au moyen du colorant "Superchrome Garnet Y". Le fer et d'autres impuretés doivent être éliminés au préalable par électrolyse sur cathode de mercure. La séparation aluminium-béryllium peut être évitée.

ZUSAMMENFASSUNG

Beschreibung einer raschen Methode zur Bestimmung von Aluminium in Beryllium durch Kathodenstrahlenpolarographie unter Verwendung des Farbstoffes Superchrom Garnet Y. Störende Schwermetalle werden durch Elektrolyse mit einer Quecksilberkathode entfernt. Eine Trennung des Aluminiums von Beryllium ist nicht notwendig.

REFERENCES

- 1 E. S. MELICK, U.S.A.E.C. report TID-7555 (1958).
- 2 U.S.A.E.C. report 71D-7015, section 1 (1958).
- 3 L. E. SMYTHE AND R. N. WHITTEM, *Analyst*, 86 (1961) 83.
- 4 M. PERKINS AND G. F. REYNOLDS, *Anal. Chim. Acta*, 18 (1958) 625.
- 5 B. A. COONEY AND J. H. SAYLOR, *Anal. Chim. Acta*, 21 (1959) 276.
- 6 T. M. FLORENCE AND L. E. SMYTHE, 4th Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, U.S.A., 1960, U.S.A.E.C. report TID-7606.
- 7 T. M. FLORENCE, *Anal. Chim. Acta*, 21 (1959) 418.

EINFACHES DESTILLATIONSVERFAHREN ZUR TITRIMETRISCHEN BESTIMMUNG VON KOHLENDIOXYD

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Die beiden grundlegenden Probleme der Kohlendioxydbestimmung bestehen in der Isolierung und Messung des Kohlendioxyds. Vor kurzem beschäftigten sich BELCHER, THOMSON UND WEST¹ eingehend mit dieser Frage. Genannte Autoren fingen das bei der Verbrennung organischer Stoffe entstehende Kohlendioxyd in Bariumhydroxydlösung auf und titrierten den Überschuss des Bariumhydroxyds mit Säure zurück. Die Ergebnisse ihrer Versuche lassen sich kurz wie folgt zusammenfassen: Die Absorption des Kohlendioxyds ist ein langsamer Prozess und das kohlendioxydhaltige Gasmisch muss in Form sehr kleiner Bläschen und in langsamem Strom durch die absorbierende Flüssigkeit geleitet werden. Die quantitative Überführung des Inhalts des Absorptionsgefäßes in den Titrierkolben bedeutet dabei ein besonderes Problem. Den auf die Aufnahme der Luftkohlenensäure zurückführbaren Fehler schalten die genannten Autoren mit unter identischen Verhältnissen durchgeführten blinden Proben aus.

Mit dem Problem der Titration beschäftigten sich mehrere Forscher, die zitierte Mitteilung gibt einen guten Überblick über die erreichten Ergebnisse. Um die bei der Rücktitration des Bariumhydroxydüberschusses durch Adsorption entstandenen Fehler auszuschalten, wird vorgeschlagen, die Messlösung in kleinen Portionen zuzugeben.

SCHULEK *et al.*² saugten das Kohlendioxyd in einen Bariumhydroxydlösung enthaltenden evakuierten Kolben. Der Überschuss des Bariumhydroxyds wurde dann nach mehrmaligem Umschütteln und entsprechender Wartezeit unter Anwendung von Pentan als Sperrflüssigkeit zurücktitriert. Mit diesem Verfahren konnte einesteils der auf die unvollständige Absorption des Kohlendioxyds zurückführbare Fehler und anderenteils die Umspülung der zu titrierenden Flüssigkeit und die störende Wirkung der Luftkohlenensäure ausgeschaltet werden. Das Verfahren erwies sich als geeignet zur Bestimmung des Kohlendioxydgehalts von Karbonaten und des bei der Verbrennung organischer Stoffe gebildeten Kohlendioxyds.

Zur Isolierung des bei verschiedenen Reaktionen gebildeten Kohlendioxyds schien uns die Anwendung des Destillationsprinzips vorteilhaft zu sein. Offen stand dabei lediglich die Frage, unter welchen Bedingungen die vollkommene Absorption des Kohlendioxyds in der als Vorlage verwendeten Bariumhydroxydlösung unter gleichzeitiger Fernhaltung des eventuell vorhandenen Kohlendioxydgehalts der Atmosphäre gewährleistet ist.

Zwecks Ausschaltung der störenden Wirkung der Luftkohlenensäure wird die Barium-

hydroxydlösung mit Pentan überschichtet. Unter solchen Bedingungen ist die störende Wirkung auf ein Mindestmass herabgesetzt. Das Pentan bedeckt die Lösungsoberfläche nicht nur als Flüssigkeit, sondern verdampft infolge seiner Flüchtigkeit auch teilweise, füllt nach Ausdrücken der Luft mit den Dämpfen den gesamten Luftraum des Kolbens vollständig aus und hält die Luftkohlendensäure auf diese Weise auch von der an der Kolbenwand haftenden Bariumhydroxydlösung fern. Absorption und Titration erfolgen in demselben Gefäss, ein Umstand, der hinsichtlich der Genauigkeit der Messung einen besonderen Vorteil bedeutet.

Die Durchführung der Destillation weicht von den allgemein bekannten Methoden darin ab, dass bei diesem Verfahren keine Bläschen durch die absorbierende Lösung passieren können. Diese Einschränkung muss streng befolgt werden, damit mit den aus der Lösung austretenden Gasbläschen auch keine Kohlensäure verloren geht. Dieses Prinzip wurde durch WINKLER³ bei der Trennung geringer Bromidmengen durch destillieren in Form von elementarem Brom sowie durch SCHULEK UND VAS-
TAGH⁴ zur Destillation des Ammoniaks verwendet.

Diese beschriebenen Verfahren mussten zur Bestimmung der Kohlensäure durch Auskochen derart verfeinert werden, dass die vollkommene Absorption der Kohlensäure gesichert werden konnte. Dies ist durch Einführung bzw. Ausarbeiten des Prinzips der stufenweisen Abkühlung der Dämpfe erreicht worden.

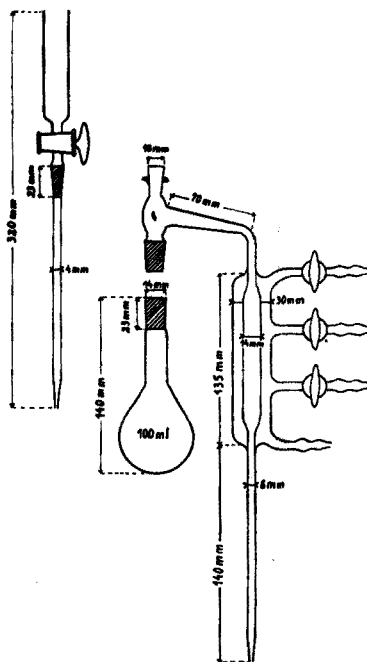


Fig. 1.

Zu diesem Behufe wurde der SCHULEK'sche Destillationsapparat (Fig. 1) an seinem Kühlerteil etwas abgeändert. Der Kühlmantel besitzt anstatt 2, 4 Ein- bzw. Ausflussröhrchen, aus welchen die drei oberen mit Glashahn versehen sind. Das untere Röhrchen wird als Einfluss-, die drei oberen abwechselnd als Ausflussröhrchen benutzt,

wodurch der Kühler bzw. die durchströmenden Dämpfe in drei Stufen abgekühlt werden können. Somit ist aber auch die bequeme Destillation bzw. Absorption der Dämpfe und Gase ohne durchströmenden Gasbläschen gesichert.

Man arbeitet nun wie folgt. Zuerst wird die Apparatur durch lebhaftes Kochen des entsprechend vorbereiteten Reaktionsgemisches aber ohne Kühlung luftleer gemacht. Nun wird die Absorptionsflüssigkeit als Vorlage — nachdem die erste Stufe der Kühlung eingestellt worden ist — unter weiter genau angegebenen Versuchsbedingungen vorgeschaltet. Der Vorlagekolben wird dem Kühlerrohr sanft angedrückt und die zweite Stufe der Kühlung in Gang gesetzt. Die Absorptionsflüssigkeit steigt nun in dem Kühlerrohr. Die Höhe des Aufsteigens kann durch Schliessen des zweiten bzw. durch Öffnen des dritten Abflussröhrchens eingestellt bzw. geändert werden. Lässt man nun durch das eingeschliffene Trichterröhrchen das geeignete Reagens oder die Untersuchungslösung behutsam in den Destillierkolben einfließen, so kann das freigemachte Kohlendioxyd bequem abdestilliert und die Absorption desselben durch die Bariumhydroxyd-Lösung „ohne Gasbläschen“ durchgeführt werden. Genaue Vorschrift wird in dem Abschnitt BESCHREIBUNG DES VERFAHRENS angegeben.

Während der Destillation muss für gleichmässiges Sieden Sorge getragen werden. Dies lässt sich mit entsprechend vorbereitetem und zerkleinertem Bimsstein (Körn- grösse 1.5–2 mm), sowie mit adäquater Regelung der Heizung erreichen. Der Kolben

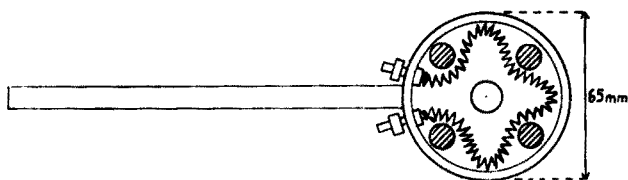


Fig. 2.

wird mit einem kleinen elektrischen Heizkörper erwärmt, dessen Leistung mit Hilfe eines Schiebewiderstandes geregelt werden kann. Der Heizkörper (siehe Fig. 2) ist eine auf Isoliermaterial niedriger Wärmekapazität befestigte Heizspirale, die in direktem Kontakt mit dem Destillierkolben steht. Eine wesentliche Vorbedingung bei der Konstruktion des Heizkörpers ist, dass die Aufheizung bzw. Abkühlung des Kolbens mit der Veränderung der Stromstärke rasch erfolgt. Die Menge des im Laufe der Destillation übergehenden Kohlendioxyds lässt sich mit der Intensität des Siedens regeln, so muss nötigenfalls durch entsprechende Einstellung des Schiebewiderstandes dafür gesorgt werden, dass das plötzlich freiwerdende Kohlendioxyd nicht in Form von Blasen in den Vorlagekolben gelangt.

Zur Sicherung einer „blasenfreien“ Destillation stehen uns also zwei Möglichkeiten zur Verfügung: einerseits die in drei Abstufungen regelbare Wasserkühlung, andererseits die Heizung. Die Regelung der Heizung ist bei richtig geführter Destillation praktisch nicht notwendig. Nach Einsetzen des Siedens lässt sich die Destillation bei gleichmässiger Heizung durchführen; lediglich für eine entsprechende Regelung der Kühlung muss gesorgt werden. Man stellt die Strömungsgeschwindigkeit des Kühlwassers während der Destillation so ein, dass das Wasserniveau im Kühlmantel beim Übergang auf eine mässigeren Kühlungsintensität leicht absinkt. Zu diesem Zwecke

soll das Ende des an den oberen Ausflusstutzen angeschlossenen Gummischlauches bezogen auf die beiden unteren relativ hoch stehen, damit das Wasser dann frei zurückströmen kann.

Die beschriebene Destillationsmethode ist zur Bestimmung des Kohlendioxyd-gehalts wasserlöslicher und in Wasser schwer löslicher Karbonate, sowie Kohlendioxyd-haltiger Lösungen und des bei der Oxydation oder Zersetzung organischer Stoffe gebildeten Kohlendioxyds geeignet. Bei der Bestimmung des Kohlendioxyd-gehalts schwer löslicher Karbonate wird die mit Bariumhydroxyd alkalisch gemachte wässrige Suspension des Karbonats im Destillierkolben untergebracht, das System mit dieser entlüftet und die zum Freimachen des Kohlendioxyds notwendige Säure durch den Hahntrichter zugegeben. Zur Messung des bei Oxydationsprozessen gebildeten Kohlendioxyds wird das System in der Regel durch Kochen der wässrigen Lösung des Oxydationsmittels entlüftet und die Lösung des zu oxydierenden Stoffes dann durch den Hahntrichter zugegeben.

Wir führten mit der oben umrissenen Methode Messungen im 0.1 und 0.01 N Massstabe durch und fanden dabei, dass das Verfahren die bequeme und genaue Bestimmung von 22–0.22 mg CO₂ ermöglicht. Ein grosser Vorteil der Methode besteht darin, dass bei der Bestimmung von 20–2 mg CO₂ im 0.1 N Massstabe keine „blinde“ Destillation durchgeführt werden muss. Die störende Wirkung der Luftkohensäure ist unter solchen Bedingungen nicht grösser als der Tropfenfehler. Zur Bestimmung geringerer Kohlendioxydmengen wird 0.01 N Bariumhydroxydlösung verwendet. Die Ergebnisse der „blinden“ Destillation sind unter solchen Bedingungen beachtlich; während der Destillation und Titration gelangen 0.2–0.3 ml 0.01 N Bariumhydroxyd entsprechende Kohlendioxydmengen in das System.

Bei der Titration des Kohlendioxyds im 0.01 N Massstabe werden die Ergebnisse auch durch das Volumen der Lösung beeinflusst, es soll daher sorgfältig darauf geachtet werden, dass die Lösungsvolumina zu Beginn der Titration gleich gross sind. Wir führten unsere Messungen mit Lösungsvolumina von 50 ml durch. An den Titrationskolben wurde das Volumen von 50 ml bezeichnet und die Lösungen wurden nach der Destillation mit ausgekochtem destilliertem Wasser auf 50 ml ergänzt. Nach einer entsprechenden Praxis beträgt die Genauigkeit der Bestimmung im 0.01 N Massstabe ± 0.03 ml 0.01 N Bariumhydroxydlösung, entsprechend ± 7 μ g Kohlendioxyd.

Wir bestimmten mit dieser Methode zuerst den Kohlendioxydgehalt von Kaliumhydrokarbonatlösungen und Kalzitproben. Auf Grund der Ergebnisse dieser Messungen wurden die Bedingungen der Destillation und Titration sowie die Genauigkeit des Verfahrens festgestellt. Aus der Reihe der Oxydationsreaktionen führten wir die Oxydation des Oxalats mit Kaliumpermanganat durch und bestimmten die Menge des gebildeten Kohlendioxyds. Hierzu sei erwähnt, dass es uns gelang, die Bestimmung der sehr stabilen komplexen Oxalate $[K_3Co(C_2O_4)_3 \cdot 3.5 H_2O]$ und $[K_3Cr(C_2O_4)_3 \cdot 3 H_2O]$ über die bei ihrer Oxydation gebildete Kohlensäure durchzuführen.

Wir bestimmten auch den Kohlendioxydgehalt der mit Kalciumoxyd karbonatfrei gemachten normalen Natriumhydroxydlösung sowie der 0.1 N Bariumhydroxydlösung und der (50%-igen) Sörensen'schen „karbonatfreien“ Natronlauge. Bei diesen Bestimmungen wurden die Lösungen im Destillationskolben unter eine Pentanschicht eingebracht und die Entlüftung durchgeführt.

Zu den Spülungen sowie zur Ergänzung der Lösungsvolumina usw. verwendeten

wir in jedem Falle frisch ausgekochtes destilliertes Wasser, das nach dem Abkühlen mit einer 0.5 cm dicken Pentan-Phase überschichtet wurde. Die Bariumhydroxyd-lösungen werden in den üblichen automatischen Büretten gelagert, jedoch auch in diesen noch zusätzlich mit Pentan überschichtet.

BESCHREIBUNG DES VERFAHRENS

Reagenzien

0.1 N Bariumhydroxydlösung (mit 5% Bariumchlorid); 0.01 N Bariumhydroxyd-lösung (mit 5% Bariumchlorid und 30% Äthanol); 0.1 bzw. 0.01 N Salzsäure; 20%-ige Schwefelsäure; 2%-ige Salzsäure; 0.3%-ige alkoholische Thymolblaulösung; 5%-ige Kaliumpermanganatlösung; Bimsstein (Körngrösse 1.5–2 mm); Pentan.

Bestimmung des Kohlendioxydgehalts wasserlöslicher Karbonate

Aus der zu untersuchenden Substanz wird mit vorher ausgekochtem und abgekühltem destilliertem Wasser eine Stammlösung hergestellt. 10.00 ml dieser Lösung sollen bei der Bestimmung im 0.1 N Massstabe 10–20 mg, bei Bestimmung im 0.01 N Massstabe 1–2 mg Kohlendioxyd enthalten.

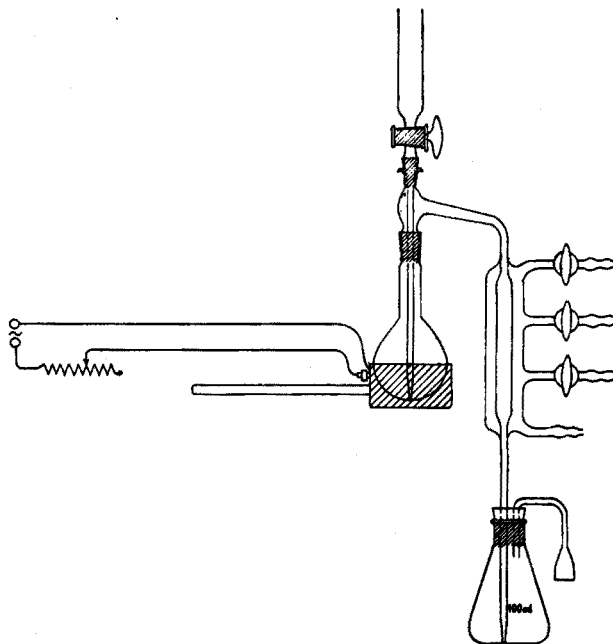


Fig. 3.

Das Einlaufrohr des Hahntrichters im Destillationskolben wird mit ausgekochtem destilliertem Wasser blasenfrei aufgefüllt. Zweckmässig saugt man das Wasser von unten in das Rohr und verschliesst dann den Hahn.

Der 100-ml Kolben des Destillationsapparats wird mit 5 ml Schwefelsäure beschickt und diese mit Wasser auf ca. 50 ml ergänzt. Man bringt nun einige Körner Bimsstein in den Kolben, stellt den Apparat zusammen und schaltet die Heizung ein. Nach

Einsetzen des Siedens wird der Schiebewiderstand so eingestellt,¹³ dass die Lösung lebhaft und gleichmässig siedet. Nachdem aus dem Ausflussrohr des Kühlers ein lebhafter Wasserdampfstrom entweicht, wird 1 Min gewartet, dann öffnet man den unteren Hahn am Kühler, verschliesst die beiden oberen und schaltet das Kühlwasser ein. In einen 100-ml fassenden Erlenmeyer-Schliffkolben werden 5 ml Pentan gegossen und dann aus einer automatischen Bürette 15,00 ml Bariumhydroxydlösung einlaufen gelassen. Bei der Bestimmung geringer CO₂-Mengen im 0,01 N Massstabe wird das Volumen von 50 ml am Kolben vorher bezeichnet. Man spült nun die Innenwand des Kolbens mit 5 ml ausgekochtem destilliertem Wasser nach, und befestigt den Kolben dann an dem am Ausflussrohr des Kühlers befindlichen, doppelt durchbohrten Korke (Fig. 3). Durch die eine Bohrung des Korkes geht dabei das Kühlerrohr, durch die andere wird über ein ungebogenes Glasrohr eine Trockenröhre angeschlossen, die mit Bariumhydroxydlösung angefeuchtete Watte enthält. Der Korkstopfen kann am Kühlerrohr auf- und abgeschoben und der Kolben so leicht gehoben oder gesenkt werden. Das Ende des Ausflussrohrs soll dabei locker am Boden des Kolbens aufliegen. Nun wird der mittlere Hahn am Kühler geöffnet und der untere verschlossen, worauf die Bariumhydroxydlösung im Kühlerrohr bis ungefähr ins untere Drittel ansteigt. Man pipettiert hierauf 10,00 ml der vorbereiteten Lösung in den Hahntrichter und lässt diese dann durch vorsichtiges Öffnen und Schliessen des Hahnes in kleineren Portionen (zu ca. 0,5 ml) in den Destillationskolben einlaufen. Unterdessen wird die Höhe der Bariumhydroxydlösung im Kühlerrohr beobachtet, und falls notwendig, wird die dritte Kühlungsstufe, durch Öffnen des obersten Hahnes und Schliessen des mittleren, eingeschaltet. Der Hahntrichter wird hierauf zuerst mit 10 und dann mit 5 ml ausgekochtem destilliertem Wasser nachgespült. Auch beim Spülen ist darauf zu achten, dass nur kleine Anteile des Wassers in den Kolben gelassen werden, da im entgegengesetzten Fall das Sieden aussetzen kann, und die Bariumhydroxydlösung aus der Vorlage in den Destillationskolben zurückgezogen wird. Nach der Spülung des Hahntrichters wird der Vorlagekolben vorsichtig um 1–2 mm gesenkt und dadurch der Austausch der Bariumhydroxydlösung zwischen dem Inneren des Kühlerrohres und dem Vorlagekolben infolge der Auf- und Abwärtsbewegung der Flüssigkeit beschleunigt. Die Destillation wird 15–20 Min hindurch fortgesetzt. Man öffnet nun den unteren Hahn des Kühlers, worauf die Bariumhydroxydlösung aus dem Kühlerrohr verdrängt wird. Der Vorlagekolben wird nun so weit gesenkt, dass das Ende des Kühlerrohres über die Flüssigkeitsoberfläche zu stehen kommt, setzt das Sieden noch 1 Min hindurch fort, wodurch das Innere des Kühlerrohres mit Wasser ausgespült wird und beendet dann das Sieden. Nach Abnahme des Vorlagekolbens (bei Messungen im 0,01 N Massstabe ist sein Inhalt mit ausgekochtem destilliertem Wasser(!) auf 50 ml zu verdünnen) wird die Vorlageflüssigkeit in Gegenwart von 10 Tropfen Thymolblau-Indikatorlösung mit 0,1 bzw. 0,01 N Salzsäure bis zum Farbumschlag auf grün titriert. Während der langsam durchgeführten Titration soll die Flüssigkeit energisch gerührt werden. Sobald die blaue Farbe zu verblassen beginnt, wird die Lösung energisch durchgeschüttelt und diese Operation bis zum Erreichen des Endpunktes öfters wiederholt. Bei Bestimmungen im 0,01 N Massstabe wird mit ausgekochtem destilliertem Wasser, dessen Volumen dem Volumen der zu untersuchenden Lösung und der Spülflüssigkeit entspricht, eine blinde Probe durchgeführt. Der Unterschied zwischen den Ergebnissen der beiden Titrationen ist mit der Menge des Kohlendioxyds proportional. Im 0,1 N Massstabe ist die blinde Probe nicht notwendig, in diesem Falle

werden die 15 ml der Bariumhydroxydlösung (in Gegenwart von 5 ml Pentan als Sperrflüssigkeit) mit 0.1 N Salzsäure titriert. 1 ml 0.1 N bzw. 0.01 N Salzsäure entspricht 2.2005 bzw. 0.22005 mg Kohlendioxyd.

Die Ergebnisse unserer Untersuchungen sind in Tabelle I zusammengefasst.

TABELLE I
BESTIMMUNG DES CO₂-GEHALTS IN KHCO₃-LÖSUNG

Einwaage CO ₂ als KHCO ₃ - ^a Lösung, mg	Verbrauch 0.1 N Bariumhydroxydlösung, ml		Gefunden CO ₂	
	Einzel	Durchschnitt	mg	Δ%
21.64	9.83	9.82	21.61	-0.1
	9.82			
10.86	4.93	4.93	10.85	-0.1
	4.94			
5.44	2.47	2.47	5.44	0.0
	2.48			
Verbrauch 0.01 N Bariumhydroxydlösung, ml				
	Einzel	Durchschnitt		
2.067	9.37	9.38	2.064	-0.1
	9.39			
1.025	4.65	4.64	1.021	-0.4
	4.63			
0.411	1.86	1.86	0.409	-0.4
	1.85			

^a Der CO₂-Gehalt der KHCO₃-Lösung wurde durch Messung mit Bariumhydroxyd auch direkt kontrolliert.

Bestimmung des Kohlendioxydgehalts des Kalzits

0.04–0.07 g grob zerkleinertes Kalzit (Islandischer Kalkspat) wird analytisch genau eingewogen und mit ausgekochtem destilliertem Wasser in den Destillationskolben gespült. Der Kolbeninhalt wird auf 30–50 ml ergänzt und mit 1 ml 0.1 N Bariumhydroxydlösung alkalisch gemacht. Nach Zugabe von Bimsstein wird der Apparat unverzüglich zusammengestellt und die Heizung eingeschaltet. Die Entlüftung und Einstellung des Vorlagekolbens führt man genau so durch wie im vorangehenden Abschnitt beschrieben wurde. Als Vorlageflüssigkeit werden 20.00 ml 0.1 N Bariumhydroxydlösung verwendet. Durch den Hahntrichter lässt man 10 ml 2%-ige Salz-

TABELLE II
BESTIMMUNG DES KALZITS ÜBER KOHLENDIOXYD

Einwaage Kalzit mg	Verbrauch 0.1 N Bariumhydroxydlösung ml	Gefunden Kalzit	
		mg	%
62.9	12.50	62.6	99.45
67.0	13.29	66.5	99.27
64.2	12.72	63.7	99.16

säure in kleinen Anteilen in den Kolben einlaufen. Die Destillation wird 15–20 Min hindurch fortgesetzt, dann wird der Inhalt des Vorlagekolbens in Gegenwart von 10 Tropfen Thymolblau-Indikatorlösung mit 0.1 N Salzsäure titriert. 1 ml 0.1 N Salzsäure entspricht 5.0045 mg Kalzit.

Die Ergebnisse dieser Messungen sind in Tabelle II zusammengefasst.

Bestimmung von Oxalaten über das bei der Oxydation mittels Kaliumpermanganat gebildete Kohlendioxyd

Die zu untersuchende Oxalatlösung soll im ml 1–2 mg Oxalat-Ionen enthalten. Im Destillationskolben werden 5 ml 5%-ige Kaliumpermanganatlösung mit 5 ml

TABELLE III

BESTIMMUNG DES NATRIUMOXALATS ÜBER DAS BEI DER OXYDATION MIT PERMANGANAT GEBILDETE KOHLENDIOXYD

Einwaage Na-Oxalat ^a g/200 ml	Zur Bestimmung eingemessene Lösung ml	Verbrauch 0.1 N Ba(OH) ₂ -Lösung ml		Gefunden Na ₂ (C ₂ O ₄)	
		Einzel	Durchschnitt	mg	%
0.3392	10.06	5.03	5.03	16.85	98.8
		5.02			
		5.03			
	5.04	2.52	2.52	8.44	98.8
		2.52			
		2.53			
2.01	1.01	1.01	1.01	3.38	99.2
		1.01			

^a 99.0%-ig. Das Präparat wurde durch direkte Bestimmung mit Kaliumpermanganat kontrolliert.

TABELLE IV

BESTIMMUNG KOMPLEXER OXALATE ÜBER DAS BEI DER OXYDATION MIT PERMANGANAT GEBILDETE KOHLENDIOXYD

Formel	C ₂ O ₄ ²⁻ %	
	Berechnet	Gefunden
K ₃ Cr(C ₂ O ₄) ₃ · 3 H ₂ O ^a	54.17	54.19
K ₃ Co(C ₂ O ₄) ₃ · 3.5 H ₂ O ^a	52.46	52.50

^a Der Wassergehalt der Verbindungen wurde nach der Karl Fischer Methode kontrolliert.

20%-iger Schwefelsäure angesäuert. Man ergänzt das Volumen mit ausgekochtem destilliertem Wasser auf 30–50 ml, stellt den Apparat nach Zugabe von Bimsstein zusammen und kocht die Lösung aus, bzw. entlüftet den Apparat nach der bereits beschriebenen Methode. Als Vorlage werden 10.00, bzw. 20.00 ml 0.1 N Bariumhydroxydlösung verwendet. Durch den Hahntrichter lässt man 10.00 ml der vorbereiteten Lösung in kleinen Anteilen einlaufen und spült mit 10 und 5 ml ausgekochtem destilliertem Wasser nach. Die Zeit des Siedens richtet sich nach der Art der Bindung des Oxalats. Bei komplexen Oxalaten grosser Stabilität ist 30–40 Min hindurch fortgesetztes Sieden notwendig, beim Natriumoxalat genügen 15–20 Min. Bei den länger dauernden Destillationen muss das verdampfte Wasser mit ausgekochtem

destilliertem Wasser ersetzt werden. Nach beendeter Destillation wird der Inhalt des Vorlagekolbens in Gegenwart von 10 Tropfen Thymolblau-Indikatorlösung mit 0.1 *N* Salzsäure titriert. 1 ml 0.1 *N* Salzsäure entspricht 2.2005 mg Oxalat-Ionen.

Die Ergebnisse unserer Messungen sind in den Tabellen III und IV zusammengefasst.

Bestimmung des Kohlendioxydgehalts von Laugen

Vor Beginn der Bestimmung wird die Oberfläche der zu untersuchenden Lösung mit einer 4–5 mm dicken Pentanschicht bedeckt. Der Destillationskolben wird mit ausgekochtem destilliertem Wasser ausgespült und mit 5 ml Pentan beschickt. Man bringt nun einen gemessenen Anteil der zu untersuchenden Lösung in den Kolben, ergänzt mit ausgekochtem destilliertem Wasser auf 30–50 ml und stellt den Apparat nach Zugabe von Bimsstein zusammen. Das Pentan wird unter voller Kühlung in ein Becherglas abdestilliert, dann lässt man das Wasser aus dem Kühlmantel abfließen. Das Pentan wird aus dem Bechergläse ausgegossen und nachdem ein lebhafter Dampfstrom aus dem Kühlerrohr entweicht, wird die Vorlage wie üblich angebracht. Als Vorlageflüssigkeit dient der erwarteten Kohlendioxydmenge entsprechend 0.05 oder 0.01 *N* Bariumhydroxydlösung. Die zu untersuchende Lösung wird im Destillationskolben — durch den Hahntrichter — mit vorher ausgekochter 20%-iger Schwefelsäure angesäuert (nötigenfalls verwendet man 1–2 Tropfen Methylrot-Indikatorlösung).

In Tabelle V sind die Messergebnisse bezüglich des Kohlendioxydgehalts einiger Laugen zusammengefasst.

Der Apparat wurde aus „Rasotherm“-Glas hergestellt. Der Hahntrichter bzw. der Kolben sind an den Kühleraufsatz mit 11/24 bzw. 13.5/24 Normalschliffen angeschlossen. Der Apparat wird nur beim Kühler an einem Gestell eingespannt, der Kolben wird mit 2 Federn am Aufsatz befestigt. Am Aufsatz, bzw. am Kolben, befinden sich zu diesem Zwecke je 2 Glashäckchen. Ähnlich kann auch der Hahntrichter fixiert werden. Das Ende des Einlaufrohres des Hahntrichters, sowie das Ende des Kühlerrohres, sind bis auf einen Innendurchmesser von 1.5–2 mm verengt. Die Bohrung

TABELLE V
BESTIMMUNG DES KOHLENDIOXYDGEHALTS VON LAUGEN

Lauge	Eingem. Lösung ml	Für das CO ₂ verbrauchte Ba(OH) ₂ -Lösung ml		Gefunden CO ₂	
		Einzeln	Durchschnitt	mg	in äquiv. %-ten
Mit CaO-Brei behandelte 1.25 <i>N</i> Natriumhydroxydlösung	20.05	(0.05 <i>N</i>)	(0.05 <i>N</i>)	6.44	1.177
		5.85			
		5.87	5.85		
		5.84			
50%-ige (12.5 <i>N</i>) Natriumhydroxydlösung nach 24-stündiger Sedimentation	4.99	(0.05 <i>N</i>)	(0.05 <i>N</i>)	8.74	0.636
		7.94			
		7.94	7.94		
		7.93			
0.1 <i>N</i> Bariumhydroxydlösung (5% Bariumchlorid enthaltend)	20.00	(0.01 <i>N</i>)	(0.01 <i>N</i>)	0.051	0.115
		0.23			
		0.23	0.23		
		0.24			

des Hahnes im Hahntrichter ist 1–1.5 mm weit, die Hähne des Kühlers besitzen 3-mm Bohrungen. Der Innendurchmesser des Einlaufrohres des Hahntrichters beträgt 3 mm, sein Ende steht 3–5 mm über dem Boden des Kolbens. Der Hahntrichter fasst ca. 15 ml. Die übrigen Daten des Apparats sind aus der Abbildung ersichtlich.

ZUSAMMENFASSUNG

Die Destillation des Kohlendioxyds lässt sich bei entsprechender Regelung der Kühlung, bei Atmosphärendruck durchführen. Die störende Wirkung des Luftkohlendioxyds wird durch Anwendung von Pentan als Sperrflüssigkeit ausgeschaltet. Im 0.1 und 0.01 N Massstabe lassen sich mit dieser Methode 22–0.22 mg Kohlendioxyd mit einer Genauigkeit von ± 0.2 –2% bestimmen.

SUMMARY

Carbon dioxide can be distilled at atmospheric pressure if the cooling is properly controlled. A suitable procedure is described. Interference from atmospheric carbon dioxide is prevented by the use of pentane as sealing liquid. Titrations with 0.01–0.1 N solutions allow determination of 0.22–22 mg of carbon dioxide with an accuracy of ± 2 –0.2%.

RÉSUMÉ

Une méthode est décrite pour le dosage titrimétrique de l'anhydride carbonique, avec distillation à la pression atmosphérique. Pour des teneurs en CO₂ de 0.22 à 22 mg, la précision est de ± 2 –0.2%.

LITERATUR

- ¹ R. BELCHER, J. H. THOMSON UND T. S. WEST, *Anal. Chim. Acta*, 19 (1958) 309.
- ² E. SCHULEK, J. TROMPLER, Á. ENDRŐI-HAVAS UND I. REMPÖR, *Anal. Chim. Acta*, 24 (1961) 11.
- ³ L. W. WINKLER, *Z. angew. Chem.*, 28 (1915) 478.
- ⁴ E. SCHULEK UND G. VASTAGH, *Z. anal. Chem.*, 92 (1933) 352.

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A SPECIFIC AND SENSITIVE SPOT TEST FOR CADMIUM UTILIZING GLYOXAL-BIS(2-HYDROXYANIL)

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Although it is a relatively common metal, cadmium has remained one of the most difficult to detect. The problems associated with its detection are apparent when it is realized that the precipitation of yellow cadmium sulfide with all of its associated complications is still considered one of the best means of detecting this element. The precipitation of the cadmium iodide complex using the iron(II) complex with α, α' -dipyridyl¹ is probably the most generally useful test reaction available up to the present. The red precipitate is so intensely colored that excellent sensitivity is obtained. Although the test is selective for anionic iodo complexes, the metals that form such complexes are those that would ordinarily be associated with cadmium and are, therefore, critical. It might be mentioned that metals such as lead, silver and thallium

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which are precipitated by iodide also give positive interferences due to the absorption of the reagent on the respective precipitates. Specificity can only be approached by removing the chloride group of metals and then masking other potential interfering metals as ammine complexes. Various organic reagents such as diphenylcarbazide and diphenylthiocarbazone have been employed with only moderate success. The most successful of such reagents has been *p*-nitro diazo amino azobenzene which forms a violet to blue lake in the presence of cadmium. Most interfering metals can be complexed by the addition of tartrate².

Preliminary studies of glyoxal-bis(2-hydroxyanil) disclosed its potential value as a reagent for cadmium. Excellent sensitivities were obtained, and pH control did not appear critical. A number of metals react with the reagent, but preliminary investigations indicated the likelihood that most of these could be masked through use of various complexing agents.

Under the highly alkaline conditions of the test, it was evident that tartrate would have to be present to prevent the general formation of hydroxides. In addition, the reactions of lead and thallium with the reagent were also masked with tartrate. The interference due to silver was eliminated with thiosulfate, as were reactions of copper and gold. Fluoride was used to further condition the test by masking the reactions of iron, uranium, calcium, strontium and barium.

The use of a solution of the above complexing agents gave a selective test with only cobalt, nickel and cadmium reacting. The test was made specific for cadmium by utilizing anion exchange resin beads and concentrating the metal ion on the resin as the tetraiodo complex.

EXPERIMENTAL

Reagents and chemicals

Unless otherwise specified, all solutions were made with AnalaR grade chemicals and distilled water. (1) Glyoxal-bis(2-hydroxyanil) solution: 1% in 95% ethyl alcohol. The reagent was prepared according to FEIGL³. (2) Piperidine: Eastman Organic (practical grade). (3) Masking mixture: a solution containing equal volumes of the following was prepared: (a) sodium thiosulfate, 20% aqueous, (b) sodium tartrate, 20% aqueous, (c) sodium fluoride, saturated aqueous. (4) Potassium iodide: 50% aqueous. (5) Metal ion solutions: stock solutions containing 10 mg/ml were prepared using appropriate salts. (6) Dowex 2-X8 anion exchange resin (50-100 mesh in Cl⁻ form). A suitable quantity of resin was packed in a small column and washed with 1 N HCl to remove trace metal contaminants. The purified resin was then washed with distilled water and air dried.

PROCEDURE

The following procedure is proposed. A drop of metal ion solution is placed in the depression of a white spot plate. Two drops of the masking mixture and two drops of the potassium iodide solution are added. About 20 ion exchange beads are added, and the mixture is stirred and allowed to equilibrate for a minute (the equilibration time can be varied depending upon the amount of cadmium present). The supernatant solution is then drawn from the spot plate depression and discarded. A medicine dropper, drawn to a fine point, serves nicely for this operation since care must be

taken that the beads are not also drawn off. The beads are then washed three times with distilled water, the washings being drawn off and discarded as previously described. Two drops of distilled water, a drop of glyoxal-bis(2-hydroxyanil) solution and a drop of piperidine are added. A positive cadmium test is indicated by a blue color forming on the resin beads. The time of color formation and the intensity of the stain are dependent upon the amount of cadmium present. It is also to be noted that the color is not stable on the resin. Fading takes place generally within a period of several minutes.

Table I gives a list of all the ions studied in the course of this work. Of all the ions listed, only the cadmium ion gave a positive test.

To determine the extent of possible interferences from the various ions listed in

TABLE I
IONS STUDIED FOR POSSIBLE INTERFERING EFFECTS

Li	Na	K	Cu(II)	Rb	Ag(I)	Cs	Au(III)
Be	Mg	Ca	Zn	Si	Cd	Ba	Hg(I)
Hg(II)	Al	Ga	Ce(III)	Ce(IV)	Tl(I)	In	Y
Ti(IV)	Ge	Zr	Sn(II)	Sn(IV)	Pb(II)	Th	V(II)
V(V)	As(V)	Sb(III)	Bi(III)	Cr(III)	U(VI)	Mn(II)	Fe(III)
Co(II)	Ni	Ru(III)	Rh(III)	Pd(II)	Ir(IV)	Pt(IV)	Os(IV)
BO ₂ ⁻	CO ₃ ⁻²	SiO ₃ ⁻²	NO ₂ ⁻	NO ₃ ⁻	HPO ₄ ⁻²	P ₂ O ₇ ⁻⁴	S ⁻²
S ₂ O ₃ ⁻²	SO ₃ ⁻²	SO ₄ ⁻²	CrO ₄ ⁻²	SeO ₃ ⁻²	SeO ₄ ⁻²	MoO ₄ ⁻²	TeO ₃ ⁻²
TeO ₄ ⁻²	WO ₄ ⁻²	F ⁻	Cl ⁻	ClO ₃ ⁻	ClO ₄ ⁻	MnO ₄ ⁻	Br ⁻
BrO ₃ ⁻	I ⁻	IO ₃ ⁻	CN ⁻	Fe(CN) ₆ ⁻³	Fe(CN) ₆ ⁻⁴	SCN ⁻	NH ₄
Acetate	Oxalate	Malonate	EDTA	Succinate	Tartrate	Citrate	

Table I upon the detection of cadmium, the procedure given above was modified as follows. A drop of the metal ion solution (10 mg/ml) whose interference was to be studied was placed in the depression of a white spot plate together with a drop of cadmium solution (1 mg/ml). The remainder of the procedure was the same as that originally given.

A control test was run in parallel with the interference studies. The control was identical to the interference test, except that a drop of distilled water was used instead of the cadmium solution.

There were no interferences, either positive or negative, from any of the ions tested, nor did colored ions interfere.

The sensitivity of the cadmium test is given by: Limit of identification of Cd: 0.05 μ g. Dilution limit: 1 : 1,000,000.

DISCUSSION

Those metal ion solutions which had to be prepared in highly acidic media to prevent hydrolysis were neutralized with 6 M sodium carbonate solution before proceeding with the spot test.

Various bases were investigated as to their usefulness for adjusting the pH of the reaction mixture, e.g., ammonium hydroxide, sodium hydroxide, pyridine, morpholine, diethylamine and piperidine. Piperidine was chosen because of its enhancement of the sensitivity of the reaction. An attempt was made to combine the glyoxal-bis-

(2-hydroxyanil) and the piperidine into a single solution, but the mixture was found to be unstable.

Preliminary tests indicated that tartrate would have to be added to prevent hydroxide formation under the alkaline conditions of the reaction. Additional observations indicated that other masking agents would be needed to further condition the test. For example, the formation of silver oxide and interferences from Cu(II) and Au(III) are masked with thiosulfate, while reactions of Fe(III), U(VI), Ca, Sr and Ba are eliminated with fluoride.

The basis for the use of the anion exchange resin is the formation of the cadmium iodo complex with its subsequent absorption on the resin. This provides an excellent method of separation from cobalt and nickel which also react with the reagent to give a red-brown and blue color respectively.

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SUMMARY

A test for cadmium based on the use of glyoxal-bis(2-hydroxyanil) is proposed. The reaction is carried out on beads of an anion exchange resin on which the cadmium has been concentrated as the tetraiodo complex. Separations inherent in the procedure make the test specific. The limit of identification is 0.05 μg .

RÉSUMÉ

Les auteurs proposent pour l'identification du cadmium une réaction à la touche, spécifique et sensible, au moyen de bis(2-hydroxyanil)glyoxal. La réaction s'effectue sur résine Dowex, et donne une coloration bleue.

ZUSAMMENFASSUNG

Es wird eine Nachweisreaktion (Tüpfelprobe) für Cadmium unter Verwendung von Glyoxal-bis-(2-hydroxyanil) beschrieben. Cadmium wird als Cadmiumjodokomplex auf Anionenaustauscherharz-Perlen adsorbiert, die nach Zusatz des Reagenzes und Piperidin eine blaue Farbe annehmen.

REFERENCES

- ¹ F. FEIGL AND L. I. MIRANDA, *Ind. Eng. Chem., Anal. Ed.*, 16 (1944) 141.
- ² F. P. DWYER, *Australian Chem. Inst. J. & Proc.*, 2 (1937) 26.
- ³ F. FEIGL, *Spot Tests in Inorganic Analysis*, 5th ed., Elsevier, Amsterdam, 1958, p. 534.

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Short Communication

Determination of traces of water in gases by means of a modified Keidel electrolytic hygrometer

Using the principle suggested by KEIDEL¹ we have developed an electrolytic hygrometer which has distinct advantages over commercially available instruments. As is well known, the meter is based on the principle of quantitative water absorption

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by a phosphorus pentoxide matrix between two platinum wires spaced closely to reduce the time of response. Subsequent electrolysis of all the water absorbed converts the water to oxygen and hydrogen and continuously regenerates the phosphorus pentoxide. In the KEIDEL cell the coiled thin platinum wires are located within a narrow (diameter 1 mm) teflon capillary. This capillary, however, can easily be blocked, especially in the presence of higher olefines, which tend to polymerize under the influence of the phosphorus pentoxide. The capillary cannot readily be cleaned. This disadvantage is eliminated in our construction, in which the two platinum wires are coiled on the outside of a teflon or glass cylinder. The two shallow circular grooves, necessary for exactly spacing the two spiralized platinum wires (diameter 0.5 mm) 0.2 mm apart, can be easily turned or etched. This part of the sensing cell can be removed for cleaning purposes. Further details² are given in Fig. 1.

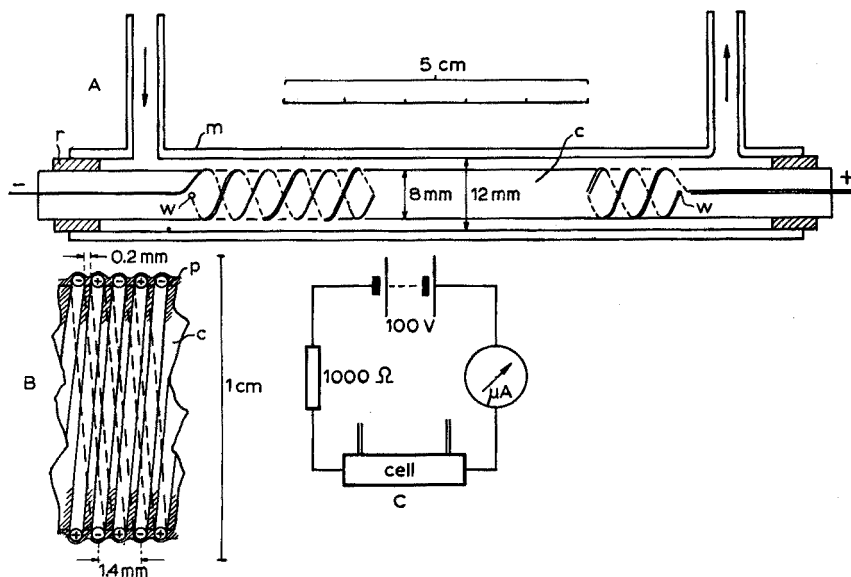


Fig. 1. Electrolytic hygrometer. A: Sensing element with enlarged detail B (longitudinal section). C: Electrical scheme. c, teflon or glass cylinder on which the two platinum wires are coiled. m, glass mantle. p, thin layer of dehydrated phosphoric acid. r, piece of butylrubber tube, attached so that no water can enter the cell. w, fixed end of the platinum wire.

Starting procedure

After the platinum wires have been cleaned and made grease-proof, they are coated with a very thin film of phosphoric acid, 80–90% by weight. The cell is conditioned by electrolyzing the acid to dryness, so that the residual current amounts to some tens of microamperes. During this procedure the cell is rinsed with a stream of dry nitrogen. Normally, the cell is used with a gas flow of 100 ml/min and a working d.c. voltage of 100 V.

Discussion

If the gas flow rate is constant (100 ml/min), then the current necessary to ensure complete conversion of the absorbed water to hydrogen and oxygen (one Faraday,

i.e. 96,500 C/0.5 mole of water) amounts to 17.9 μA for each mg of water present per cubic meter gas at 760 mm and 20°. Expressing the water content in p.p.m. (v/v), this factor becomes 13.4 μA .

The range of the cell is from 5–2000 mg of water per cubic meter. Both the absorption and the electrolysis proceed with 100% efficiency, hence no additional calibration is necessary. The standard deviation is about 5%. The so-called 63%-response is achieved within 1.5 min. It is interesting to note that phosphoric acid spattering on the inner wall of the cylindrical glass mantle does not noticeably disturb the measurement. Several instruments of this type have been satisfactorily used for four years.

Central Laboratory, Staatsmijnen in Limburg,
Geleen (The Netherlands)

E. BARENDRECHT

¹ F. A. KEIDEL, *Anal. Chem.*, 31 (1959) 2043.

² *Netherlands Patent Application*, Stamicarbon N.V., Heerlen, Nr. 223,599, June 15th, 1959.

Received June 24th, 1961

Anal. Chim. Acta, 25 (1961) 402–404

Addendum

Determination of magnesium and aluminium in zinc-base die-casting alloys¹

In the above paper, brief mention was made of the possibility of applying the method described for determination of magnesium in aluminium alloys. We have since found that silica interferes in this method by causing coprecipitation of magnesium with Fe, Mn and Al. The method given (2nd paragraph, p. 239) should therefore be modified as follows.

The main constituent (aluminium) was removed by dissolving the alloy in sodium hydroxide. The insoluble residue was filtered off on paper and the residue and paper were digested with nitric and sulphuric acids, nitric acid being removed by fuming. More nitric acid was added as required to ensure complete removal of organic matter. Under these conditions, silica is insoluble. After digestion and dilution, silica was filtered off along with lead sulphate. The Fe, Mn and Al remaining were then eliminated with ammonia and ammonium persulphate, before the magnesium was determined as described originally. The addition of potassium cyanide before titration with EDTA masks any zinc which may coprecipitate with $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$.

H. J. van der Rijn, N.V. Research Laboratory,
Naarden (The Netherlands)

L. BLOCH

¹ L. BLOCH, *Anal. Chim. Acta*, 23 (1960) 233.

Received June 28th, 1961

Anal. Chim. Acta, 25 (1961) 404

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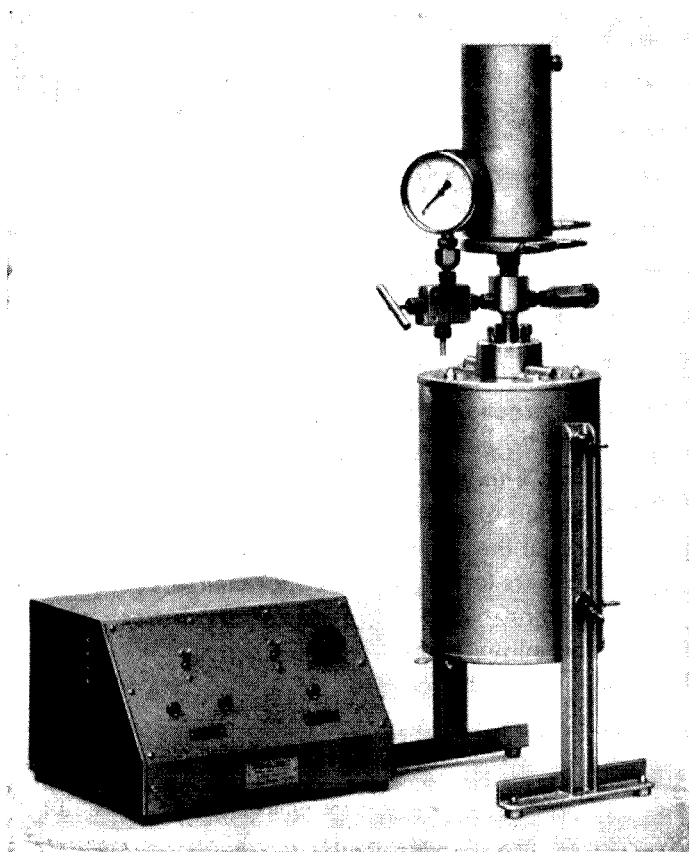
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L'autoclave est agité intérieurement par le va et vient vertical d'une tige munie de palettes, entraînée **magnétiquement** à travers la paroi de l'enceinte sous pression, sans **aucun presse-étoupe**.

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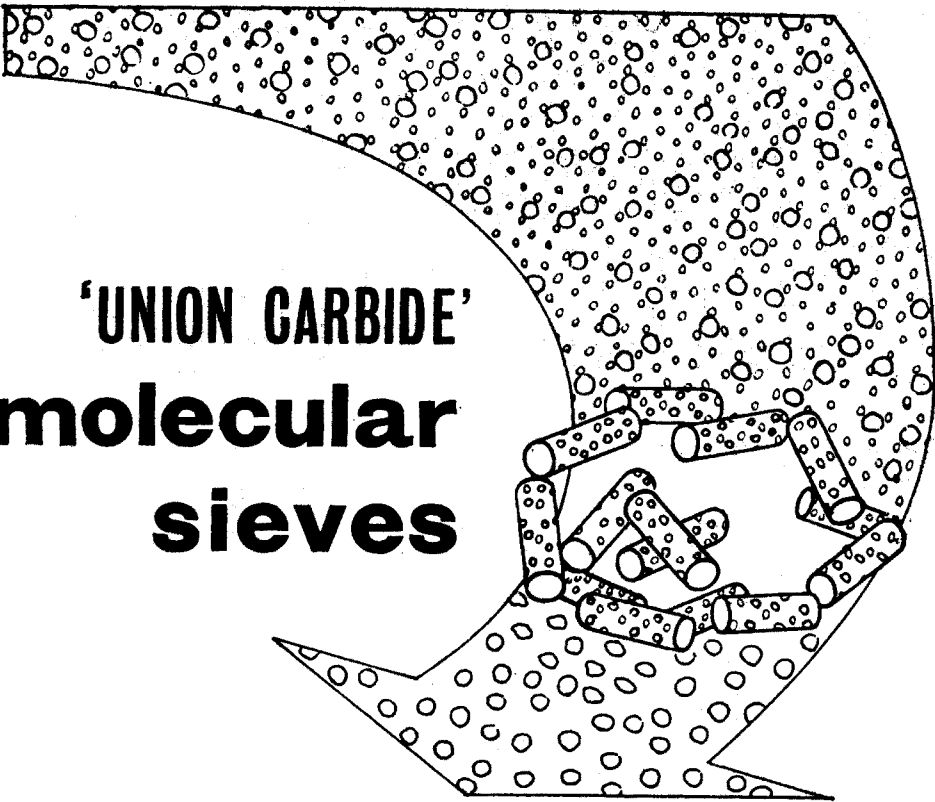
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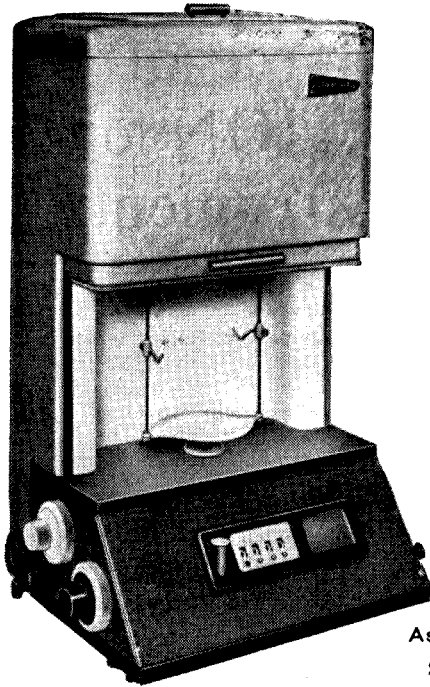
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