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SUMMARIES OF ARTICLES PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 26, No. 6, June 1962

THE ISOLATION OF RADIO-MANGANESE BY DISTILLATION AS PERMANGANIC ACID

The selective isolation of manganese by distillation as permanganic acid was investigated. Contamination from Fe, Cr and Co was negligible. It was found possible to isolate carrier-free ^{54}Mn from cyclotron-irradiated iron targets. The time needed for the distillation was about 15 min with yields of 85–90%.

J. PIJCK AND J. HOSTE, *Anal. Chim. Acta*, 26 (1962) 501–505

AN ENZYMATIC METHOD FOR THE DETECTION OF ESTERS

An enzymatic method for the detection of esters has been developed. The use of various esterases as an analytical tool has been examined. It has been found that lipase can be used for the detection of esters under specified conditions. The relative rates of hydrolysis observed in the case of various esters have been explained on the basis of the generally accepted mechanism. The enzymatic method has been compared with the hydroxamic acid test.

P. W. WEST AND M. QURESHI, *Anal. Chim. Acta*, 26 (1962) 506–513

CARBAZOLES, PHENAZINES AND DIBENZOFURAN IN PETROLEUM PRODUCTS; METHODS OF ISOLATION, SEPARATION AND DETERMINATION

Alkylindoles, -carbazoles and -phenazines were isolated from a petroleum distillate by adsorption on activated aluminum oxide and desorption with methanol. After removal of methanol and dilution with benzene, the concentrate was extracted with 72% perchloric acid to obtain the alkylindoles and alkylcarbazoles as soluble perchlorates. These compound types were then isolated from the acidic layer by addition of water and extraction with benzene. A concentrate of the benzene extract was separated by gas chromatography into alkylindoles and 6 different carbazoles, the latter being characterized by ultraviolet and mass spectrometric techniques. The carbazoles were determined photometrically with 2-bromo-2-nitroindandione-1,3 reagent and by gas chromatography. Phenazine and several alkylphenazines were isolated from the nitrogen compound concentrate as solid perchlorates, liberated by alkali treatment of their perchlorates, and separated by gas chromatography; ultraviolet and mass spectra were used for their identification. Dibenzofuran was identified in the residual concentrate after the acid extraction.

G. K. HARTUNG AND D. M. JEWELL, *Anal. Chim. Acta*, 26 (1962) 514–527

SPECTROPHOTOMETRIC DETERMINATION OF RARE EARTH ELEMENTS AND THORIUM WITH ARSENAZO

The simultaneous spectrophotometric determination of rare earth elements (lanthanum and gadolinium) and thorium with arsenazo is described. In 0.05 *N* nitric acid, thorium alone forms a colored complex with the reagent; at pH 7.2 both thorium and the rare earths form colored complexes. Satisfactory results were obtained with weight ratios of Th/rare earths ranging from 0.2 to 10.

H. ONISHI, H. NAGAI AND Y. TOITA, *Anal. Chim. Acta*, 26 (1962) 528–531

A NEW ROUTINE METHOD FOR DETERMINATION OF IODINE IN PLANT MATERIALS

A new method is suggested for determination of iodine in grass and crop samples. The sample is decomposed with sulphuric, nitric and perchloric acids. Iodine is determined in the diluted digest. The method is excellent for routine work, being faster and simpler than previous methods.

G. W. F. H. BORST PAUWELS AND J. CH. VAN WESEMAEL, *Anal. Chim. Acta*, 26 (1962) 532–540

THE DETERMINATION OF PHENOL AND KINETIC STUDIES ON THE MONOBROMINATION OF PHENOL BY A PULSE COULOMETRIC TECHNIQUE

A method for the coulometric determination of phenol is described in which constant current pulses are used to electrogenerate bromine and a current recorder is used to follow the bromination reaction of phenol. Solutions containing 10^{-4} to $7 \cdot 10^{-6}$ *M* phenol are determined with a precision of 1%. A general method for determining the kinetics of bromination reactions is postulated and used for the determination of the rate constant of the monobromination of phenol. The rate constant for the reaction in which the reacting species are the neutral phenol molecule and the bromine molecule was found to be $1.6 \cdot 10^5$ l/mole sec.

G. S. KOZAK AND Q. FERNANDO, *Anal. Chim. Acta*, 26 (1962) 541–547

THE SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN SMALL AMOUNTS OF RADIOACTIVE GRAPHITE BY THE CATHODE LAYER TECHNIQUE

A modification of the cathode layer technique is suitable for the analysis of radioactive graphite using copper and cobalt as internal standards. The sample is ground with the internal standard mixture and introduced into a specially designed electrode which is burned in a d.c. arc. The cathode layer portion of the arc plasma is examined using a medium quartz spectrograph with photographic recording. The spectra are evaluated visually, by comparison with standard spectra, or by non-recording microphotometry using the "blackening separation" method. Using a 5-mg sample of graphite, the effective concentration range for Al, B, Ba, Be, Bi, Ca, Cr, Fe, Mg, Mn, Mo, Ni, Pb, Si, Sn, Ti and V is from 10 to 500 p.p.m. and the coefficient of variation for single exposures at the 100-p.p.m. level varies from 2 to 6% according to the element determined.

M. S. W. WEBB, J. C. COTTERILL AND T. W. JONES, *Anal. Chim. Acta*, 26 (1962) 548–556

THE EXTRACTION OF MERCURY BY DITHIZONE RETAINED ON SILICA GEL

A silica gel–dithizone–chloroform phase is suitable for the quantitative batch extraction of certain metals. The extraction of mercury from a chloride phase by such a support has been investigated and the effect of varying acidity, free ligand acid concentration, and chloride ion concentration has been determined.

T. B. PIERCE AND P. F. PECK, *Anal. Chim. Acta*, 26 (1962) 557–567

STUDIES ON THE SOLVENT EXTRACTION OF SOME CADMIUM CHELATES

Eighteen different chelating agents have been investigated as possible extractants for radiolabelled $10^{-5.1}$ *M* cadmium from aqueous solutions into chloroform. The experimentally-determined extraction data have been analyzed theoretically by measurement of metal chelate and chelating agent association constants and distribution constants.

G. K. SCHWEITZER AND D. R. RANDOLPH, *Anal. Chim. Acta*, 26 (1962) 567–571

CHELATING PROPERTIES OF BIS(8-HYDROXY-2-METHYL-5-QUINOLYL)METHANE

A new chelating reagent, bis(8-hydroxy-2-methyl-5-quinolyl)methane, has been prepared and characterized. It does not react with aluminum but does chelate with many other metals. Analytical data did not permit a decision on the possibility that some of these chelates are polymeric.

J. P. PHILLIPS AND J. T. LEACH, *Anal. Chim. Acta*, 26 (1962) 572–574

THE METAL COMPLEXES OF SOME AZO AND AZOMETHINE DYESTUFFS

PART I: SPECTRA IN WATER, AND IN DIOXAN/WATER, IN THE WAVELENGTH RANGE 320–600 mμ

The visible spectra of the highly sensitive colorimetric reagent 4-(2-pyridylazo)-resorcinol (I), and of the coloured complexes formed with copper(II), nickel(II), cobalt(II), lead(II), and uranium(VI) were obtained in water and in aqueous dioxan. The structures of these complexes were determined by spectrophotometric methods, and chelation by (I) established as essentially terdentate. Comparison is made with the visible spectra of salicylidene-2-aminopyridine (II), 2-(*o*-hydroxyphenyl-imino-methyl)-pyridine (III), and benzeneazoresorcinol (IV), and of the metal complexes of (II), (III), and (IV). The red coloration obtained with 4-(2-pyridylazo)-resorcinol is explained by the presence of a pseudo-phenanthroline system and an *o-o'*-disubstituted azo system, the active groups in chelation being the pyridine nitrogen atom, the azo nitrogen farthest from the heterocycle, and the *o*-hydroxyl group.

W. J. GEARY, G. NICKLESS AND F. H. POLLARD, *Anal. Chim. Acta*, 26 (1962) 575–582

CHLORPROMAZINE HYDROCHLORIDE AS AN ANALYTICAL REAGENT

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LEE KUM-TATT AND H. K. TONG, *Anal. Chim. Acta*, 26 (1962) 583–588

STUDIES ON ADSORPTION INDICATORS

PART I. TITRATION OF IODIDE IN PRESENCE OF CHLORIDE. MECHANISM OF THE COLOUR CHANGES DURING ARGENTOMETRIC TITRATIONS WITH CONGO RED AS ADSORPTION INDICATOR

Congo red is a suitable indicator for the titration of iodide in presence of chloride with silver solution at pH 5–5.5. The behaviour of congo red as an adsorption indicator is described in detail. The silver compound of congo red has been isolated and its properties investigated.

K. N. TANDON AND R. C. MEHROTRA, *Anal. Chim. Acta*, 26 (1962) 589–594

SPOT TEST EXAMINATION OF MATERIALS FOR AROMATIC COMPOUNDS BASED ON SULFONATION

(Short Communication)

F. FEIGL AND V. GENTIL, *Anal. Chim. Acta*, 26 (1962) 595–596

THE ISOLATION OF RADIO-MANGANESE BY DISTILLATION AS PERMANGANIC ACID

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(Received October 9th, 1961)

INTRODUCTION

The isolation of manganese from a complex inorganic mixture can be performed by different techniques: precipitation (generally as MnO_2), solvent extraction of chelate systems or ion-exchange[1], the last allowing carrier-free separation of radio-manganese. All these methods however are time-consuming and inselective.

Little attention has been paid to the selective separation of manganese by distillation as permanganic acid described by STRICKLAND AND SPICER[2]. According to this technique manganese is distilled as $HMnO_4$ when manganese(II) solutions are heated in the presence of periodate in a 10 *M* sulphuric acid medium. The method was applied in the separation of manganese in two high-chromium steels, giving quantitative and reproducible recoveries.

It was our purpose to investigate this procedure for use in trace analysis after neutron activation and for the preparation of carrier-free ^{54}Mn from iron cyclotron targets. Furthermore, experimental data were desired as to the behaviour of several elements under the given distillation conditions.

EXPERIMENTAL

A series of distillations were performed in the apparatus described by STRICKLAND AND SPICER[2]. 1-mg aliquots of manganese(II) were distilled from 50 ml of 10 *M* sulphuric acid in the presence of 1 g of potassium periodate. Distillation took place from a 500-ml flask equipped with a separatory funnel for the introduction of the reagents, a splash-bulb and a water-cooled condenser.

The volume was kept constant by addition of 40% nitric acid, as the distillation proceeded; 200 ml of distillate were collected. The time needed to complete the distillation was about 1 h. Deposits of manganese dioxide on the glass apparatus were unavoidable, even when the nitric acid added had previously been saturated with potassium periodate. The recoveries, determined spectrophotometrically, ranged between 43 and 68% and were not quantitative.

It was found desirable to reduce the volume of the distillation apparatus in order to reduce the distillation time. An all-glass apparatus was constructed (see Fig. 1) with a 50-ml capacity flask. Inlets were provided for the addition of nitric acid and for the introduction of an inert gas into the reaction mixture. Manganese recoveries

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were determined by spectrophotometry or by tracer techniques using ^{54}Mn. Interferences of iron, cobalt and chromium were also studied with ^{59}Fe, ^{60}Co and ^{51}Cr tracers.

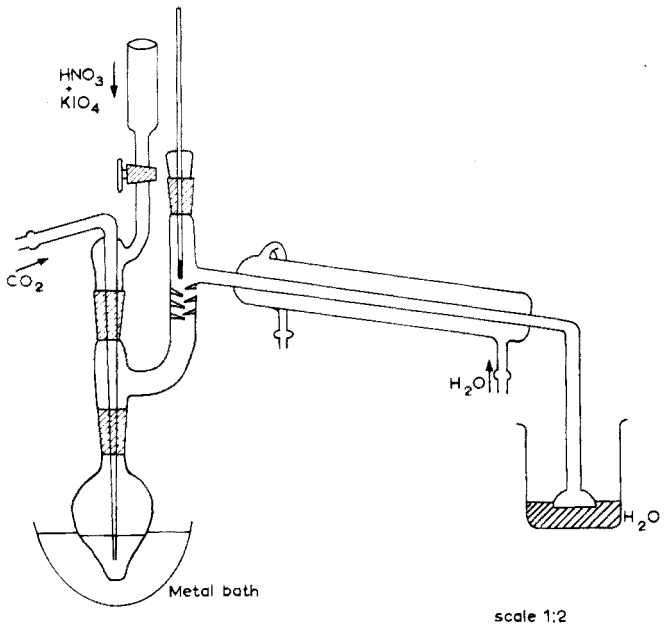

Fig. 1.

PROCEDURE

A stock solution was prepared containing 5 ml of standard manganese(II) solution, 28 ml of 36 *N* sulphuric acid, 2 g of potassium periodate, and tracer solutions, and diluted with water to 50 ml.

10 ml of this solution were introduced into the distillation flask and heated on a metal bath. When the distillation began, 40% nitric acid (containing 10 g of potassium periodate/100 ml) was added dropwise, while a steady stream of carbon dioxide was passed via a capillary through the reaction mixture to ensure smooth boiling. The distillate was collected in a 100-ml beaker. After about 15 min the distillation was stopped.

When manganese recoveries were determined by spectrophotometry the distillate was heated for 10 min to remove carbon dioxide, 1 g of potassium periodate was added and the heating was continued for 5 min. The cooled solution was transferred to a 50-ml volumetric flask and diluted to the mark with water. Spectrophotometric standards were prepared by heating 10 ml of stock solution with 15 ml of 6 *N* sulphuric acid and 1 g of potassium periodate and diluting the cooled solution to 50 ml. The determinations were made at 540 mμ with a Beckman DU spectrophotometer.

Radiometric recoveries of the tracers were calculated by measuring the activities of 4-ml aliquots from the 50-ml distillates. All activity measurements were made by γ-counting with a well-type NaI(Tl) detector. Radiochemical identification and purity control of the distillates were performed by γ-ray spectrometry.

It appeared that iron, cobalt and chromium are not distilled under the given conditions.

For the experiments with synthetic iron cyclotron targets, aliquots of iron powder (100–1000 mg) were dissolved in the distillation flask in a minimum amount of aqua regia, taken to near dryness and redissolved in 5 ml of 14 *N* nitric acid, which was then evaporated to near dryness. Tracer solutions were added with activities equi-

TABLE I

DISTILLATION OF MANGANESE AS PERMANGANIC ACID

Composition of distillation mixture	*Manganese recovery (%)*	*Recovery of interfering element (%)*
Mn(II) 0.1 mg	62	
	73	
	69	
	72	
	77	
	68	
Mn(II) 0.1 mg	67	
Fe 100 mg	66	
	71	
	68	
Mn(II) 0.1 mg	61	^{51}Cr 0
+ ^{51}Cr	62	0
	48	$4 \cdot 10^{-2}$
	57	$4 \cdot 10^{-2}$
	63	$6 \cdot 10^{-2}$
Mn(II) 0.1 mg	71	^{51}Cr $9 \cdot 10^{-2}$
Fe 100 mg	74	0
+ ^{51}Cr	70	$5 \cdot 10^{-2}$
Mn(II) 0.1 mg	64	^{60}Co 0
+ ^{60}Co	61	$3 \cdot 10^{-3}$
	70	0
	61	0
Mn(II) 0.1 mg	63	^{60}Co 0
Fe 100 mg	64	0
+ ^{60}Co	60	$4 \cdot 10^{-3}$
	48	0
Mn(II) 0.1 mg	48	^{59}Fe 0
+ ^{59}Fe	47	0
	65	0
	58	0
	53	0
Mn(II) 0.1 mg	62	^{59}Fe $4 \cdot 10^{-2}$
Fe 100 mg	60	$3 \cdot 10^{-2}$
+ ^{59}Fe	64	$2 \cdot 10^{-2}$
^{54}Mn +		
0.01 mg Mn(II)	61	
0.1 mg Mn(II)	70	
1 mg Mn(II)	61	
10 mg Mn(II)	11	

valent to expected cyclotron yields, together with sulphuric acid, potassium periodate and aliquots of water, calculated to make the medium approximately 10 *M* in sulphuric acid.

RESULTS

The results of different series of distillations with manganese carrier and ^{59}Fe, ^{51}Cr and ^{60}Co tracers, with or without iron carrier are summarized in Table I. The influence of the manganese carrier concentration is given in the same table.

The results from carrier-free distillations of ^{54}Mn and from distillations of synthetic cyclotron targets are summarized in Table II. The quantities of ^{54}Mn and ^{60}Co tracers

TABLE II

DISTILLATION OF CARRIER-FREE ^{54}Mn AND ISOLATION OF ^{54}Mn FROM CYCLOTRON TARGETS

Distillation mixture		*Recovery (%)*	
^{54}Mn		^{54}Mn	93
			83
			101
			92
Cyclotron targets		^{54}Mn	^{60}Co contamination (spectrometry)
^{54}Mn + ^{60}Co[a]			
Fe(III)	100 mg	87	0
	100 mg	87	0
	100 mg	90	0
	100 mg	87	0
	100 mg	87	0
	100 mg	91	0
	250 mg	89	0
	250 mg	84	0
	500 mg	59	0
	1,000 mg	40	0

[a] $^{54}Mn/^{60}Co$ activity ratio 1:16

added to the synthetic targets are based upon the theoretical thick target yields described in the literature[3]. It appears that the induced ^{59}Fe activity can be neglected in comparison to the ^{54}Mn and ^{55}Co activities. The $^{54}Mn/^{55}Co$ ratio was calculated to be about 1/16.

DISCUSSION

It appears from Tables I and II that good recoveries, varying from 60 to 90%, can be expected. These results are not quantitative due to deposition of manganese dioxide in the distillation apparatus. The yield can be increased by passing hydrogen chloride through the condenser, thus solubilizing the precipitated manganese dioxide. This treatment does not introduce iron or cobalt into the distillate, as was proved by tracer experiments with ^{59}Fe and ^{60}Co.

No contamination is to be feared from ^{59}Fe or cobalt radioisotopes. Extremely small quantities of ^{51}Cr were detected in the distillate, but these are not likely to interfere, because iron targets for cyclotron irradiation are normally chromium-free.

Furthermore, ^{54}Mn (0.8 MeV) can be selectively counted in the presence of ^{51}Cr (0.3 MeV) by energy discrimination.

If distillation takes place in the presence of carrier, 1 mg of manganese must be considered as the upper limit giving a satisfactory yield. ^{54}Mn can be separated in a carrier-free state from irradiated iron cyclotron targets. Time needed for a distillation is 15 min for a target of about 100 mg.

As the formation of insoluble iron salts disturbs the smooth distillation, the target weight should be kept as low as possible. The overall yield was found to be 85–90%.

ACKNOWLEDGEMENT

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SUMMARY

The selective isolation of manganese by distillation as permanganic acid was investigated. Contamination from Fe, Cr and Co was negligible. It was found possible to isolate carrier-free ^{54}Mn from cyclotron-irradiated iron targets. The time needed for the distillation was about 15 min with yields of 85–90%.

RÉSUMÉ

Les auteurs ont examiné la séparation du manganèse par distillation, sous forme d'acide permanganique. Cette méthode a permis d'isoler le radiomanganèse. La contamination due au fer, chrome et cobalt est négligeable. Le temps nécessaire pour la distillation est d'environ 15 min, avec des rendements de 85–90%.

ZUSAMMENFASSUNG

(54)-Mangan kann nach Umwandlung in Permangansäure durch Destillation von Trägersubstanzen wie Eisen, Chrom oder Kobalt abgetrennt werden. Die Destillation verläuft rasch mit einer Ausbeute von 85–90%.

REFERENCES

1 G. W. SEDICOTTE, *The Radiochemistry of Manganese*. National Academy of Sciences, Nuclear Science Series NAS-NS, 3018, 1960.
2 J. D. H. STRICKLAND AND G. SPICER, *Anal. Chim. Acta*, 3 (1949) 543.
3 J. W. IRVINE, JR., *Nucleonics*, 3, No. 2 (1948) 5.

AN ENZYMATIC METHOD FOR THE DETECTION OF ESTERS

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Esters as a class are more difficult to detect than compounds with similar functional groups, *i.e.*, aldehydes, ketones and carboxylic acids. This difficulty arises from two causes:

(*1*) The ester group is resonance stabilized and is, therefore, less reactive than the aldehydic and ketonic groups.

(*2*) The ester group does not have an easily ionizable atom, as in the case of carboxylic acids. At the same time, there are other closely related substances, such as acid halides and anhydrides, which interfere in the detection of esters.

Hence very few good tests are known for esters as a class. The classical method depending upon the hydrolysis of esters is tedious and lengthy. FEIGL's[1] hydroxamic acid test is a great improvement on the classical method. Unfortunately, a number of common substances, *e.g.*, chloroform, formamide, acetamide, most aldehydes, lactones, trichloroacetic acid, benzotrichloride, acetonitrile etc., give a positive hydroxamic acid test. This test, therefore, suffers from a lack of specificity. Because enzymes are relatively specific in their behavior, it seemed likely that a selective test for esters could be evolved based on enzymatic action. Initial studies of enzymatic tests for esters were made by VAN EYKEN[2]. Although the results were not completely definitive, they indicated enough promise that the more extensive studies reported here were undertaken.

A number of esterases were examined for this purpose. Steapsin, wheat germ lipase, horse serum lipase and, to a limited extent, glandular lipase were allowed to react with various esters. Almost all the common esters were investigated. Some substituted and sterically hindered esters were also tested. The pH of ester–esterase mixtures was adjusted to neutrality to methyl red using ammonium hydroxide of appropriate concentration. This step was necessary because a number of substances which are not esters react with lipase giving immediate release of hydrogen ions. The presence of the ester was inferred if the yellow color of the mixture changed to orange or pink on standing for a few minutes. To choose the proper esterase for this test, esters were acted upon by various esterases under identical conditions. Lipase in general gave the best results. Interferences from organic compounds with other functional groups were also studied, and efforts were made to remove them. It was also observed that the relative reactivity of the esters with esterases could in general be explained on the basis of generally accepted mechanisms.

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EXPERIMENTAL METHODS AND RESULTS

Preparation of reagents

(*1*) *Lipase solution.* Pancreatic lipase (steapsin) was weighed and the necessary amount of distilled water added to make a 10% solution. The contents were thoroughly stirred with a glass rod until a homogeneous emulsion was formed. A few drops of toluene were added, and the emulsion was again thoroughly shaken. The lipase solution so prepared was stable for 24 h at room temperature (approx. 26°).

(*2*) *Methyl red.* A 0.20% solution in distilled water.

(*3*) *Ammonium hydroxide.* The strength of the ammonium hydroxide solutions need not be exact. Various dilute solutions ranging from 0.1 *N* to 0.01 *N* were used.

Reagent grade chemicals were used throughout without further purification.

Acetophenone was shaken with sodium carbonate and then distilled. Benzyl alcohol was also freshly distilled. Steapsin, wheat germ lipase and horse serum lipase were procured from the local market.

General method

Three drops of lipase solution were added to three drops of the solution to be tested. A drop of methyl red was added. If the solution became pink, it was made yellow by the addition of the least possible quantity of ammonium hydroxide. If more than 3 drops of 0.1 *N* ammonium hydroxide were required to make the original substance (3 drops) neutral to methyl red, it could be assumed that the substance was either an ester that had been highly hydrolysed or that it was probably an acid, an anhydride or an acid halide. After neutralization, the contents were shaken vigorously for 3–5 min. A change of color from yellow to light orange or pink indicated the presence of an ester. Another drop of indicator was added if the change in color was not clearly visible. Of the common substances, benzaldehyde, nitroethane, nitrobenzene and bromobenzene interfered. If the test was slightly modified as given below, nitroethane still interfered, but nitrobenzene, bromobenzene and benzaldehyde did not.

Modified ester test

To 3 drops of the substance were added 3 drops of lipase, 1 drop of indicator and 3 drops of distilled water. Dilute ammonium hydroxide was then added to make the mixture just alkaline. The solution was then shaken for 10 min, and the color of the aqueous layer noted. In the presence of an ester, the mixture will be light orange or pink; otherwise, colorless.

Comparison of esterases

For purposes of comparison, 5% solutions of pancreatic, wheat germ and horse serum lipase were each adjusted to a pH of 6.2 using dilute ammonium hydroxide or hydrochloric acid as required.

The ester test as outlined above was performed with these esterases. The colors in the various test tubes were visually compared. In case hydrolysis was negligible in 5 min, the colors were compared after about 4 h. The results are summarized in Table I.

Extension of the ester test

When it became clear that pancreatic lipase, in general, gave the best results, the

ester test was tried with additional esters. The results are summarized in Table II.

The ester test was repeated with pure samples of different types of organic compounds. The following compounds gave a negative ester test: ethyl alcohol, methyl

TABLE I

COMPARISON OF PANCREATIC, WHEAT GERM AND HORSE SERUM LIPASES

Name of esters	*Effectiveness of lipases in the ester test (in decreasing order)*
Methyl acetate, ethyl acetate, benzyl acetate (hydrolysis negligible), amyl butyrate, ethyl anisate (hydrolysis negligible)	Pancreatic lipase Wheat germ lipase Horse serum lipase
Ethyl propionate, ethyl butyrate, methyl benzoate, methyl salicylate and ethyl phthalate (negative test), ethyl cinnamate, ethyl acetoacetate, benzyl benzoate (negative test)	Pancreatic lipase Horse serum lipase Wheat germ lipase
Vinyl acetate, bornyl acetate (after 12 h), ethyl bromoacetate	Wheat germ lipase Horse serum lipase Pancreatic lipase
Ethyl malonate, phenyl benzoate (after 1 h)	Horse serum lipase Pancreatic lipase Wheat germ lipase
Ethylene diacetate	Horse serum lipase Wheat germ lipase Pancreatic lipase
Isopropyl phthalate, oxalate	Quick hydrolysis; all equally good

alcohol, acetaldehyde, acetamide, ether, glycerine, toluene, chloroform, bromobenzene, carbon tetrachloride, acetophenone, urea, aniline, ethyl amine, β-naphthol, acetic acid, sucrose, glucose.

Nitroethane and benzaldehyde gave a positive ester test. Sometimes bromo-

TABLE II

THE ESTER TEST WITH PANCREATIC LIPASE ONLY

Esters	*Remarks*
Isopropyl benzoate	Positive test in 15 h
Isoamyl salicylate	Negative test
Isobutyl acetate	Positive test in 10 min
Isopropyl propionate	Positive test in 1 h
Isobutyl formate	Positive test in 5 min
Ethyl citrate, *n*-butyl citrate, dimethyl phthalate, ethyl cyanoacetate	Positive test in 1 min
Isopropyl trimethylacetate, methyl diisopropylacetate, methyl dimethylethylacetate, *sec*-octyl trimethylacetate	Positive test only after 12 h

benzene, nitrobenzene and benzyl alcohol also gave positive tests. However, when the modified ester test is used, they give a negative result.

Test for an ester in the presence of other substances

Sometimes it is required to test for an ester in the presence of other substances. Therefore, ethyl acetate was mixed with different organic substances, and the ester test was performed on the mixtures. The results are summarized in Table III.

TABLE III

TEST FOR ESTERS IN THE PRESENCE OF OTHER SUBSTANCES

No.	*Composition of mixture*	*Time in min for positive test*	*Remarks*
1	Ethyl acetate + ether (1 : 1)	5	
2	Ethyl acetate + ether (1 : 10)	40	
3	Ethyl acetate + benzene (1 : 1)	10	
4	Ethyl acetate + acetamide (1 : 1)	5	
5	Ethyl acetate + glycerine (1 : 1)	5	
6	Ethyl acetate + sucrose (1 : 1)	5	
7	Ethyl acetate + dextrose (1 : 1)	5	
8	Ethyl acetate + acetaldehyde (4 : 1)	5	
9	Ethyl acetate + ethyl alcohol (1 : 1)	5	
10	Ethyl acetate + propionaldehyde (4 : 1)	5	
11	Ethyl acetate + benzyl alcohol (1 : 1)	13	shake for 10 min and allow to stand for 3 min; observe upper layer
12	Ethyl acetate + toluene (1 : 1)	10	observe the lower layer
13	Ethyl acetate + chloroform (1 : 1)	8	observe the upper layer
14	Ethyl acetate + bromobenzene (1 : 1)	10	run a blank with pure bromobenzene
15	Ethyl acetate + carbon tetrachloride (1 : 1)	10	observe the upper layer
16	Ethyl acetate + acetophenone		as in number 11
17	Ethyl acetate + nitrobenzene (1 : 1)		Shake for 10 min. Add another drop of indicator. Notice the upper layer. Compare with pure nitrobenzene
18	Ethyl acetate + nitrobenzene (1 : 3)		as in number 17
19	Ethyl acetate + nitrobenzene (1 : 1) at 50°	5	

Comparison with the hydroxamic acid test

Since the hydroxamic acid test is the best one known for the detection of esters, it is of interest to compare the two tests. The important points are summarized in Table IV.

DISCUSSION

The scope and limitations of the enzymatic method for the detection of esters

The results summarized in Table I indicate that of the three lipases tried, steapsin (the pancreatic lipase) gives the best results. Glandular pancreatic lipase was also used for a few experiments (results are omitted for the sake of brevity). This lipase was

found to act on phenyl benzoate better than the pancreatic lipase. In all other cases, steapsin either did better than, or was as good as, the gland lipase. Mixture of various lipases were also tried without any beneficial result. The use of activators, such as calcium chloride, albumin etc., was investigated in conjunction with the various lipases. It was found that the addition of activators did more harm than good to this test. When steapsin is used free from activators (as described under experimental), the ester test is quick and simple if applied to test pure substances. Thirty-eight "unknowns", comprising almost all the common organic classes of substances, were studied by this method. The esters used in the unknowns were: ethyl acetate, ethyl propionate, methyl benzoate, benzyl acetate, methyl salicylate, ethyl phthalate and amyl butyrate. They are fairly representative of aliphatic and aromatic esters. The non-esters included in the unknowns were: aldehydes, ketones, urea, acid chlorides, anhydrides, amides, alcohols, sugars, acids, toluene, chloroform and bromobenzene. Esters were detected in all cases where they were present. Of the non-esters, only benzaldehyde, nitroethane and bromobenzene gave positive tests. It therefore appears that the enzymatic approach provides a fairly reliable test. Benzaldehyde gives a positive ester test owing to autoxidation. However, interferences due to nitroethane, bromobenzene and nitrobenzene can be eliminated if a 20% emulsion of the unknown in water is used for this test. A positive test is obtained in the case of an ester; otherwise, a negative test is obtained.

Table IV shows that a number of substances which are not esters give a positive

TABLE IV

COMPARISON BETWEEN THE HYDROXAMIC ACID TEST AND THE ENZYMATIC TEST

Basis of comparison	*Hydroxamic acid test*	*Enzymatic test*
Number of tests usually performed	Three tests are recommended	Usually one test is necessary
Effect of time	It is best to notice the color within 5 min. The color may diminish with time	The color is noticed after 5 min. The color becomes intense with time
Tests with lactones	Positive test	Negative test
Test with esters of inorganic acids	Negative test	Negative test
Test with chloral hydrate	Positive test	Negative test
Test with chloroform and bromoform	Positive test	Negative test
Test with formaldehyde and benzaldehyde	Weakly positive test	Weakly positive test
Most amides	Positive test	Negative test
Acid esters	Weak test	Weak test
Acetonitrile	Positive test	Negative test

hydroxamic acid test. In such instances, the enzymatic method is more valuable. For instance, such common substances as lactones, anhydrides, formic and phthalic acids, acetamide, chloral hydrate and chloroform give a positive test with the hydroxamic acid method, but show no interference with the enzymatic method.

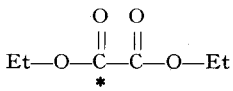
Correlation of the structure of esters with their relative rates of hydrolysis

The mechanism of the hydrolysis of esters is not fully known. The simplest way is to

consider enzymes as bifunctional catalysts having ionizable positive and negative groups[3]. The oxygen atom of the carbonyl and the alcoholic groups in an ester are susceptible to attack by the enzyme, the former being attached to the electronegative part of the enzyme, and the latter to the electropositive part. The intermediate so formed breaks up to give the products of hydrolysis. It is possible to explain the facts observed during this investigation on the basis of this assumption.

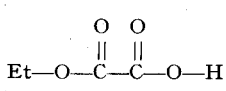
It has been found that ethyl bromoacetate and ethyl cyanoacetate are hydrolyzed much faster than ethyl acetate. This follows from the fact that the methyl group is a weak electron-releasing group which decreases the electropositive character of the carbonyl carbon atom. The bromo and cyano groups are electron-attracting groups which increase the electropositive character of the carbonyl carbon atom by pulling away electrons. This accounts for the increase in the rate of hydrolysis.

Esters of dibasic and tribasic acids have been found to hydrolyze very rapidly. Consider the case of diethyl oxalate.

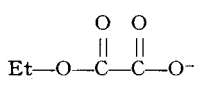


The electron-attracting carbonyl group (marked with an asterisk) pulls electrons from the unmarked carbonyl group, thus increasing the electropositive character of the carbon atom. Therefore, the hydrolysis of the esters of dibasic and tribasic acids is enhanced.

The acid esters of the dibasic acids are not easily hydrolyzed. Hydrolysis takes place if the pH is shifted to 5, whereas normally the optimum pH for the hydrolysis by lipase is 8. Taking the acid ester of oxalic acid as an example, it has the formula:



(1)



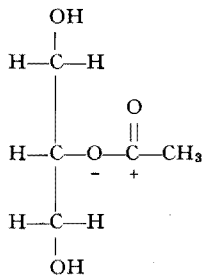
(2)

When the pH is on the basic side, the ester exists mostly in the ionic form (2). The negatively charged carboxylate group decreases the electropositive character of the carbonyl carbon atom of the ester. It is also possible that the negatively charged carboxylate group offers a better site for the proton to attach itself than does the alcoholic oxygen atom. When the pH is shifted to 5, the ester exists mostly in the un-ionized form (1), and there is no longer a charged electron-releasing group in the ester molecule. The hydrolysis, therefore, takes place more easily.

The hydrolysis of esters of secondary alcohols is of special interest. It is known that lipase hydrolyzes the triglycerides to 1,2-diglyceride and then to 2-monoglyceride. The action of pancreatic lipase then ceases. It has been taken to imply that lipase action is specific for primary hydroxyl groups. Our findings that lipase hydrolyzes many esters of secondary alcohols show this to be untrue.

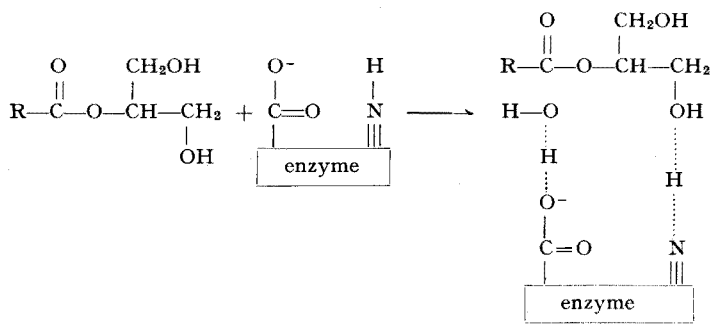
A suspicion has been expressed[4] that MATTSON AND BECK were unable to hydrolyze the ester bond at the secondary hydroxyl group as they did not use bile salts as activators. The function of bile salts is not to act as activators, but only as emulsifiers. It appears more probable that the reason is neither in the specificity of lipase for the ester bond of the primary hydroxyl group nor in the absence of activators, but rather

is a functional characteristic of the compound.

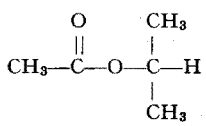


2-Monoglyceride

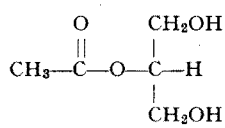
Here the terminal hydroxyl groups offer a better site for the proton of the $-NH_4^+$ group rather than the oxygen atom of the ester bond. This might be depicted as follows:



If such an explanation is true, it is to be expected that glycol monoacetate will not be hydrolyzed by the lipase even though it does not contain the ester bond of a secondary hydroxyl group. Isopropyl acetate is also very easily hydrolyzed which lends weight to the reasoning that it is not the secondary nature of the ester bond which is responsible for the lack of activity of the lipase.



Isopropyl acetate



2-Monoglyceride

Finally, it is noted that highly hindered esters give positive tests only after lengthy standing (Table II) which lends further support to the mechanism proposed above.

ACKNOWLEDGEMENT

The authors are grateful to DR. JAMES G. TRAYNHAM for supplying them with a number of esters and for his helpful suggestions. The financial support given to one of us (M.Q.) by the Continental Oil Company is gratefully acknowledged.

SUMMARY

An enzymatic method for the detection of esters has been developed. The use of various esterases as an analytical tool has been examined. It has been found that lipase can be used for the detection of esters under specified conditions. The relative rates of hydrolysis observed in the case of various esters have been explained on the basis of the generally accepted mechanism. The enzymatic method has been compared with the hydroxamic acid test.

RÉSUMÉ

Les auteurs ont développé une méthode enzymatique pour l'identification des esters, au moyen de lipase. Une comparaison a été faite avec l'essai à l'acide hydroxamique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zum Nachweis von Estern mit Hilfe von Enzymen. Die bei der Hydrolyse entstandene Säure wird durch den Farbumschlag von Methylrot nachgewiesen. Die enzymatische Methode wird mit dem Hydroxamsäuretest verglichen.

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CARBAZOLES, PHENAZINES AND DIBENZOFURAN IN PETROLEUM PRODUCTS; METHODS OF ISOLATION, SEPARATION AND DETERMINATION

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INTRODUCTION

The adverse effects of nitrogen compounds in various phases of petroleum refining have been apparent to the industry for some time. It is known that these compounds reduce the stability of refined products through gum formation and also impart color and odor[1]. In addition, they adversely affect the activity of cracking and other catalyst types employed in petroleum processing[2]. Therefore, to apply the most effective methods and conditions for the removal of these impurities, it is important that the types of nitrogen compounds present in a distillate be known.

Generally, both basic and nonbasic nitrogen compound types occur in petroleum distillates. While the basic nitrogen compounds can be obtained by hydrochloric acid extraction of the oil, the isolation of the nonbasic components is not as easily accomplished. Activated aluminum oxide has been used for this purpose[3] but has the disadvantage that aromatics are also adsorbed. Thus, elution with methanol yields a concentrate which contains both the nonbasic nitrogen compounds and aromatic hydrocarbons. During the search for an improved concentration step it was found that indoles, carbazoles, and phenazines reacted with 72% perchloric acid permitting separation from the aromatic hydrocarbon phase. The technique is based on the finding that indole and carbazole nitrogen exhibits basic properties toward perchloric acid[4,5] and that the resulting perchlorates are soluble in perchloric acid. Furthermore, gas chromatography on a silicone oil-firebrick column was successfully applied for the separation of the alkylindoles and carbazoles present in this concentrate, and ultraviolet spectroscopy and mass spectrometry were used for their characterization.

While the detection and quantitative determination of pyrroles and indoles can be achieved easily[6,7], the quantitative determination of carbazoles in petroleum products has been done only to a limited extent[3,8,9]. A method of WANAGS, which uses 2-bromo-2-nitroindandione-1,3 as color reagent[10,11], showed a minimum of interference from other nitrogen compounds and was, therefore, found suitable for the determination of carbazoles in petroleum products.

The occurrence of phenazines in petroleum distillates has not been reported in the literature previously. After the liberation of the phenazines from the perchlorates, the phenazines were separated by gas chromatography on a silicone oil-firebrick column and characterized by ultraviolet spectroscopy and mass spectrometry.

Although the major effort of this investigation was concerned with the identification of nitrogen compounds in a hydrogenated furnace oil, the accidental isolation

and identification of dibenzofuran from the oil appeared interesting enough to be reported, since this oxygen compound as well as the indoles, carbazoles, and phenazines showed resistance to catalytic hydrogenation.

EXPERIMENTAL

A hydrogenated light catalytically cracked furnace oil having a boiling range of 450 to 650°F (232–343°C) was used for this investigation. The total nitrogen content of the oil was determined by the Kjeldahl method, the amount of basic nitrogen by potentiometric titration, and the content of pyrroles plus indoles colorimetrically with *p*-dimethylaminobenzaldehyde reagent. The results of these determinations were as follows:

Total nitrogen:	160 p.p.m.
Basic nitrogen:	25 p.p.m.
Pyrroles + indoles:	5.7 p.p.m.
Carbazoles:	40 p.p.m.
Unidentified nitrogen:	89.3 p.p.m.

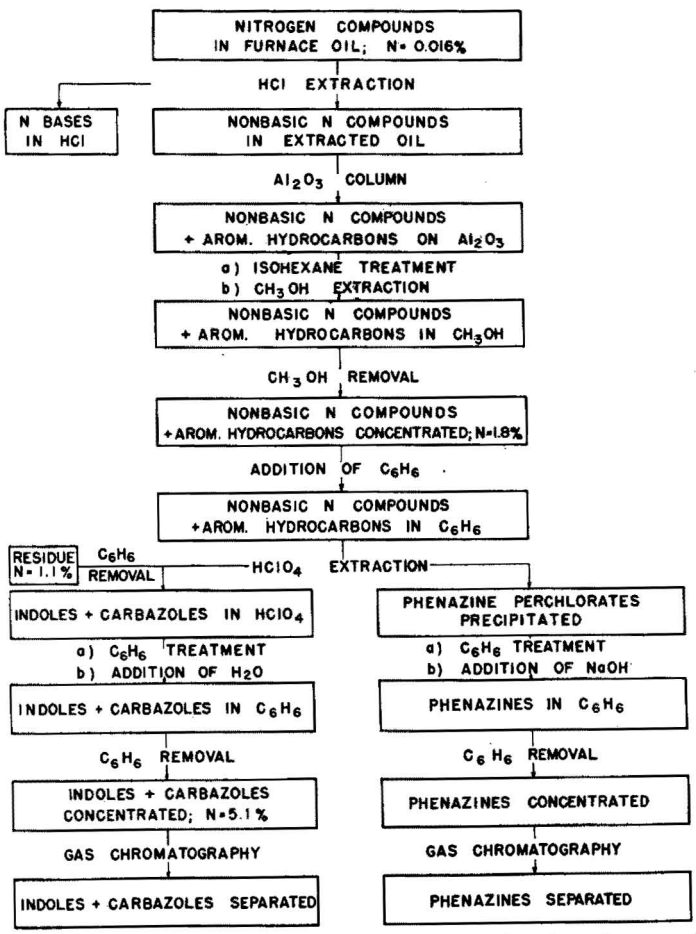

Fig. 1. Isolation of indoles, carbazoles, and phenazines from furnace oil.

Isolation of carbazoles

A 250 ml portion of the hydrogenated oil was extracted with three 50 ml portions of normal hydrochloric acid to remove the basic nitrogen compounds. The extracted oil was percolated through a column of activated aluminum oxide (Alcoa, Grade F-20; 50 cm long, 1.9 cm I.D.) for adsorption of the nonbasic nitrogen compounds. The column was washed with 500 ml of isohexane to remove nonadsorbed oil followed by elution with 500 ml of methanol (spectroanalyzed) for desorption of the nitrogenous material. The solvent was removed on a steam bath and the concentrate diluted with 50 ml of benzene. The solution was then extracted with five 10 ml portions of 72% perchloric acid for separation of the carbazoles from aromatic hydrocarbons present in this concentrate (Fig. 1).

A dark precipitate of solid perchlorates resulting from this acid treatment was separated by filtration on a glass-fiber filter and reserved for the isolation of phenazines as described later.

The perchloric acid extracts were combined and re-extracted with three 10 ml portions of benzene. The acid layer was diluted with water (1 : 4) to liberate the carbazoles from their perchlorates and then extracted with benzene. This benzene extract was stripped of solvent and a mixture of nonbasic nitrogen compounds containing the carbazoles was obtained as a residue. The residue was analyzed and found to contain 5.1% nitrogen.

Separation of carbazoles by gas chromatography

The residue containing the nonbasic nitrogen compounds obtained from the extraction with perchloric acid was dissolved in a small amount of benzene. The diluted sample was then introduced into a gas chromatography column (stainless steel, 20 ft. × 1/4 in. I.D.) containing 20% by weight of silicone oil on 42–60 mesh firebrick. The column was kept at 255°, the flash chamber at 310°, and the outlet at 280°. A Gow-Mac thermal conductivity cell was used as detector with helium as the carrier gas. The helium pressure was maintained at 15 psig. Fig. 2 shows the chromatogram

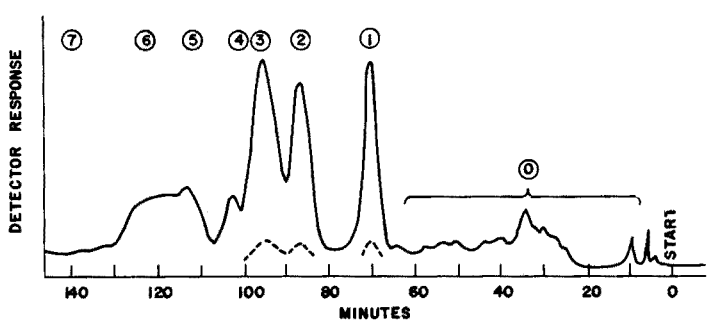

Fig. 2. Gas chromatographic separation of carbazoles on silicone oil: (0) Indoles; (1) Carbazole; (2) C_1-Carbazole; (3) C_2-Carbazole; (4) C_3-Carbazole; (5) C_4-Carbazole; (6) C_5-Carbazole; (7) Not identified.

and Table I the retention times of the individual fractions obtained from the carbazole concentrate. The dotted line of peaks 1, 2, and 3 in Fig. 2 was obtained on the recorder with an attenuation less sensitive than that used for the other part of the

TABLE I

GAS CHROMATOGRAPHIC SEPARATION OF CARBAZOLES ON SILICONE OIL

Fraction	*Compound (Largest m/e)*	*Retention time min**	*Log. ret. time*
0	Indoles	0 – 66	——
1	Carbazole (167)	70	1.844
2	C_1-Carbazole (181)	85	1.928
3	C_2-Carbazole (195)	94	1.972
4	C_3-Carbazole (209)	103	2.012
5	C_4-Carbazole (223)	113	2.052
6	C_5-Carbazole (237)	125	2.096
7	Not identified	> 136	——

*Time at peak maximum.

chromatogram. Since peaks 1, 2, and 3 in Fig. 2 were off-scale using the same attenuation throughout, the peaks were drawn manually in the ratio corresponding to the two different attenuations.

Interchangeable sections of stainless steel tubing (2 feet long, 3/8 inch I.D. and open at both ends), slipped over the heated outlet tube were used as receivers for the separated compounds. The receivers were heated to the outlet temperature on the instrument side and kept at room temperature at the opposite end. The tubes were exchanged according to the peaks on the chromatogram. The resulting fractions appeared as white solids and were reserved for further investigations by ultraviolet spectroscopy, mass spectrometry, and quantitative colorimetric determinations, after they had been removed from the receivers with methanol.

Characterization of carbazoles

The fractions obtained from the gas chromatographic separation were investigated by ultraviolet absorption techniques employing a Cary recording spectrophotometer-Model 11, mass spectrometric techniques, and colorimetry.

The compounds comprising group 0 on the gas chromatogram in Fig. 2 were mainly alkylindoles. This was shown by ultraviolet spectroscopic investigation of fractions corresponding to individual peaks and by spot tests with *p*-dimethylaminobenzaldehyde. A more detailed investigation of the peaks in group 0 was not intended because of the relatively low content of indoles in the oil (5.7 p.p.m.) and because separation and identification techniques for alkylindoles were described previously[12]. Figs. 3 and 4 show the ultraviolet absorption spectra of the separated carbazoles in methanol. Because of overlapping of fractions from the gas chromatography unit, some of the ultraviolet spectra represent mixed carbazoles – especially those of fractions 2 and 3 as well as of those from fractions 5, 6, and 7. All spectra show major absorption peaks or shoulders at wavelengths of 233–239 mμ, 245–250 mμ, 256–260 mμ, 290–295 mμ; minor peaks are noted in some of the spectra at 322 mμ and 335 mμ.

In addition, all fractions were studied with the aid of a Consolidated Electrodynamics Corporation mass spectrometer, Model 21–103, modified in this laboratory with a high-temperature inlet system. Table I lists the largest *m/e* values which correspond to the largest molecular weights in the high voltage spectra of the individual gas chromatographic fractions. These data indicate the molecular weights of carbazole and C_1- through C_5-carbazole. In this paper, C_1-, C_2-, C_3-, etc. refer to methyl-, ethyl-, propyl-, or any combination of these alkyl groups.

The most intense *m/e* values were 167 in the spectrum of fraction 1, *m/e* 181 in that of fraction 2, and 195 in fraction 3. In the spectra of fractions 4, 5, and 6, *m/e* 195 was the most intense value. This can be explained by the formation of C_2-carbazole fragments from C_3-, C_4-, or C_5-carbazoles in the mass spectrometer. Moreover, the high intensity of *m/e* 195 does not indicate that a C_2-carbazole is present as the major

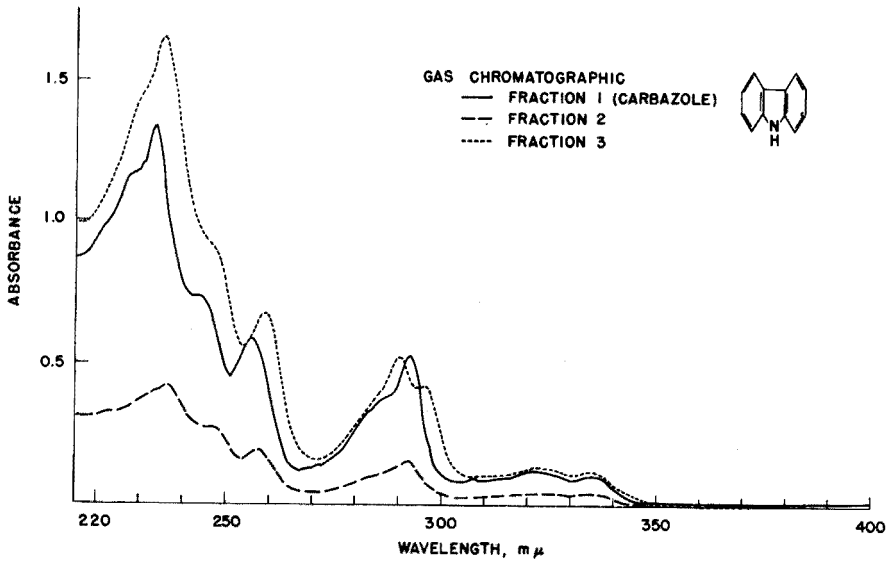

Fig. 3. Ultraviolet absorption spectra of alkyl carbazoles isolated from furnace oil.

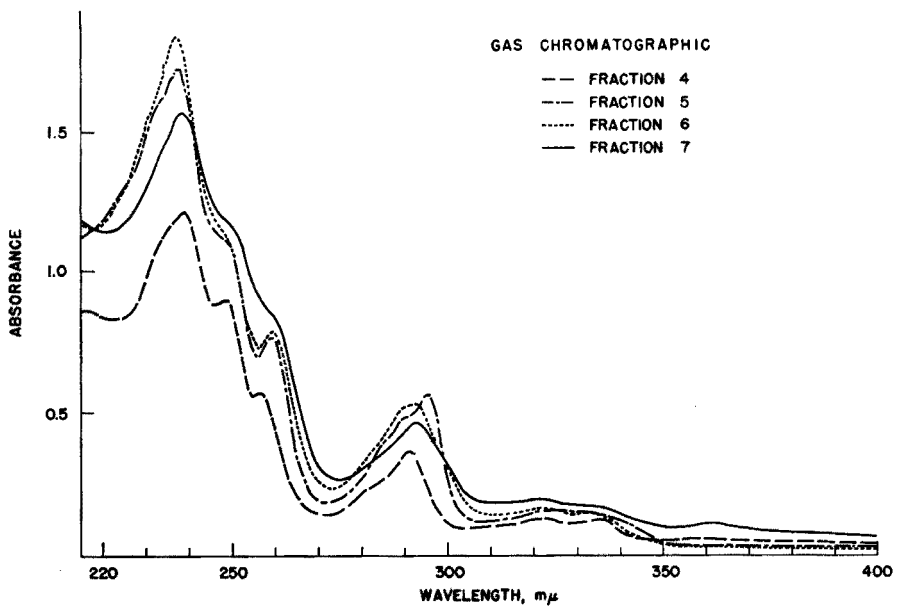

Fig. 4. Ultraviolet absorption spectra of alkyl carbazoles isolated from furnace oil

component in fractions 4, 5, or 6, since peak intensities in a mass spectrum cannot be used for quantitative determinations without calibration by authentic compounds even in case of a series of homologs. Such authentic alkylcarbazoles were not available for calibration purposes.

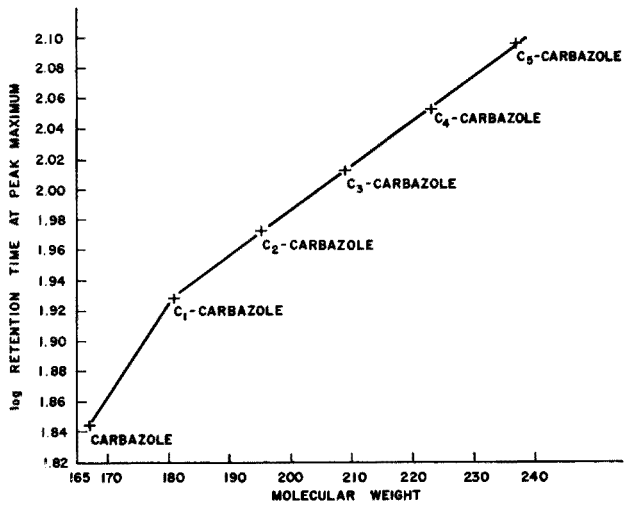

Fig. 5. Correlation between molecular weights and retention times of carbazoles.

To confirm the data obtained from the gas chromatographic separation and mass spectrometry of the carbazoles, the plot shown in Fig. 5 was prepared. This graph shows that the log of the retention time increases linearly with the molecular weight of the alkylcarbazoles. It will be noted that carbazole, the first member of the homologous series, does not fall on the straight line. This nonconformity was expected and is discussed in some detail by PECSOK[13]. The presence of unidentified compounds in the carbazole concentrate made an absolute determination of the retention times of the C_4- and C_5-carbazoles difficult. These compounds showed retention times between those of fractions 5 and 6 (Fig. 2) resulting in poor resolution of the carbazoles in that range of the gas chromatography curve.

The unfractionated nonbasic nitrogen concentrate, obtained by extraction with perchloric acid, was also investigated by mass spectrometry. The digitized mass spectrum of this concentrate contains the *m/e* values of a homologous series of carbazoles (167, 181, 195, 209, 223, 237, 251) and is shown in Table II.

This suggests the presence of both carbazole and C_1- through C_6-carbazoles. Although the digitized mass spectrum includes molecular weights up to 429, the mass spectrum itself showed even higher molecular weights up to 472.

An examination of Fig. 6A shows that the low voltage mass spectrum of the concentrate is composed primarily of peaks of carbazoles (167, 181, 195, 209), thus demonstrating the selectivity of the perchloric acid extraction for these compounds. No attempt was made to calculate the quantities of the individual carbazoles from the mass spectra because the peak heights did not correlate with the weight or mole

TABLE II

DIGITIZED HIGH VOLTAGE MASS SPECTRUM OF THE CARBAZOLE CONCENTRATE

m/e	*peak intensity*	*m/e*	*peak intensity*
133	770	207	1692
147	1047	208	1230
149	346	209	206
152	310	220	455
166	347	223	26
167	1746	237	16
177	446	251	32
178	430	266	436
180	1830	280	663
181	2394	354	310
182	368	414	100
190	718	429	177
192	623		
194	664		
195	1074		
206	7890		

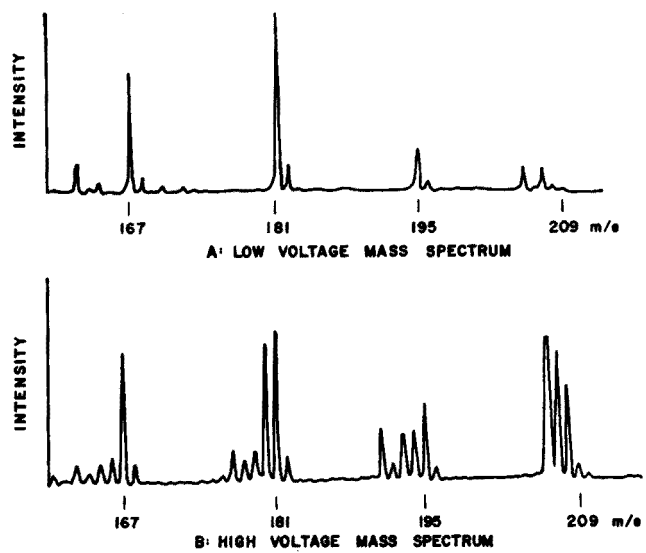

Fig. 6. Mass spectra of a concentrate of alkyl carbazoles. A) low voltage spectrum, B) high voltage spectrum.

percent distribution of the individual carbazoles. The high voltage spectrum in Fig. 6B shows some additional peaks which are partially due to fragmentation of the higher molecular weight compounds.

High voltage mass spectrometric examination of the total carbazole concentrate also indicated the presence of penta- and hexamethyl carbazole (*m/e* 237, 251) or other alkylcarbazoles having these molecular weights, but in a much smaller quantity.

These heavier molecular weight carbazoles (C_5 and higher) could not be recovered from the gas chromatography column and, thus, were not detected.

A virgin atmospheric gas oil was selected to demonstrate the applicability of the perchloric acid extraction method to other petroleum distillates. Fig. 7 shows the ultraviolet absorption spectra of some unidentified alkylcarbazoles which were isolated from the gas oil in the same manner as described for the carbazoles from the hydrogenated oil. The retention times for the individual fractions at 15 psig. helium and 255° column temperature are also shown in Fig. 7.

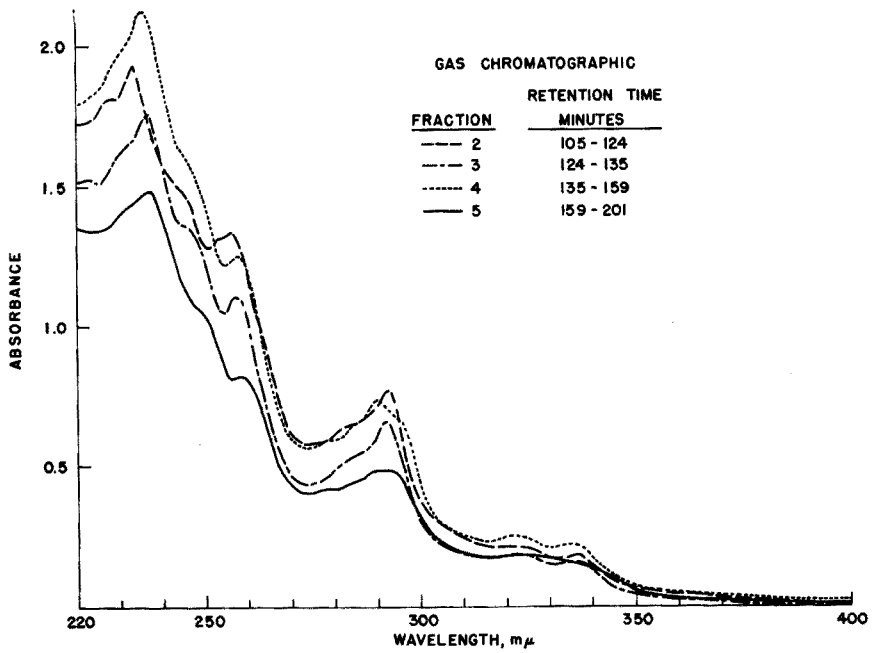

Fig. 7. Ultraviolet absorption spectra of alkyl carbazoles isolated from a virgin atmospheric gas oil.

Quantitative determination of carbazoles

The plot illustrated in Fig. 8 shows that either the colorimetric method or the peak area measurement of a gas chromatogram can be used for the quantitative determination of the separated alkylcarbazoles. A straight line was obtained by plotting the absorption at 525 mμ of each fraction after reaction with 2-bromo-2-nitroindandione-1,3 versus the peak areas obtained from the gas chromatogram. Since the peak areas of a gas chromatogram are directly related to weight in a series of homologous compounds, and since the points for the different alkylcarbazoles fall on a straight line, it was concluded that the carbazoles were recovered quantitatively from the gas chromatography column and that both the peak areas and the colorimetric method can be used for quantitative determinations of alkylcarbazoles. Fig. 8 also shows that C_2-carbazole is the major component among the alkylcarbazoles separated by gas chromatography.

The 2-bromo-2-nitroindandione-1,3 reagent was prepared according to WANAGS'

procedure[14,15] and was used for the determination of the carbazoles. Since *p*-dimethylaminobenzaldehyde reacts only with pyrroles and indoles, and not with carbazoles, and since 2-bromo-2-nitroindandione-1,3 yields colors with all three groups of compounds, it was possible to calculate the amount of carbazoles by difference. The

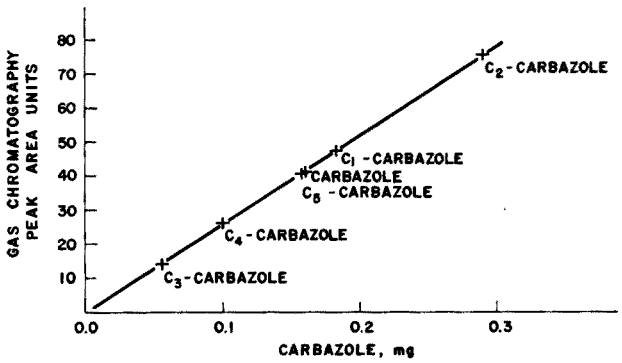

Fig. 8. Determination of carbazoles colorimetrically and by gas chromatography.

procedure recommended for the determination of carbazoles when pyrroles and/or indoles are present is as follows. Exactly 1.0 ml of the reagent, which contains 7.6 g of 2-bromo-2-nitroindandione-1,3 in 152 ml of glacial acetic acid, is added to a sample containing 0.1 to 1.0 mg of carbazole and the solution is diluted to 20.0 ml with glacial acetic acid. The sample is heated for 4 h in a water bath for maximum color development. The solution is then transferred to a cuvette and measured photometrically at 525 mμ against a reagent blank. The absorbances are converted to the equivalent concentrations of carbazole by means of a previously prepared calibration curve. The absorbance due to the presence of pyrroles and/or indoles is subtracted from the original absorbance and is determined with the aid of two calibration curves using *p*-dimethylaminobenzaldehyde as the first, and 2-bromo-2-nitroindandione-1,3 as the second reagent. Indole was employed as the calibration standard.

Phenazines

During the perchloric acid extraction procedure, a black precipitate was formed which was insoluble in both the benzene and acid layers. This precipitated material was isolated from the two liquid phases by filtration through a glass-fiber filter paper, washed with benzene and finally dried by air. An attempt to determine the melting point of the dry material resulted in a small explosion at about 130°. Treatment with concentrated aqueous sodium hydroxide and benzene, however, decomposed a portion of the solid perchlorates and liberated some of the nitrogen compounds. The benzene layer was separated from undissolved residue and the aqueous layer. Most of the benzene was then stripped off and the residue subjected to gas chromatography. A 20% by weight silicone oil on firebrick packing was used in a column 20 feet long by 1/4 inch I.D. A column temperature of 288° and a flash chamber temperature of 318° were employed. Helium at 15 psig. was used as the carrier gas. The resulting chromatogram is shown in Fig. 9. Five fractions were collected in 10 ml test tubes cooled by dropping water. Fractions 4 and 5 were collected on a time basis, since only minor peaks were

noticed on the chromatogram. Fraction 4 had a retention time between 39 and 67 min and fraction 5 between 67 and 100 min. The isolated cuts were taken up in 4 ml portions of methanol and examined by ultraviolet spectroscopy. Table III lists the absorption maxima of each spectrum and Fig. 10 shows the absorption spectra.

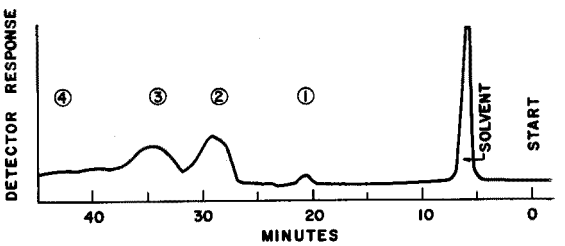

Fig. 9. Gas chromatographic separation of phenazines on silicone oil.

TABLE III

ULTRAVIOLET ABSORPTION MAXIMA OF PHENAZINES SEPARATED BY GAS CHROMATOGRAPHY

Fraction	*Absorption maxima (mμ)*				
1			257		
2	240	250	255	318	360
3	240	252	257	322	363
4		252	259		365
5		254			
Phenazine		248			362

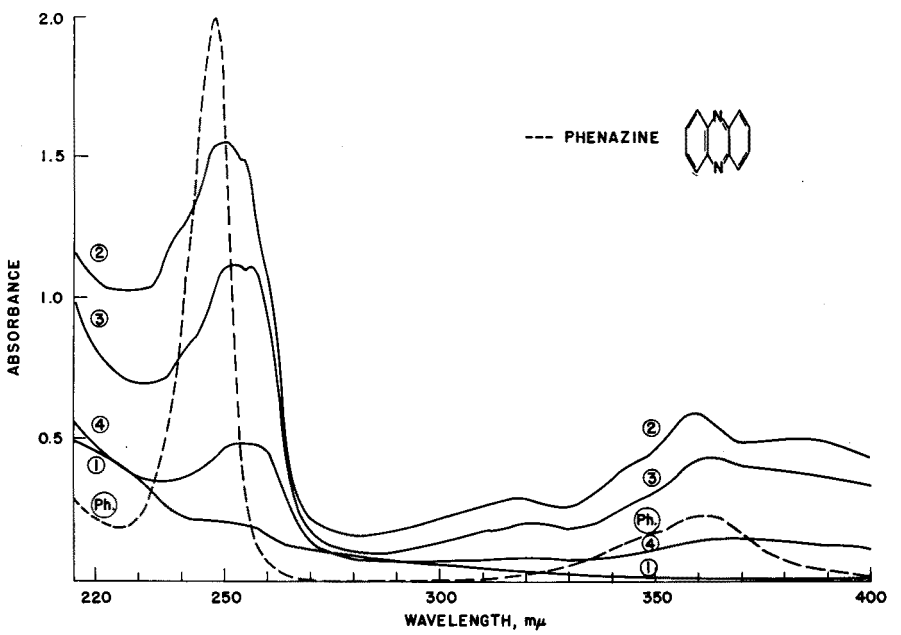

Fig. 10. Comparison of ultraviolet absorption spectra of separated alkyl phenazines with that of pure phenazine.

The presence of phenazines in fractions 2 and 3 was suggested by the yellow color of these fractions and substantiated by the ultraviolet spectra which are compared with that of phenazine in Fig. 10. Fractions 2 and 3 from the gas chromatographic separation were also investigated by mass spectrometry. Although both fractions contained silicone oil from the column packing, it was possible to recognize the *m/e* values of 180 (for phenazine) in fraction 3 and of 194 (for methylphenazine) in fraction 4.

Dibenzofuran

In an attempt to characterize the remainder of the material not extracted with perchloric acid for other types of nitrogen compounds, further separations were made by gas chromatography. The silicone oil column and the conditions used were identical with those described previously for the separation of the carbazoles. Fractions were collected according to the peaks of the gas chromatogram and were investigated by ultraviolet spectroscopy and mass spectrometry as described before. The ultraviolet absorption spectrum of the peak having a retention time of 12 min in the gas chromatographic separation is shown in Fig. 11 together with the spectrum of pure

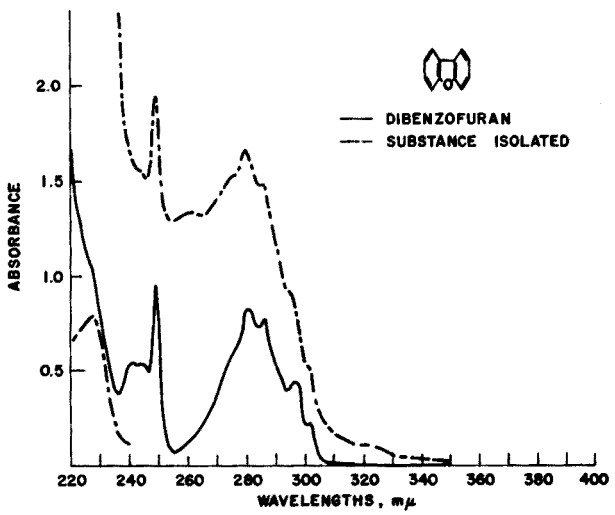

Fig. 11. Ultraviolet absorption spectrum of the isolated and the pure dibenzofuran.

dibenzofuran; the similarity of both spectra is evident. Phenanthrene, having a retention time of 22 min, was used as internal standard in this separation. Furthermore, pure dibenzofuran showed the same retention time on the gas chromatography column as the isolated substance. A comparison of the mass spectra of both substances showed the most intense *m/e* value to be 168 which is the molecular weight of dibenzofuran.

DISCUSSION

The presence of carbazoles in petroleum and its distillates as well as in shale-oil is known from several investigations[3,8,9,16], and a number of methods have been proposed for their isolation. These involve reactions with liquid sulfur dioxide[17], chloro-

sulphonic acid[18], concentrated sulfuric acid[19], formation and decomposition of the alkali metal carbazolates[20], distillation techniques[21], paper chromatographic methods[22,23], and ion exchange resins[24]. These approaches either decompose nitrogen compounds or have other undesirable features[17]. Perchloric acid (72%), on the other hand, does not decompose the alkylcarbazoles at room temperature and may be considered analogous to the extraction of basic nitrogen compounds with aqueous hydrochloric acid. Although carbazoles are not basic in glacial acetic acid[25,26], in 72% perchloric acid they have basic properties and form perchlorates. Therefore, because of the solubility of the carbazole perchlorates in this acid, a separation from condensed aromatic hydrocarbons is possible. Such a separation has considerable merit since aromatic hydrocarbons interfere in the gas chromatographic separation of the alkylcarbazoles and the evaluation of the mass spectra. The carbazole perchlorates are easily decomposed by addition of water[5]. This permits the liberation of the carbazoles for extraction into a solvent.

Silicone oil-firebrick as a packing material for the separation of carbazoles proved to be useful due to its thermal stability at high temperatures. Although silicone oil was occasionally found in gas chromatographic fractions, this presented no problem since the coating material did not show ultraviolet absorption.

Carbazole and C_1-, C_2-, C_3-, C_4-, and C_5-carbazoles were found in the hydrogenated oil. It is interesting to note that chromatography, as applied in this investigation, was unable to separate carbazole from N-methylcarbazole. This suggests that the methylcarbazole isolated in the present study and which was separated from carbazole is different from N-methylcarbazole. The investigation by mass spectrometry did not reveal which alkyl substituents were present in the individual alkylcarbazoles isolated from the oil. According to BOER[27] 70 to 80% of the alkyl carbon in aromatic hydrocarbons found in petroleum consists of methyl groups. It is reasonable to expect that this ratio also applies to the alkylcarbazoles isolated in this investigation. On the basis of the peak areas from gas chromatographic separations, the C_2-carbazoles constitute the major portion of the total carbazoles. This is in agreement with mass spectrometric results obtained on alkylcarbazoles from a catalytically cracked stock[3]. On the other hand, it has been found that carbazole and indole derivatives with three carbon atoms were most abundant in a virgin oil[3].

It should be mentioned that the residue remaining after the perchloric acid extraction had a nitrogen content of 1.1%. This residue gave a positive color reaction with 2-bromo-2-nitroindandione-1,3, which indicated that possibly some highly substituted carbazoles did not dissolve in perchloric acid, or that some other unidentified compounds also reacted with the reagent. A mass spectrum obtained on this concentrate showed molecular weights up to 472. Since the major portion of the nitrogen compounds present in a recently investigated crude oil have molecular weights above 320[28], the possibility of the presence of nitrogen compounds in the oil examined in our investigation having molecular weights up to 472 was not surprising.

The perchloric acid extraction procedure was also successfully applied to another petroleum distillate. After separation by gas chromatography and investigation of the separated fractions by ultraviolet spectroscopy, spectra of carbazoles were obtained, thus demonstrating the general applicability of the extraction method.

To our knowledge, phenazine and its alkyl derivatives have not been isolated previously from petroleum distillates. These constitute another type of nonbasic nitrogen

compounds which had not been identified in petroleum and its products. Although no satisfactory peaks were obtained in the gas chromatographic separation of the alkylphenazines, it is believed that a better resolution is possible under conditions different from those described here. It is interesting to note that the alkylphenazines, as well as the alkylindoles and -carbazoles mentioned previously, resisted catalytic hydrogenation. This is true also for dibenzofuran, which was identified along with the nitrogen compounds. The finding of dibenzofuran in the present study confirms a recent suggestion by APPLEBY *et al.*[29], that certain mass spectral data were consistent with the presence of alkylated dibenzofurans in a petroleum distillate. These oxygen-containing compounds are believed to be responsible to a certain extent for coke formation on cracking catalysts. In another investigation[30], mass spectral data of petroleum fractions also suggested the presence of dibenzofurans. Likewise, benzofuran was identified previously in a neutral shale oil naphtha fraction[31]. The presence of dibenzofuran in petroleum may be of interest since this compound is known to be formed biosynthetically[32].

ACKNOWLEDGEMENTS

The authors wish to thank MR. R. E. SNYDER for helpful advice and the various personnel of the Physical Sciences Division for their cooperation in the work involved.

SUMMARY

Alkylindoles, -carbazoles and -phenazines were isolated from a petroleum distillate by adsorption on activated aluminum oxide and desorption with methanol. After removal of methanol and dilution with benzene, the concentrate was extracted with 72% perchloric acid to obtain the alkylindoles and alkylcarbazoles as soluble perchlorates. These compound types were then isolated from the acidic layer by addition of water and extraction with benzene. A concentrate of the benzene extract was separated by gas chromatography into alkylindoles and 6 different carbazoles, the latter being characterized by ultraviolet and mass spectrometric techniques. The carbazoles were determined photometrically with 2-bromo-2-nitroindandione-1,3 reagent and by gas chromatography. Phenazine and several alkylphenazines were isolated from the nitrogen compound concentrate as solid perchlorates, liberated by alkali treatment of their perchlorates, and separated by gas chromatography; ultraviolet and mass spectra were used for their identification. Dibenzofuran was identified in the residual concentrate after the acid extraction.

RÉSUMÉ

Les auteurs proposent une méthode pour isoler les carbazole phénazine et dibenzofuranne dans un distillat de pétrole, par adsorption sur alumine activée et désorption au moyen de méthanol. Une méthode est également décrite pour leur séparation, leur identification et leur dosage, en utilisant la chromatographie en phase gazeuse, ainsi que les techniques par spectrométrie de masse et dans l'ultra-violet.

ZUSAMMENFASSUNG

Die Isolierung, Trennung und Bestimmung von Carbazolen, Phenazinen und Dibenzofuran in Petroleumprodukten kann durch Adsorption an aktiviertem Aluminiumoxyd und Desorption mit Methanol erfolgen. Zur Trennung und Bestimmung werden Gaschromatographie, Messungen im Ultraviolett und Massenspektrometrie angewandt. Phenazine werden als Perchlorate isoliert und mit den erwähnten Methoden getrennt und bestimmt.

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SPECTROPHOTOMETRIC DETERMINATION OF RARE EARTH ELEMENTS AND THORIUM WITH ARSENAZO

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Arsenazo (Neothoron) is a sensitive and selective reagent for thorium; it forms a colored complex in fairly acidic solutions[1-3]. At higher pH values, however, the reagent forms colored complexes with various metals including the rare earths[4-6]. Because the separation of traces of rare earths from thorium is not always easy, it is desirable to have a method that permits the determination of the former in the presence of the latter. KUZNETSOV AND PETROVA[7] have developed a thermospectrophotometric method, which utilizes the fact that the absorbances of the rare earth–arsenazo complexes change with temperature, whereas that of the thorium–arsenazo complex does not.

The purpose of the present work was to develop a simple method for the determination of both rare earths (lanthanum and gadolinium have been used) and thorium with arsenazo by changing the acidity of the medium. The method is based on the fact that in a 0.05 *N* nitric acid medium the absorbance is due to the thorium complex alone, while at pH 7 the absorbance is due to both the thorium and rare earth complexes.

HOLCOMB AND YOE[3] have determined both uranium and thorium with arsenazo by changing the pH of the sample solution. The lack of selectivity of arsenazo reactions at high pH thus offers, under appropriate conditions, a valuable method for the determination of two different elements.

EXPERIMENTAL

Reagents

Arsenazo, 0.10 g in 100 ml of water. A product of Dotite Neo-Thorin (Dojindo & Co., Ltd., Kumamoto, Japan) was used without further purification.

Triethanolamine buffer was prepared by mixing 400 ml of 15% (w/v) triethanolamine solution, 330 ml of 1 *N* nitric acid, and 70 ml of water. The pH was adjusted to 7.2 $\pm$ 0.1 with dilute nitric acid or ammonium hydroxide.

A standard thorium solution (1 mg Th/ml) was prepared by dissolving 2.380 g of $Th(NO_3)_4 \cdot 4H_2O$ in 1 l of 0.1 *N* nitric acid. This solution was standardized by titrating with EDTA using Xylenol Orange as indicator[8].

Standard solutions of lanthanum (1 mg La/ml) and gadolinium (1 mg Gd/ml) were

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prepared by igniting their oxides, dissolving weighed amounts of the oxides in a slight excess of nitric acid, and diluting to an appropriate volume with water.

Apparatus

Absorbance measurements were made with a Hitachi Model EPU-2A spectrophotometer, using 1-cm cells. A glass-electrode pH meter (Horiba Model M-3) was used for pH measurements.

Calibration curves

(*a*) Curve 1. Transfer, for example, 0, 20, 50, 80 and 110 μg of Th (the pH of the thorium solution should be about 3) to 25-ml volumetric flasks and add nitric acid to make the acidity 0.05 *N* after diluting to volume. Add 1.0 ml of 0.1% arsenazo solution, mix and dilute to the mark with water. Measure the absorbance of the solution at 580 mμ, using the reagent blank as the reference.

(*b*) Curve 2. Transfer the same amounts of thorium as above to 25-ml volumetric flasks and add 1.0 ml of 0.1% arsenazo solution. Add 5.0 ml of triethanolamine buffer solution and dilute to the mark with water. Measure the absorbance at 580 mμ against the reagent blank. If necessary, confirm that the pH of the solution is 7.2 $\pm$ 0.1.

(*c*) Curve 3. Transfer, for example, 0, 20, 40, 70 and 100 μg of La or Gd (the pH of the working standard solution should be 3–4) to 25-ml volumetric flasks. Then continue as described for curve 2.

PROCEDURE

Transfer an aliquot of the sample solution (pH about 3) to a 25-ml volumetric flask. Develop the color as described for curve 1 and measure the absorbance (A_1). Determine the amount of thorium from curve 1.

Transfer another aliquot (of the same volume as above) of the sample solution to a 25-ml volumetric flask. Develop the color as described for curve 2 and measure the absorbance (A_2).

From curve 2 determine the absorbance (A_3) for the amount of thorium found from curve 1. Then from curve 3 determine the amount of lanthanum or gadolinium that corresponds to ($A_2 - A_3$).

All experiments were carried out at room temperatures with a range of 24° to 29°.

RESULTS AND DISCUSSION

Determination of thorium

Conditions for the spectrophotometric determination of thorium with arsenazo have already been studied in detail[2,3]. Although interference of nitrate has been reported[2], tests have shown that the calibration curves at 0.05 *N* hydrochloric acid and 0.05 *N* nitric acid are practically the same. A range of 10 to 140 μg of thorium is suitable for the determination. The molar absorptivities for thorium at 0.05 *N* nitric acid and pH 7.2 are $2.2 \cdot 10^4$ and $2.9 \cdot 10^4$, respectively (580 mμ). At pH 7.2 Beer's law holds for the range 0 to 110 μg Th per 25 ml. The absorbance of the thorium complex in 0.05 *N* nitric acid and at pH 7.2 remains nearly constant for 3 h.

Determination of rare earth elements

Different pH values have been recommended by different workers for the determi-

nation of rare earths, *i.e.*, 9.0[6], 8.0[4] and 7.0[5]. The absorbance of arsenazo solution increases with increase in pH[5]. In the present work, a pH of 7.2 was chosen. Undoubtedly a pH of 7.0 could also be used.

Although larger amounts of arsenazo have been added to develop the color with rare earths[5,6,9], the use of 1 ml of 0.1% arsenazo solution gave satisfactory results. This may be due to the purity of the reagents used.

FRITZ *et al.*[4] have obtained a molar absorptivity of $2.47 \cdot 10^4$ for lanthanum. BANKS *et al.*[5] have given a value of $(2.75 \pm 0.05) \cdot 10^4$ for the apparent molar absorptivity of a mixture of rare earths. On the other hand, the results obtained by SHIBATA *et al.* give molar absorptivities of $4.9 \cdot 10^4$ and $2.3 \cdot 10^4$ for lanthanum[6] and cerium(III)[9], respectively. The present authors have obtained values of $2.4 \cdot 10^4$ and $2.5 \cdot 10^4$ for lanthanum and gadolinium, respectively. Apparently SHIBATA's value for lanthanum is incorrect and a factor of $\frac{1}{2}$ is necessary. (We have discussed this with DR. SHIBATA.)

Determination of thorium and rare earth elements

The absorbance at pH 7 is equal to the sum of the absorbances of the thorium and rare earth complexes.

TABLE I

DETERMINATION OF THORIUM AND LANTHANUM WITH ARSENAZO

Taken		*Found*	
Th, μg	*La, μg*	*Th, μg*	*La, μg*
0	51.3	5, 5	51, 51
10	103	13, 13	100, 101
10	42.8	12, 12	40, 40
30	85.5	32, 32	81, 81
20	20.5	21, 21	19, 19
50	51.3	52, 52	49, 49
30	20.5	32, 32	19, 19
80	34.2	82, 82	29, 29
40	10.3	41, 41	10, 10
90	17.1	92, 92	14, 14
50	5.1	51, 51	6, 6
50	0	51, 51	2, 1

TABLE II

DETERMINATION OF THORIUM AND GADOLINIUM WITH ARSENAZO

Taken		*Found*	
Th, μg	*Gd, μg*	*Th, μg*	*Gd, μg*
0	50	5, 5	47, 47
10	40	12, 12	43, 43
20	20	20, 20	20, 20
50	50	51, 51	48, 48
40	10	40, 40	10, 10
50	5	51, 51	5, 5
50	0	51, 51	1, 1

Results obtained in applying the proposed method are collected in Tables I and II. Satisfactory results are shown with 10 to 90 μg of thorium and 5 to 100 μg of lanthanum. The weight ratio of Th/La ranges from 0.1 to 10. Similar results are also shown with mixtures of thorium and gadolinium (the Th/Gd ratio 0.25 to 10).

Although only lanthanum and gadolinium were used in the present investigation, the proposed method would undoubtedly be applicable to other rare earth elements.

The effects of other elements on the determination of thorium[1-3] and rare earths[4-6] have already been studied. Many elements including traces of iron and aluminum interfere with the determination at pH 7.2.

SUMMARY

The simultaneous spectrophotometric determination of rare earth elements (lanthanum and gadolinium) and thorium with arsenazo is described. In 0.05 *N* nitric acid, thorium alone forms a colored complex with the reagent; at pH 7.2 both thorium and the rare earths form colored complexes. Satisfactory results were obtained with weight ratios of Th/rare earths ranging from 0.2 to 10.

RÉSUMÉ

Une méthode spectrophotométrique est proposée pour le dosage simultané des terres rares et du thorium, au moyen d'arsènazo, leurs complexes colorés se formant à des pH différents.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur gleichzeitigen Bestimmung der seltenen Erden und des Thoriums mit Hilfe von Arsenazo. Sie beruht auf der pH Abhängigkeit der Komplexbildung mit dem Reagenz.

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A NEW ROUTINE METHOD FOR DETERMINATION OF IODINE IN PLANT MATERIALS

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INTRODUCTION

For over 4 years the method applied in our laboratory for the determination of iodine in crop samples was that recommended by the Central Veterinary Laboratory (Ministry of Agriculture, Fisheries and Food, Great Britain)[1]. In this method 200 mg of dried plant sample are digested with 80 ml of 18 *N* sulphuric acid and 4 g of potassium permanganate at 195°. After the digestion oxalic acid is added and the iodine formed by reduction is distilled. Iodine is then determined colorimetrically by means of its catalytic action on the rate of reduction of cerium(IV) by arsenic(III) in an acidic medium. Though this method generally gave satisfactory results it is time-consuming and can only be handled by experienced analysts. Furthermore, much time is required for the recrystallisation of permanganate and oxalic acid. For these reasons a simpler method was sought in which distillation could be omitted and the recrystallisation of chemicals avoided.

Very few methods have been described in the literature for the analysis of iodine in crops. Distillation after acid digestion has been used by both JOHNSON AND BUTLER[2] and HOUSTON[3]. Numerous methods for the determination of iodine in blood have been published (for reviews, see[4,5]) but none of these methods appeared sufficiently attractive for application in a routine determination of iodine in crop samples. In the methods depending on alkaline ashing, the temperature and the duration of the decomposition are very critical, whereas those based on an acid digestion followed by distillation require too much time. Some methods in which the distillation is replaced by removal of iodine in a current of air[6] or in which iodine is diffused at 60°[7] are also rather laborious despite a certain simplification.

The method of ZAK[8], in which blood samples are oxidised with chloric acid in the presence of chromate and the iodine is directly determined in the diluted digest, is a very rapid method which might be applied as a routine method for crop analyses. It has, however, the disadvantage that the chloric acid reagent has to be freshly prepared regularly. We have sought for a digestion mixture which is easily obtainable and does not yield any substances which could interfere with the colorimetric determination following the decomposition. For this reason the so-called Neumann acid was chosen; this consists of a mixture of equal volumes of sulphuric and nitric acid, and is applied

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in the analysis of several crops. As the decomposition is often more successful when some perchloric acid is present we followed the latter procedure.

For the investigation of the reliability of the method, radioactive iodine (^{131}I) was used as a tracer.

EXPERIMENTAL

Reagents

Unless otherwise mentioned analytical grade chemicals from Merck were used.

Neumann acid: a mixture of 1 volume of concentrated sulphuric acid (s.g. 1.84) and 1 volume of concentrated nitric acid (s.g. 1.40).

Perchloric acid: (s.g. 1.67).

Acid arsenic solution: 9.8 g of arsenic trioxide was dissolved in 14 ml of 10 *N* sodium hydroxide; 600 ml of water was added and the mixture neutralized with 10 *N* sulphuric acid; 42 ml of concentrated sulphuric acid was added followed after shaking by 10 ml of concentrated hydrochloric acid. The mixture was diluted to 1 l.

Dilution liquid: 3.0 *N* sulphuric acid.

Ceric solution: 5 g of cerium ammonium sulphate (British Drug Houses Ltd; low in other rare earths) was dissolved in 70 ml of 5 *N* sulphuric acid by gentle heating. After filtering the solution was diluted with distilled water to 100 ml. For use the solution is diluted with 3 volumes of 3.5 *N* sulphuric acid. This solution can be kept for a few weeks. The cerium ammonium sulphate is previously purified by washing 15 g of the salt with 75 ml of distilled 96% ethanol.

Standard iodine solution: 1 mg of iodine as KIO_3 in 1 liter of water.

Method of checking with radioactive iodine

0.1–0.2 μC ^{131}I (carrier free) as NaI is pipetted into a 50-ml measuring flask in which 200 mg of crop sample have been placed. After the decomposition 1 ml of the radioactive solution in a porcelain crucible (Weta no. 3127) was placed in a lead castle; it was measured by means of a Philips scintillation counter no. 4111 and the recovery was calculated.

Procedure for determination

200 mg of crop sample was dried at 105° and placed in a 50-ml measuring flask. After this 7.5 ml of Neumann acid was added with shaking to moisten the sample completely and then 1 ml of perchloric acid was pipetted in. The digest was then heated over a period of 1 h to 160–190° by means of an electric hot plate (type Inventum no. 224/22; first position with a surface temperature of 200°). The surface temperature was then raised to 275° (second position) until the first occurrence of a yellow colour (the temperature of the digest was 195–215°). The total duration of the decomposition was about 90 min.

After being cooled, the digests were diluted with water to 40 ml with constant shaking. Then 1 ml of acid arsenic solution was added; the solution was then diluted to 50 ml, and shaken again.

After one or two days of standing at room temperature (18–24°) the solutions were shaken a few times; 5 ml of each solution was then pipetted into a colorimeter tube, into which 0.4 ml of acid arsenic solution had been pipetted beforehand. The contents

of the colorimeter tubes were shaken twice and then placed in a waterbath, adjusted to exactly 30°.

After about 20 min 1 ml of the ceric solution was added in succession to each tube at intervals of 1 min. The transmittance at 420 mμ was measured by a colorimeter (Lumetron) 30 sec after the addition of the cerium. The transmittance was again measured 20 min after the first determination. It is thus possible to carry out one series of 20 determinations at a time if one measurement is executed every minute. The difference in transmission between the two colorimeter readings less the value of the blank decomposition is a measure of the iodine content. With every series of 18 samples two blanks are included. The iodine contents can be read from a calibration curve. The points of this curve are established by digesting amounts from 0 to 0.5 ml of the standard iodine solution in the same way as for the crop samples.

When the iodine content is so low that the difference in transmission less the blank value, is not more than 4, a third measurement is carried out after 120 min. The iodine contents are then read from a test curve which has been prepared in a similar way.

When the iodine content is so high that the second reading of the transmission is greater than 75% within 20 min, the solution must be diluted. The dilution can be effected by adding dilution liquid. In this case the iodine contents should be read from a test curve which has also been prepared by application of a corresponding dilution.

DISCUSSION

Influence of perchloric acid

Digestion with Neumann acid alone led to great losses of added radioactive iodine. In two different measurements the recovery was only 20 and 51% respectively. However, addition of perchloric acid decreased the losses of iodine considerably (see Table I). Even 0.1 ml of perchloric acid was nearly sufficient for a quantitative recovery. It appeared safer, however, to add 1 ml of perchloric acid to each digest.

TABLE I

VARIATION OF THE RECOVERY OF ^{131}I ADDED TO 200 mg OF CROP SAMPLE WITH THE AMOUNT OF PERCHLORIC ACID

ml $HClO_4$	*Recovery* %	$\sqrt{\frac{\Sigma d^2}{n(n-1)}}$	$\sqrt{\frac{\Sigma d^2}{(n-1)}}$	*n*
—	80	6	22	13
0.1	93	3	5	2
1.0	93.9	0.9	4.1	21

d = deviation of the average
n = number of determinations

Amount of sample taken

The recoveries of inactive iodate added did not appear to differ significantly on varying the amount of sample from 50 to 200 mg. With 300 mg, however, 5 to 10% of the iodine was not recovered while with 400 mg as much as 15 to 30% was lost. 200 mg of crop sample is therefore the most suitable amount for reliable decomposition.

Temperature of digestion

Fig. 1 shows the influence of the final temperature of the digestion on the acidity of the digest diluted to 50 ml. The decrease of acidity in the temperature range of 150–200° can probably be ascribed to volatilization of nitric acid which is still present. The acidity decreases very sharply in the range of 210–225°. The liquid becomes deep yellow in this range; it is likely that this further decrease of acidity is caused by decomposition of the perchloric acid present. At 240–270° the liquid turns colourless

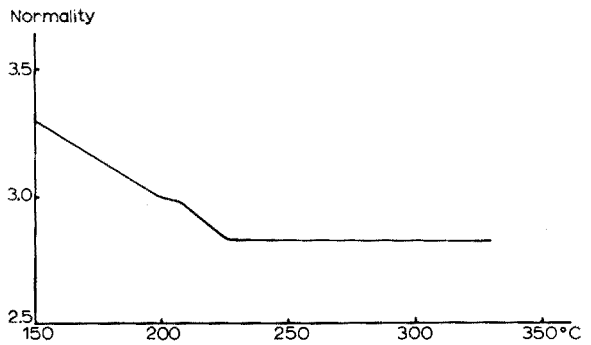

Fig. 1. Relation between the normality of the digest after dilution to 50 ml and the final temperature of digestion.

again. Apparently all the perchloric acid has then disappeared. The amount of recovery of added ^{131}I was independent of heating up to at least 280°. No significant differences in iodine contents were established when samples of known iodine content were digested at temperatures in the range of 160 to 280°. On digestion at temperatures below 160° only part of the iodine was recovered. Presumably the decomposition was incomplete.

The initial appearance of the yellow colour was used to determine the end-point of the digestion, for it was not necessary then to place a thermometer in the liquid. This temperature was about 195–215°.

Method of dilution

After dilution of the digest the iodine volatilizes slowly. The volatilization appears to depend strongly on the temperature at which the liquid is kept (see Fig. 2). Addi-

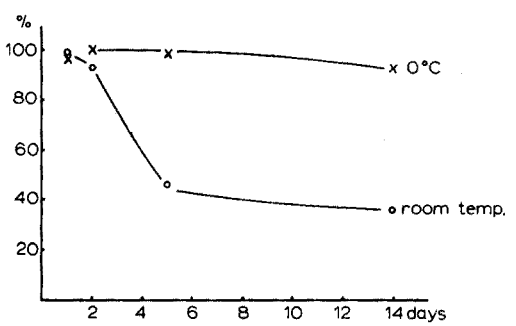

Fig. 2. Relation between the percentage of iodine remaining in the diluted digest and the time of storage at 0° and room temperature respectively (no arsenic(III) was added).

tion of 1 ml of acid arsenic solution made the losses decrease sharply. Possibly the iodide is slowly converted to iodine and then reduced to the less volatile iodide by the arsenic(III), so that the risk of volatilization decreases again. It should, however, be noted that on addition of greater amounts of arsenic the loss of iodine increases again (see Fig. 3)*.

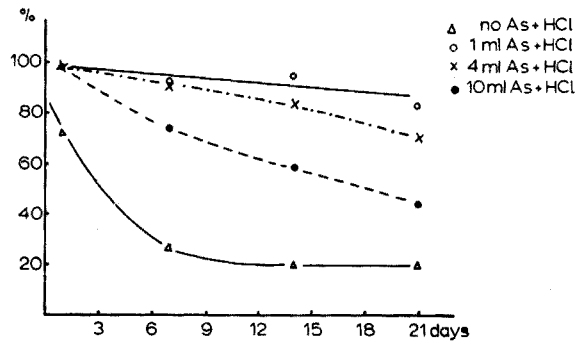

Fig. 3. Relation between the percentage of iodine in the diluted digest and the time of storage on adding different quantities of acid arsenic solution. The temperature of storage was about 20°. The final volume was 50 ml.

Though the losses could not be completely suppressed by addition of acid arsenic solution the decrease in the iodine content after 1 day was never more than 10%. It was not necessary to make a correction for these losses because the measuring points of the calibration curve were subject to identical losses after dilution.

Finally it should be remarked that the acid arsenic solution should never be added directly to the undiluted digest because this would lead to very severe losses of iodine. As a matter of fact concentrated sulphuric acid reoxidizes the hydriodic acid formed by reduction. At an acidity of 3.5 *N* the losses by this reaction are not very great. For this reason the digest should be diluted to at least 40 ml before the arsenic can be added. On further dilution to 50 ml the concentration of the sulphuric acid decreases still more.

The occurrence of interfering and retarding factors

Occasionally the catalytic reduction of cerium(IV) by arsenic(III) seemed to be retarded, so that a determination completed shortly after the digestion period gave incorrect results. In some cases, this retardation was still perceptible one day after the digestion. It seemed that the temperature of storage of the digest after dilution to 50 ml had considerable influence on the extent of retardation.

A given sample of grass was digested with the acid mixture and the solutions obtained after dilution and addition of 1 ml of acid arsenic solution were left to stand for a night at different temperatures. The next day the iodine content was determined colorimetrically (see Fig. 4). The results obtained suggest that sometimes an interfering substance remains after the digestion; this gradually hydrolyzes or volatilizes if the solution is allowed to stand for some time at a suitable temperature. The

* If the digestion is carried out at 250° then the iodine content remains fairly constant on addition of 4 ml of acid arsenic solution.

interference can be practically eliminated by standing for one day at room temperature (18–24°). Standing for another day had no effect on the results.

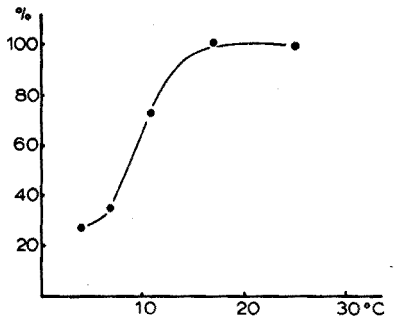

Fig. 4. Relation between the iodine measured in the diluted digest (as a percentage of the total iodine present) and the temperature of storage during the first day after decomposition and dilution. The samples investigated showed an initial arrest of the catalytic reduction of cerium.

Apart from the retardation described above we have also sometimes found a diminished sensitivity, which did not disappear after standing for one day at room temperature. Normally the difference between the transmission readings before and after the reaction (20 min) for 0.1 ml of the standard iodine solution amounted to 6 to 7. During a particular period the differences were only 3.5–4.5. This diminished sensitivity was also found for the other points in the standard curve. The factor responsible for the reduced sensitivity was the sulphuric acid used. The low differences in transmission were found with a particular batch of sulphuric acid, while two other batches produced normal values.

Calibration curve

Fig. 5 represents some typical standard curves. Differences in transmission determined after 20 and 120 min were plotted for iodine contents varying from 0 to 3000 μg per kg of crop sample. The values were obtained by means of "destruction" of

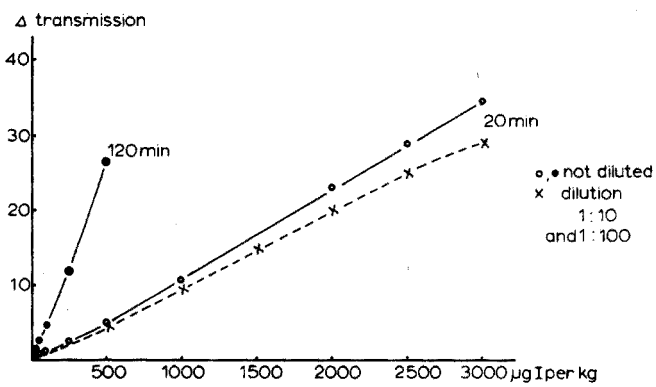

Fig. 5. Relation between the difference in transmission observed after 20 or 120 min (after deduction of the blank value) and iodine contents corresponding to fixed points of the standard curve and expressed in μg I per kg dry weight.

known quantities of potassium iodate. In several cases the curve drawn by the check points was not completely straight, being slightly less steep at lower contents. Owing to the effect of dilution the standard curves for samples with a high iodine content are situated below the average "normal standard curve". This can be ascribed to the fact that the arsenic concentration diminishes on dilution with 3.0 N sulphuric acid so that the catalytic reduction of cerium(IV) proceeds more slowly.

Comparison of the results of the new method with those of the distillation method

In Table II are shown the results of iodine determinations in grass samples varying

TABLE II

COMPARISON OF RESULTS OF IODINE ANALYSES IN GRASS BY THE DISTILLATION METHOD AND BY THE NEW METHOD

The analyses were partly repeated on different days.

μg I/kg dry matter		Difference (μg/kg)	%[c]	t[d]	$\sqrt{\frac{\Sigma d^2}{n-1}}$		$\frac{\Sigma d}{n}$				n[e]	
I[a]	II[b]				I[a]	II[b]	I[a]	%[f]	II[b]	%[f]	I[a]	II[b]
30	65	+35	202	2.7	18	33	12	40	21	32	5	11
196	160	—36	82	1.0	75	35	56	29	22	14	5	11
262	212	—50	81	1.4	77	33	54	27	31	15	5	11
411	381	—30	93	1.4	43	29	31	8	29	8	5	11
445	363	—82	82	3.6	33	59	26	6	48	13	5	11
571	516	—55	90	2.6	39	41	30	5	32	6	5	11
729	661	—68	91	1.7	79	53	56	8	41	6	5	11
643	661	+18	103	0.3	86	120	62	10	90	14	5	11
457	514	+57	112	1.7	49	71	36	8	59	11	5	8
814	784	—30	96	0.8	71	55	59	7	43	5	5	10
1316	1271	—45	97	0.4	260	58	221	17	41	3	5	11
1862	1806	—56	97	0.6	181	161	150	8	102	6	5	11
2122	2065	—57	97	0.5	194	211	138	7	168	8	5	11
2342	2147	—195	92	2.4	87	240	64	3	187	9	5	11
2282	2376	+94	104	0.5	412	261	272	12	225	10	5	11
2658	2298	—360	86	3.8	195	147	152	6	89	4	5	10
Average			94.1[g] ± 2.3[h]					8.1[i]		7.9[i]		

[a] Values obtained by the distillation method.
[b] Values obtained by the new method.
[c] Iodine contents as determined by the new method and expressed as a percentage of the iodine contents by the old method.
[d] Student's $t = \dfrac{\text{difference}}{\sqrt{\frac{\Sigma d^2}{n(n-1)_{\mathrm{I}}} - \frac{\Sigma d^2}{n(n-1)_{\mathrm{II}}}}}$
[e] Number of determinations.
[f] $\Sigma(d/n)$ expressed as a percentage of the iodine contents determined by the old and new methods respectively.
[g] The value 202 has been left out of consideration.
[h] $\sqrt{\frac{\Sigma d^2}{n(n-1)}}$
[i] Average of the percentages of the $\Sigma(d/n)$ values of the samples with an iodine content higher than 350 μg/kg dry matter.

in iodine contents between 30 and 3000 μg per kg dry matter. The same samples were also analysed according to the distillation method previously used in this laboratory. It appears that the values of $\sqrt{\Sigma d^2/(n-1)}$ and of $\Sigma(d/n)$ are approximately equal for both methods. The average deviation of mean values for samples with an iodine content higher than 350 μg per kg appeared to be about 8% both for the distillation method and for the new method. When all the determinations were made on the same day the average deviation with the new method did not appear to be higher than 3.2% for a grass sample with a mean iodine content of 1710 μg per kg.

From Table II it can be seen that the values by the new method are on average 6% lower than those determined according to the distillation method. Table III contains additional observations: in series analyses of iodine contents lower than 400 μg per kg, the new method produced values which were either equal to or higher than the values obtained by the distillation method. For samples of iodine contents higher than 400 μg the new method produced values which were relatively lower, which is in agreement with the data of Table II.

TABLE III

COMPARISON OF IODINE CONTENTS DETERMINED ACCORDING TO THE DISTILLATION METHOD AND THE NEW METHOD

μg I/kg	$\frac{\text{New method}}{KMnO_4 \text{ method}} \cdot 100\%$	Number of samples	Number of replications
100– 250	129±11	11	2
100– 250	108± 6.8	18	2
250– 400	101± 5.5	19	2
400– 650	94± 3.9	17	2
150–3000	94± 2.3	15	see Table II
10,000– 120,000	97± 3.3	7	3 or 4

Thus the absolute values of the iodine contents determined according to the new method may be somewhat on the low side. We also observed that the recovery of iodine added in the form of potassium iodate to grass samples and corresponding to increases of the iodine content between 600 and 2500 μg per kg, was only 92.6±2.5%.

It is very probable, on the other hand, that for values lower than 400 μg per kg the distillation method gives values which are to low.

GENERAL DISCUSSION

The new method seems as good as the distillation method previously used in this laboratory, as regards reproducibility. At low contents (below 350 μg per I kg) the reproducibility is even better. Differences from the absolute values are certainly not greater than 7 to 8%.

For practical purposes, such as cases where the iodine content of grass should be known in relation to possible iodine deficiency of cattle, the new method can be deemed sufficiently accurate. A very important factor is that the number of analyses which can be carried out by one analyst is at least 3 times greater than that possible by the

distillation method. Moreover, the equipment is very simple and the procedure can be quickly learned. In contrast, the distillation method requires complicated apparatus and can only be done reproducibly after much training. The most important differences between the two methods are as follows:

	New method	*Distillation method*
Mean error[a]	7.9%	8.1%
Number of samples/day per person (duplicate)	10	3

[a] for iodine contents higher than 350 μg per kg

ACKNOWLEDGEMENTS

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SUMMARY

A new method is suggested for determination of iodine in grass and crop samples. The sample is decomposed with sulphuric, nitric and perchloric acids. Iodine is determined in the diluted digest. The method is excellent for routine work, being faster and simpler than previous methods.

RÉSUMÉ

Une nouvelle méthode simple et rapide est proposée pour le dosage de l'iode dans les plantes. L'échantillon à analyser est décomposé au moyen des acides sulfurique, nitrique et perchlorique. Après dilution, l'iode est dosé colorimétriquement.

ZUSAMMENFASSUNG

Beschreibung einer einfachen und raschen Methode zur Bestimmung des Jodgehaltes von Pflanzen. Der Aufschluss erfolgt mit Schwefelsäure, Salpetersäure und Perchlorsäure; nach Verdünnen wird das Jod kolorimetrisch bestimmt.

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THE DETERMINATION OF PHENOL AND KINETIC STUDIES ON THE MONOBROMINATION OF PHENOL BY A PULSE COULOMETRIC TECHNIQUE

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INTRODUCTION

Numerous determinations with electrolytically generated bromine have been described in the literature[1] but the determination of phenol with electrogenerated bromine has received little attention. VAN ZYL AND MURRAY[2] have reported the determination of 10^{-4}–10^{-6} *M* solutions of phenol by a coulometric method in which errors of 5–13% were obtained. More recently, DEVANATHAN AND FERNANDO[3] have utilized a pulse technique for the coulometric determination of 8-quinolinol with an error of about 1%. In this method a coulometer which generates current pulses, the number of which is electromechanically registered, was used. This investigation was therefore initiated in order to determine the feasibility of using a similar method for the determination of phenol.

EXPERIMENTAL

Apparatus

The multivibrator as well as the titration cell have been previously described in detail[3,4]. A Hewlett-Packard Model 711A power supply served as the source of anode voltage, which was maintained at 200 V, and $R_1 : R_2$ = 100 kohm : 100 kohm in all experiments.

The indicator circuit consisted of a rotating platinum microelectrode and a saturated calomel reference electrode which were connected to a Speedomax Type G recorder. This indicator system was used to record the diffusion current of free bromine in the solution[3,4].

Reagents

Potassium bromide, hydrochloric acid and phenol were of reagent grade purity, and used without further purification. 8-Quinolinol was obtained from Lemke and Co. Inc. and purified by distillation under vacuum. It was then recrystallized from an ethanol–water mixture and dried in vacuo in a desiccator. The melting point of the final product was 72.5–73.5°. All solutions were made from distilled water that was purified by passage through a mixed cation–anion exchange resin bed. The effluent was again distilled with alkaline potassium permanganate and the distillate collected and used in this work.

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Titration of phenol

The central compartment of the titration cell contained 50 ml of solution which was made up as follows: 25 ml of 0.50 *M* potassium bromide, *x* ml of a standard solution of phenol in 0.10 *N* hydrochloric acid and (25 — *x*) ml of 0.10 *N* hydrochloric acid. Therefore the solution was 0.25 *M* in potassium bromide and 0.05 *N* in hydrochloric acid in all experiments. The standard phenol solution ($\sim 10^{-5}$ *M*) was prepared by weighing. Fresh standard solutions of phenol were prepared periodically. Before each determination the platinum generator and indicator electrodes were pretreated[4,5].

The power supply as well as the multivibrator were allowed to warm up for a sufficient period of time before a titration was begun. The multivibrator was switched on and the manner in which the electrogenerated bromine concentration varied with time was recorded. When the monobromination of phenol was complete the concentration of free bromine increased rapidly in a linear fashion. Extrapolation of these linear plots to the residual current line gave the end-points of the titrations. A set of typical titration curves is shown in Fig. 1.

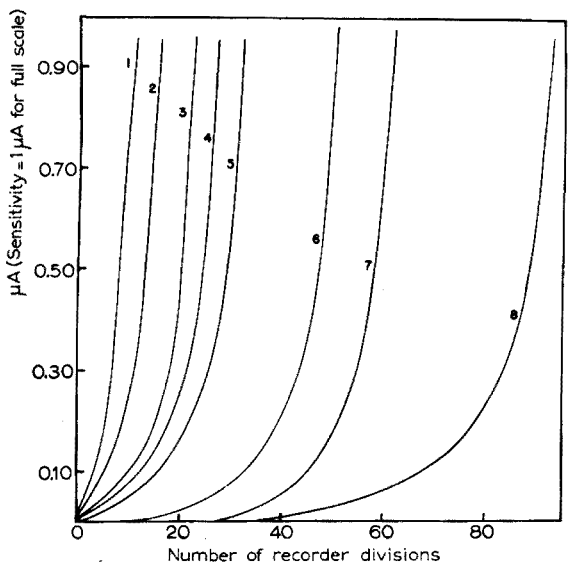

Fig. 1. Recorded titration curves for various concentrations of phenol (μg/50 ml). (*1*) 34.72; (*2*) 69.44; (*3*) 108.80; (*4*) 138.88; (*5*) 173.60; (*6*) 272.00; (*7*) 347.20; (*8*) 520.80.

Determination of pulse size

Previous workers have shown that the titration efficiency of 8-quinolinol with electrogenerated bromine is 100%[3,4]. A series of standard 8-quinolinol solutions were therefore used to determine the quantity of bromine electrogenerated per pulse and hence the coulombic magnitude of each pulse. When solutions containing 140–400 μg of 8-quinolinol in a total volume of 50 ml were titrated under conditions identical to those used for titrating phenol, it was found that the magnitude of the pulse size was $3.823 \cdot 10^{-4}$ coulombs per pulse (Table I).

TABLE I

DETERMINATION OF PULSE SIZE UTILIZING 8-QUINOLINOL

Oxine titrated (μg)	*End-point (current pulses)*	*Pulse size*	
		pulses/μg oxine	*coulombs/pulse*
154.4	1078.5	6.985	$3.807 \cdot 10^{-4}$
231.6	1611.0	6.956	$3.823 \cdot 10^{-4}$
308.8	2148.0	6.956	$3.823 \cdot 10^{-4}$
386.0	2684.7	6.955	$3.822 \cdot 10^{-4}$

RESULTS

Table II shows a set of results obtained when solutions containing 35–520 μg of phenol in 50 ml of solution were titrated with electrogenerated bromine. Fig. 2 shows that

TABLE II

THE TITRATION OF PHENOL WITH ELECTROGENERATED BROMINE

Phenol conc. (μg/50 ml)	*End-point*		
	Number of current pulses	*μg of Br_2*	*sec*
34.72	230.5	73.00	18.6
69.44	415.0	131.2	33.4
108.80	647.0	204.5	52.2
138.88	811.0	256.5	65.4
173.60	1020	322.5	82.2
272.00	1590	504.0	128
347.20	2021	639.9	163
520.80	3039	961.0	245

For all titrations, B^+ = 200 V; generating current = 12.5 mA; recorder sensitivity = 1 μA full scale and t = 25.0 ± 0.03°.

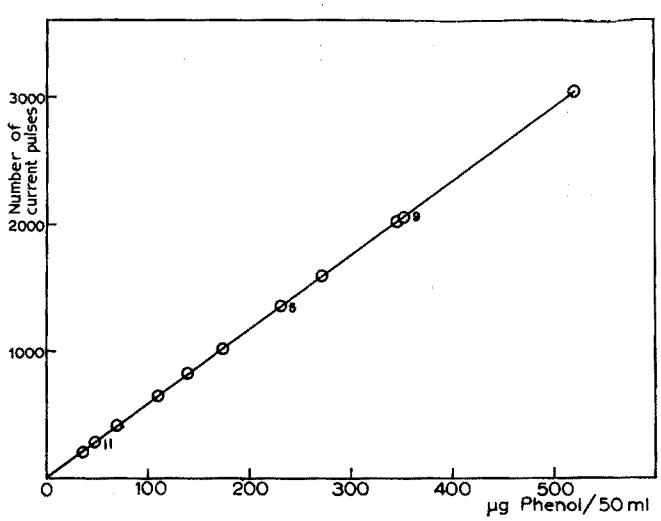

Fig. 2. Calibration curve for the determination of phenol. All points represent the average of at least 2 experiments except in the cases where the numbers denote the number of experiments carried out.

a linear relationship exists between the concentration of phenol and the number of current pulses required for each titration. The end-points in these titrations have been expressed as the number of μg of bromine, the number of current pulses and the time (in sec) required for each determination.

The precision of this method was determined by carrying out a series of titrations at three selected phenol concentrations, namely, $7.48 \cdot 10^{-5}$ M, $4.90 \cdot 10^{-5}$ M and $9.80 \cdot 10^{-6}$ M. Five to eleven determinations were carried out at each concentration. Table III summarizes the results obtained for a phenol concentration of $7.48 \cdot 10^{-5}$ M. The end-point in each of these experiments could be determined within at least half a chart division. From these results it can be seen that a solution containing 350 μg of phenol in 50 ml can be titrated with a precision of 1%.

TABLE III

TITRATION OF A $7.48 \cdot 10^{-5}$ M SOLUTION OF PHENOL FOR DETERMINING THE PRECISION OF THE METHOD

End-point (chart divisions)	*Deviation (d) (μg Br_2)*	d^2
56.0	+11.78	138.76
55.5	+ 5.89	34.69
55.2	+ 2.36	5.57
54.7	— 3.53	12.46
54.3	— 8.24	67.90
54.1	—10.60	112.36
55.2	+ 2.36	5.57
55.0	0	
55.0	0	

End-point = 55.0 $\quad \Sigma(X-m)^2 = 377.31$

Standard deviation = ± 6.87 μg Br_2 = ± 4.04 μg phenol

DISCUSSION

The theoretical relationship between the number of μg of phenol, x, and the number of μg of bromine, y, if only monobromination of the phenol occurs, is given by the equation:

$$y = 1.70\,x$$

The experimental relationship obtained between x and y is shown in Fig. 2. However it is evident that at the end-point in every titration there is a certain excess of bromine present (Fig. 3). If OB is a titration curve, E is the end-point obtained by extrapolating the linear portion of the curve and DE is therefore a measure of the excess bromine present in solution at the end-point. These amounts of excess bromine can be determined for every phenol titration and when subtracted from the total amount of bromine electrogenerated in each case, will give a new experimental relationship between x and y:

$$y = 1.87\,x - 18.0$$

When the phenol concentration is less than 100 μg/50 ml the relationship between x and y is identical with the theoretical equation, $y = 1.70\,x$. The deviation of the experimental curve at concentrations greater than 100 μg/50 ml, can be attributed to the dibromination of the phenol that has taken place in solution. The extent of dibromination increases with increasing phenol concentration since the time required

for the titration of phenol also increases with phenol concentration. Table IV shows the amount of bromine required for the theoretical monobromination of various quantities of phenol titrated. The amount of bromine that reacted in each titration (total bromine electrogenerated — free bromine at end-point) is also tabulated in

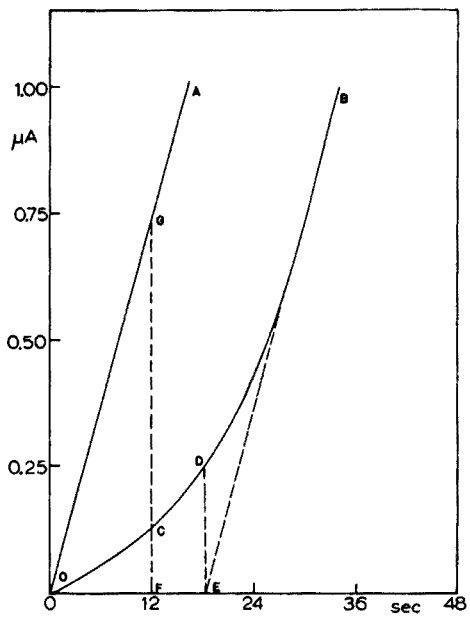

Fig. 3. Titration curves for the determination of rate constants. OA, titration curve without phenol; OB, titration curve with phenol. 3 sec ≡ 37.20 pulses ≡ 11.78 μg Br_2.

TABLE IV

RELATIONSHIP BETWEEN $[Br_2]$ THEORETICAL AND $[Br_2]$ EXPERIMENTAL FOR VARIOUS PHENOL CONCENTRATIONS

Phenol conc. (μg/50 ml)	*Bromine conc. (μg)*		
	Theor.	*Exper.*	*Excess*
138.88	236.4	242.0	+2.37%
230.40	392.0	413.3	+5.44
347.20	590.0	627.1	+6.29
351.60	597.0	634.0	+6.20
520.80	886.2	949.3	+7.12

each case. It is seen that there is an excess of bromine utilized in each titration and that this excess increases with the amount of phenol titrated or with the time required for each titration.

It is obvious therefore that the coulometric titration of phenol with electrogenerated bromine, using conventional methods, is subject to considerable error if the titration conditions are not rigidly controlled[2]. The method that is described above in which current pulses are generated at a constant rate, and the titration curve recorded on an instrument with a known chart speed, has overcome the difficulties caused by

dibromination. From the working curve shown in Fig. 2 it is seen that phenol solutions whose concentrations are as low as $7 \cdot 10^{-6}$ *M* can be titrated with a precision of 1%.

A more important application of this method is the ease with which rate constants can be determined for most bromination reactions. From the data presented above we have calculated the rate constant for the monobromination of phenol. The species which brominate the phenol molecule or the phenoxide ion in aqueous solution at low pH are, Br_2 and Br_3^-. If the pH is sufficiently low the phenoxide ion concentration in solution is extremely small. According to BELL AND RAWLINSON[6] there is little evidence to show that the tribromide ion takes part in the bromination of phenols. It is therefore assumed in this work that the reaction responsible for the monobromination of phenol is:

$$C_6H_5OH + Br_2 \rightarrow BrC_6H_4OH + H^+ + Br^-$$

The monobromophenol that is formed is a stronger acid than phenol and consequently its anionic form is present in solution in larger concentrations than that of phenol. In addition, the monobromophenoxide ion can be readily dibrominated. In this work it has been shown that when phenol solutions whose concentrations were less than 100 μg/50 ml, were titrated with electrogenerated bromide, the extent of dibromination was negligible. Therefore in all subsequent calculations it was assumed that no dibromination occurred.

The rate constant, *k*, for the monobromination of phenol is given by:

$$\frac{d[BrC_6H_4OH]}{dt} = k[C_6H_5OH][Br_2]$$

Utilizing Fig. 3 it can be seen that at any time *t*, say 12 sec, during the course of the reaction, the concentration of free bromine in solution is proportional to CF and the concentration of bromine reacted, *i.e.* the concentration of monobromophenol formed is proportional to CG. Since the size of the current pulses is known, ($3.823 \cdot 10^{-4}$ coulombs/pulse) the concentrations of bromine and BrC_6H_4OH can be calculated, in m/l. Hence the molar concentration of unreacted phenol can be determined at any time *t*, since the initial concentration of phenol is known.

A series of values of $[Br_2]$ and $[C_6H_5OH]$ could therefore be calculated for various times from which $d[BrC_6H_4OH]/dt$ could be determined and hence the value of *k*, the rate constant. Calculations for initial phenol concentrations of $1.01 \cdot 10^{-5}$ *M* to $5.91 \cdot 10^{-6}$ *M* were carried out; the concentrations of bromide and hydrogen ion in all these cases were 0.25 *M* and 0.05 *M* respectively. The value of *k* that was calculated varied from $1.5 \cdot 10^5$ to $1.8 \cdot 10^5$ l/mole sec. The average value of *k* was found to be $1.6 \cdot 10^5$ l/mole sec. To our knowledge this value has not been determined before, although a value of $1.8 \cdot 10^5$ l/mole sec has been postulated in a recent paper by BELL AND RAWLINSON[6] in which no experimental conditions for the bromination reaction are given. The method that has been proposed above is applicable to the study of the kinetics of most moderately fast bromination reactions, especially those reactions which cannot be followed by conventional techniques.

ACKNOWLEDGEMENT

The authors are grateful to the Research Corporation for financial assistance.

SUMMARY

A method for the coulometric determination of phenol is described in which constant current pulses are used to electrogenerate bromine and a current recorder is used to follow the bromination reaction of phenol. Solutions containing 10^{-4} to $7 \cdot 10^{-6}$ *M* phenol are determined with a precision of 1%. A general method for determining the kinetics of bromination reactions is postulated and used for the determination of the rate constant of the monobromination of phenol. The rate constant for the reaction in which the reacting species are the neutral phenol molecule and the bromine molecule, was found to be $1.6 \cdot 10^5$ l/mole sec.

RÉSUMÉ

Une étude a été effectuée sur le dosage coulométrique du phénol, au moyen de brome produit par électrolyse; l'enregistrement du courant permet de suivre la réaction de bromuration du phénol. Des solutions renfermant 10^{-4} à 7.10^{-6} *M* de phénol ont pu être dosées avec une précision de 1%.

ZUSAMMENFASSUNG

Beschreibung einer coulometrischen Methode zur Bestimmung von Phenol mit Hilfe von Brom, das im Reaktionsgemisch elektrolytisch erzeugt wird. Durch die aufgenommene Stromkurve lässt sich der Verlauf der Bromierungsreaktion verfolgen.

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THE SPECTROGRAPHIC DETERMINATION OF IMPURITIES IN SMALL AMOUNTS OF RADIOACTIVE GRAPHITE BY THE CATHODE LAYER TECHNIQUE

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INTRODUCTION

In recent years there has been considerable interest in the correlation of the chemical properties of graphite with impurity content and the need arose in connection with this study for the determination of impurity elements in small samples (about 50 mg) of radioactive graphite. This report outlines the technique used for analysing such samples.

PRELIMINARY CONSIDERATIONS

Before this work was envisaged considerable experience had already been gained in the analysis of graphite by the method of ashing the sample and applying conventional spectrographic methods[1–3] to the analysis of the ash. This method was not considered suitable owing to the small sample size and the sensitivity required. A method was therefore sought which could be applied directly to such samples without ashing.

The cathode layer method in which the enhanced emission of certain elements in the cathode layer of a d.c. arc is used, was developed by MANNKOPFF[4] for the analysis of a wide range of samples. MITCHELL[5] found that this method gave high sensitivity and good precision, and required only a few mg of sample. Furthermore since carbon is mixed with sample to promote good burning characteristics in the arc this method seemed particularly appropriate for the analysis envisaged.

EXPERIMENTAL

Most workers have followed MANNKOPFF AND PETERS[4] in using a narrow cathode electrode made of carbon with a deep boring approximately 1 mm × 12 mm deep holding 5 to 10 mg of the sample admixed with spectrographic buffer and internal standard mixtures. Initially this procedure was adopted because it had been stated that carbon electrodes burnt more rapidly and reproducibly than graphite. Most grades of carbon, however, were found to contain significant quantities of calcium, magnesium and boron which contributed the equivalent of 10 to 50 p.p.m. of these elements to the sample being analysed.

In spite of the greater thermal conductivity of graphite and, consequently, a potentially slower burning rate, it was necessary to make electrodes from spectroscopically pure graphite to overcome these blank difficulties. In point of fact it was

found that the burning time was only slightly increased, and no appreciable instability of the arc due to the greater cooling of the cathode resulted.

A variety of spectrographic buffers have been used by different workers in order to minimise the effect of variations in the composition of the samples, including carbon itself[5–7]. In view of the fact that samples would consist of carbon in the form of graphite, it was considered that no additional buffer would be required and in actual practice this assumption has been justified.

Since the determinations of copper and cobalt were not required, the possibility of using a mixture of the oxides of these metals as internal standard was investigated by the "falling plate" technique, when it was found that the emission of the lines of these elements were homologous with the lines of most of the elements to be determined. Figures 1a and b illustrate the curves obtained for two elements typical of the two main classes of elements. Further experiments showed that the following mixture gave satisfactory line densities: 10% copper oxide, 2½% cobalt oxide and 87½% sample.

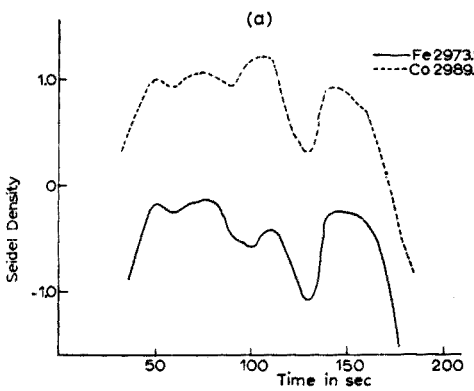

Fig. 1a. Emission curves for iron and cobalt.

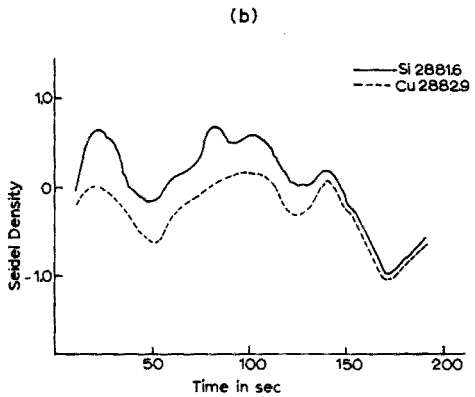

Fig. 1b. Emission curves for silicon and copper.

Initial work was carried out using conventional cathode layer electrodes 12 mm deep by 1 mm diameter and a wall thickness of about 1 mm, but these required an extended exposure time to burn to completion. A series of experiments was therefore carried out, varying the parameters of crater size, arc current and exposure time, and the optimum precision and sensitivity were obtained when an electrode 1 mm internal diameter and 7 mm deep was used at a current of 10 A with an exposure time of 3 min.

The choice of photographic plate was governed by the necessity or otherwise of determining sodium. In actual practice it was found that blank difficulties were experienced due to traces of sodium introduced with the internal standard. In these circumstances it was found more expedient to determine sodium by flame photometry on another portion of the sample and to use an Ilford Ordinary plate in conjunction with a spectrograph of medium dispersion for the present investigation.

The plate was evaluated by microphotometry using the "blackening-separation" method of MITCHELL AND SCOTT[8] and this necessitated exposing each sample through a seven-step rotating sector. In practice it was found convenient to measure Seidel

densities either by the use of a Seidel scale in the galvanometer or by use of the formula

$$\text{Seidel density } (S) = \log\left(\frac{G_0}{G} - 1\right)$$

where G_0 = clear glass deflection and G = deflection on line measured.

The selection of the cathode layer portion of the arc column was effected by means of a mask placed in front of the collimating lens of the spectrograph and alignment of the arc, which is critical, was maintained by observation of an enlarged image projected on to a screen placed at the further end of the instrument bar.

The dimensions of the mask were chosen to include 2 mm of the arc column immediately adjacent to the cathode.

The form in which the impurities were present in the graphite was not known although it was thought likely that they would be present in the form of oxides and carbides. HEGEMANN AND RÜSSMANN[9] have shown in the analysis of graphite that there was no difference in the result produced by standards made from either the oxides or the carbides of the impurity elements, presumably because the large excess of graphite present reduced the oxide to carbide in the first few sec of burning in the arc. Accordingly, synthetic standards were made by successive dilution of a mixture of all the oxides of the metals and results showed this procedure to be justified.

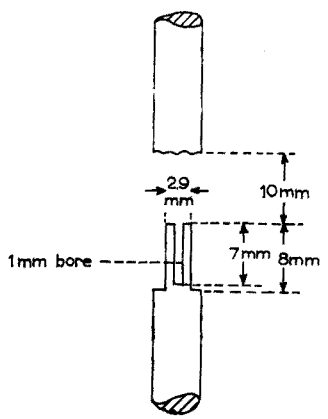

Fig. 2. Electrode assembly.

METHOD

Note

Some form of containment is necessary when handling radioactive samples. This should include at least a glove box with a suitable filter at the extraction outlet. An additional means of restricting the spread of radioactivity within the box is an inverted funnel suspended above the arc and connected through a filter to the exhaust.

Spectrographic conditions

(a) For visual evaluation. Spectrograph: Hilger medium quartz; external optics:

arc 53 cm from slit, lens F957, 43 cm from slit, rotating step sector with lens F1084 2 cm from slit; collimator mask: this should be of card or sheet metal with an aperture of 8 mm by 45 mm, painted matt black and placed symmetrically across the front of the collimator mounting; slit length: 1.8 mm; slit width: 0.010 mm; photographic plate: Ilford ordinary; top electrode (+ve): 1/4 in. diameter N.C.C., freshly broken off, not shaped; bottom electrode (—ve): 1/4 in. diameter N.C.C., specially machined (see Fig. 2); analytical gap: 10 mm; sample charge: electrodes filled to capacity using a small perspex funnel (see Fig. 3) and a rigid wire to ensure firm, even packing; current: 10 A d.c.; exposure: 3 min.

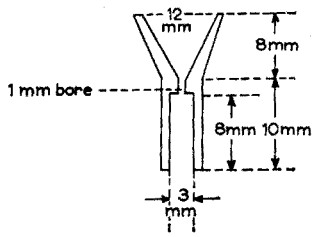

Fig. 3. Perspex funnel for loading electrodes.

(b) For microphotometry. Conditions as above except the following: slit length: 12 mm; position of 7-step sector: at slit, sector ratio 2 : 1.

Photographic processing

Develop in I.D.2 for 4 min at 20°. Rinse with water and fix in acid hypo until the plate is completely clear. Wash for 30 min in an efficient washing tank and allow to dry.

Standards

Prepare by dry grinding in an agate mortar a mixture of oxides of all elements required to be determined and adjust the concentration to 1.0% by weight of each element by the addition of 'Specpure' ammonium sulphate. By successive additions of N.C.C. graphite powder, prepare dilutions of this 1% mixture containing 1000, 500, 200, 100, 50, 20, 10, 5, 2 and 1 p.p.m. of impurity elements in the graphite.

For use as an internal standard, prepare by dry grinding a mixture containing 400 mg of copper oxide (CuO) and 100 mg cobalt oxide (Co_3O_4).

Preparation of sample

Grind for 10 min in an agate mortar 7 mg of the internal standard mixture and 49 mg of sample. By means of a perspex funnel (see Fig. 3) fill three electrodes with this mixture. Add a small portion of the mixture at a time repeatedly tamping with a rigid tungsten wire to ensure firm and even filling of the electrodes. The presence of occluded air in the cup will cause uneven volatilization of the impurities.

Spectrographic procedure

If required, first switch on the rotating step sector and allow it to attain its maximum r.p.m. Place a loaded cathode and counter electrode in the arc stand and strike

the arc at 3 A by lowering the upper electrode. Rapidly (within 5 sec) open the gap to 10 mm and increase the current to 10 A. Maintain the gap at 10 mm by continuous adjustment of cathode and anode and allow to burn for 3 min. If any spluttering occurs during the burn resulting in material being blown out of the electrode the exposure should be rejected. Repeat the above procedure to give duplicate exposures.

Interpretation of spectra

(a) Visually. Using a suitable comparator and standard plates for line identification read the spectra by comparing the densities of impurity and internal standard lines with those on the standard plate. The standard plates are prepared by mixing the standard dilutions above with the internal standard mixture and exposing an appro-

TABLE I

Element line	*Internal standard line*	*Range as p.p.m. in graphite*	*Interferences and remarks*	*Seidel density selected for microphotometry*
Al 3961.5	Co 3957.9	20–500		0.5
B 2497.7	Co 2506.5	5–500		
Ba 4934.1	Co 4867.9	10–500		
Be 3130.4	Cu 3146.8	1–50		
3131.1	Cu 3146.8	1–50		
Bi 3067.7	Co 3064.4	20–500		
Ca 3968.5	Co 3957.9	20–100		
4226.7	Cu 4275.1	20–1000	Cr 4226.7[a]	0.5
Cr 2843.3	Co 2837.2	10–500		0.6
4254.3	Cu 4275.1	10–200		
Fe 2973.2	Co 2989.6	10–500		0.3
	Co 3000.5			
	Co 3177.3			
Mg 2795.5	Co 2803.8	5–100	Weak Fe 2795.5	
2802.7	Co 2803.8	2–100		
Mn 2576.1	Co 2587.2	5–200		
2593.7	Co 2587.2	5–200		
2605.7	Co 2587.2	5–200	Weak Fe 2605.7	
2801.1	Co 2803.8	5–200	Weak Zn 2801.0	
Mo 3132.6	Cu 3146.8	50–500	Weak Ta 3132.6	
3170.3	Co 3177.3	50–500	Ta 3170.3	0.3
Ni 3002.5	Cu 2997.4	5–200		
	Co 3000.5		Co line is best	0.3
3003.1	Cu 2997.4	10–500	for microphotometry	
	Co 3000.5			
3393.0	Co 3367.1	20–500		
Pb 2833.1	Co 2837.2	20–500	Cu line is best	
	Cu 2882.9		for microphotometry	0.5
Si 2881.6	Cu 2882.9	10–500		0.5
Sn 2840.0	Co 2837.2	20–500	Cu line is best	
	Cu 2882.9		for microphotometry	0.5
Ti 2956.1	Co 2957.7	50–500		
3361.2	Co 3367.1	20–500		
V 3185.4	Co 3177.3	20–500		0.3

[a] When calcium is determined it is essential that chromium be absent from the elements in the standard mixture.

priate series of these by the method outlined for samples. The lines listed in Table I are pairs which have been found satisfactory. Other elements may be determined if they are included in the standard mixture but suitable internal standard lines would need to be sought.

(b) By microphotometry. (*1*) Using a non-recording microphotometer measure the Seidel densities of three appropriate steps of element and internal standard on the sectored pattern for samples and standards. The steps selected should bracket the recommended internal standard density given in the last column of Table I. (*2*) Plot these densities against the log relative intensities as given by the steps of the rotating sector (see Fig. 4). (*3*) Measure the difference in mm on the log relative intensity scale at the chosen Seidel density between the element and internal standard lines (see Fig. 4). (*4*) Plot these differences against the log concentration of the element for each standard (see Fig. 5). (*5*) Read off the log concentration of the element present in the sample appropriate to the difference in "blackening separation" as given in mm in (*3*).

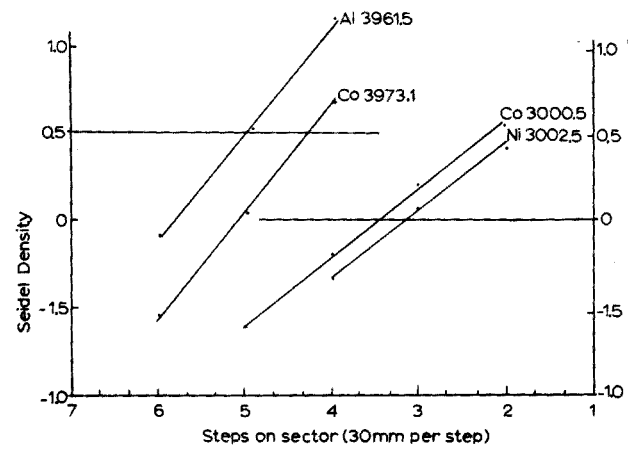

Fig. 4. Blackening separation curves for Al/Co and Ni/Co.

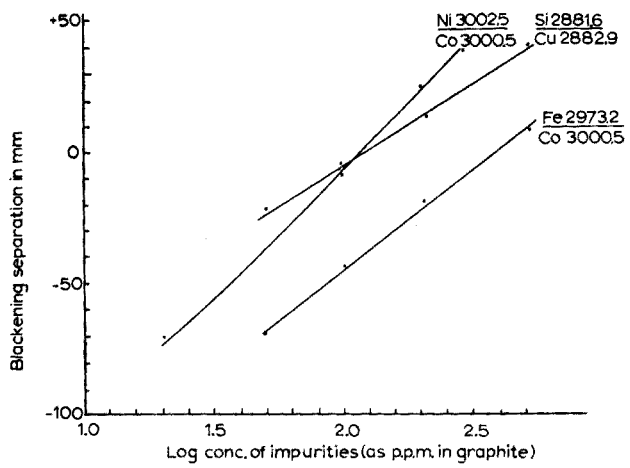

Fig. 5. Working curves for nickel, iron and silicon.

SENSITIVITY

A series of standards was exposed on a number of plates and the visual limits of detection were determined. These are shown in Table II.

TABLE II

SENSITIVITY OF ELEMENTS IN GRAPHITE

Element	*Wavelength*	*Sensitivity in p.p.m. in graphite*
Aluminium	3961.5	10[a]
Boron	2497.7	5
Barium	4934.1	10
Beryllium	3130.4	1
Bismuth	3067.7	10
Calcium	3968.5	20[a]
Chromium	2843.3	10
Iron	2973.2	10
Magnesium	2802.7	2[a]
Manganese	2593.7	5
Molybdenum	3132.6	20
Nickel	3002.5	10
Lead	2833.1	10
Silicon	2881.6	10[a]
Tin	2840.0	10
Titanium	3361.2	20
Vanadium	3185.4	10

[a] Sensitivity limited by blank

ACCURACY AND PRECISION

The precision of the method was determined by replication of a 100-p.p.m. standard on a number of plates and determining the coefficient of variation of the results obtained by non-recording microphotometer. The values obtained are shown in Table III.

TABLE III

COEFFICIENTS OF VARIATION FOR VARIOUS ELEMENTS

Element	*Coefficient of variation per determination at 100-p.p.m. level*
Nickel	3
Silicon	2.5
Vanadium	2.5
Aluminium	3.5
Chromium	3.0
Tin	5.5
Lead	6.0

The coefficients of variation for tin and lead would probably be improved by the use of an element of similar volatility as internal standard.

In order to check the accuracy of the method for the determination of calcium,

aluminium, vanadium and nickel, samples were examined by the cathode layer and iron flux methods[1] using the non-recording microphotometer in both cases and the comparative results are given in Table IV.

TABLE IV

COMPARISON OF RESULTS OBTAINED BY IRON FLUX AND CATHODE LAYER METHODS

(Results expressed as p.p.m. in graphite)

Element	*Sample A*		*Sample B*		*Sample C*		*Sample D*		*Sample E*		*Sample F*	
	C.L.	*I.F.*	*C.L.*	*I.F.*	*C.L.*	*I.F.*	*C.L.*	*I.F.*	*C.L.*	*I.F.*	*C.L.*	*I.F.*
Calcium	190	150	350	410	300	380	240	240	450	500	240	280
Aluminium	30	30	50	50	30	20	30	30	40	50	50	50
Vanadium	200	240	<10	6	210	220	190	220	160	170	<10	8
Nickel	20	20	<10	1	10	12	30	25	25	20	<10	1

The accuracy of the method for the determination of silicon was assessed by comparison of the results obtained by the present method, the iron flux method and by chemical analysis using the silicomolybdate method. The results are given in Table V.

TABLE V

DETERMINATION OF SILICON IN GRAPHITE

	p.p.m. of silicon in graphite		
Sample	*Iron flux*	*Cathode layer*	*Chemical (silico-molybdate)*
A	100	95	90
B	70	100	80
C	120	100	90
D	90	100	90
E	110	140	90
F	220	250	250

The accuracy for the determination of iron was assessed by comparison of results with those obtained by X-ray fluorescence analysis and chemical analysis (*o*-phenanthroline). The results are given in Table VI.

TABLE VI

	p.p.m. iron in graphite		
Sample	*Cathode layer*	*X-ray fluorescence*	*Chemical (o-phenanthroline)*
A	50	60	60
B	85	65	85
C	55	40	50
D	50	60	50
E	60	120	70
F	150	130	150

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to the following: Mr. J. WALKDEN of Chatham

Outstation (A.E.R.E.) for arranging the chemical analyses; to Mr. H. I. SHALGOSKY, Woolwich Outstation for X-ray fluorescence analyses and to Miss E. C. BLACKLOCK and Mr. M. L. WORDINGHAM who analysed many of the samples connected with the work of this programme.

SUMMARY

A modification of the cathode layer technique is suitable for the analysis of radioactive graphite using copper and cobalt as internal standards. The sample is ground with the internal standard mixture and introduced into a specially designed electrode which is burned in a d.c. arc. The cathode layer portion of the arc plasma is examined using a medium quartz spectrograph with photographic recording. The spectra are evaluated visually, by comparison with standard spectra, or by non-recording microphotometry using the "blackening separation" method. Using a 5-mg sample of graphite, the effective concentration range for Al, B, Ba, Be, Bi, Ca, Cr, Fe, Mg, Mn, Mo, Ni, Pb, Si, Sn, Ti and V is from 10 to 500 p.p.m. and the coefficient of variation for single exposures at the 100-p.p.m. level varies from 2 to 6% according to the element determined.

RÉSUMÉ

Les auteurs ont effectué une étude sur le dosage spectrographique d'impuretés dans un graphite radioactif, en utilisant une électrode spéciale et comme étalon interne, le cuivre et le cobalt. On a pu ainsi déterminer des teneurs de 10 à 500 p.p.m. de: Al, B, Ba, Be, Bi, Ca, Cr, Fe, Mg, Mn, Mo, Ni, Pb, Si, Sn, Ti et V.

ZUSAMMENFASSUNG

Beschreibung einer spektrographischen Methode zur Bestimmung von Verunreinigungen in radioaktiven Graphit unter Verwendung einer Spezialelektrode mit Kupfer und Kobalt als interne Standardsubstanzen. Spuren folgender Elemente können nachgewisen werden: Al, B, Ba, Be, Bi, Ca, Cr, Fe, Mg, Mn, Mo, Ni, Pb, Si, Sn, Ti und V.

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THE EXTRACTION OF MERCURY BY DITHIZONE RETAINED ON SILICA GEL

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INTRODUCTION

A solute experiencing chromatographic partition between a stationary solid phase and a mobile fluid phase will undergo a series of successive equilibrations as it passes through the stationary medium. By contrast, solvent extraction, a second versatile separation technique, requires successive batch extractions, each corresponding to only one equilibration, to separate solutes with poor separation factors, and these can be achieved only with the expenditure of considerable time and effort, or by using complicated and expensive equipment. Thus although concentration waves of solute, typical of distribution during chromatographic elution, are obtained using multistage extraction techniques[1], these procedures must be automatic or semi-automatic, if the tedium associated with a method which requires a large number of repetitions is to be avoided.

There would therefore be considerable advantages to be gained from modifying normal batch extraction procedures to operate on chromatographic principles, and a possible method would be to retain the complexing agent involved in the formation of the extractable species, on a solid support, sufficiently firmly to preclude its elution as the mobile phase passes through the column. As the mobile phase is likely to be an aqueous solution, reagents exhibiting low solubility in water are desirable, and in order to achieve an increased reaction rate between the hydrophobic complexing agent retained on the support, and a metal in aqueous solution, it is frequently advisable to incorporate an organic solvent into the solid phase. A non-aqueous phase consisting of a solid support, an organic solvent and a complexing agent has been prepared[2], which may be used for batch extractions, or slurried and packed into a column, and the use of this type of material for the separation of metals[3,4] has prompted further investigations into the behaviour of a metal undergoing extraction from an aqueous phase by such a system.

GENERAL CONSIDERATIONS

The formation of a complex ML_n in the aqueous phase of a two-phase system from a metal ion M^{+n}, present initially in the aqueous phase, and the ligand L^-, derived from the conjugate acid HL originally present in the non-aqueous phase, and the subsequent extraction of the complex, may be considered to involve four separate equilibria[5].

The ligand acid partitions into the aqueous phase, such that

$$\frac{[HL]_0}{[HL]} = p_r \tag{1}$$

where square brackets are used to represent concentrations, which are used in place of activities, and the subscript o denotes species present in the non-aqueous phase. After partition free base is liberated in the aqueous phase by the dissociation of HL such that

$$\frac{[H^+][L^-]}{[HL]} = K_a \tag{2}$$

where K_a is the dissociation constant of the acid HL. The complex is formed by the stepwise addition of n ligand ions to the metal M^{+n}, the composite formation constant K_f being given by

$$\frac{[ML_n]}{[M^{+n}][L^-]^n} = K_f \tag{3}$$

and the complex then partitions into the non-aqueous phase

$$\frac{[ML_n]_0}{[ML_n]} = p_c \tag{4}$$

Combining eqns. (1)–(4)

$$\frac{[ML_n]_0[H^+]^n}{[M^{+n}][HL]_0{}^n} = \frac{K_f p_c K_a{}^n}{p_r{}^n} \tag{5}$$

and since K_f, p_c, K_a and p_r are all constant, eqn. (5) may be rewritten

$$\frac{[ML_n]_0[H^+]^n}{[M^{+n}][HL]_0{}^n} = K' \tag{6}$$

where K' is a constant.

From considerations of mass balance, the total quantity of uncomplexed ligand L_u is given by

$$\begin{aligned} L_u &= [HL]_0 V_o + [HL] V_w + [L^-] V_w \\ &= [HL]_0 \left[V_o + \frac{V_w}{p_r} \left(1 + \frac{K_a}{[H^+]} \right) \right] \end{aligned} \tag{7}$$

where V_o and V_w are the volumes of the organic and aqueous phases respectively. Similarly for the complexed ligand

$$\begin{aligned} L_c &= n[ML_n]_0 V_o + n[ML_n] V_w \\ &= n[ML_n]_0 \left[V_o + \frac{V_w}{p_c} \right] \end{aligned} \tag{8}$$

If V_w/p_c and the factor $(V_w/p_r)(1 + K_a/[H^+])$ are both negligible by comparison with 1, eqns. (7) and (8) approximate to $L_u = [HL]_0 V_o$ and $L_c = n[ML_n]_0 V_o$ respectively,

indicating that in the event of low ligand acid dissociation, and of high partition of the acid and complex in favour of the non-aqueous phase, virtually all the complex and the free ligand are to be found in the organic phase.

Under these conditions the system bears a close overall resemblance to another two-phase separation technique, cation exchange on a resin, which also may be described by an expression similar to eqn. (6) except that o now refers to the species in the resin phase, and L^- to the resin matrix associated with one equivalent of hydrogen ions, whilst the terms $[ML_n]_0$ and $[HL]_0$ again account for all the HL and ML_n present in the system, since these species do not occur in the aqueous phase. In both cases the non-aqueous phase may be considered to provide sites for which both metal and hydrogen ions compete, and at which, during extraction, an n-valent metal may be complexed with the liberation of n-protons thus

$$M^{+n} + nHL_0 \rightleftharpoons ML_{n0} + nH^+$$

Relatively free movement of these sites is usually possible when they are provided by a complexing agent in solution, and this will reduce any metal concentration gradient that may have been established in the phase when employed in column form, for example in counter-current operation. Consequently unless this diffusion is restricted by some means, like packing the column with an inert material, the technique may well provide little or no advantage over conventional batch extraction. No such diffusion is feasible for exchange sites incorporated into a resin matrix and it is therefore possible to bring the solution being extracted into continuous contact with fresh concentrations of available exchange sites, thus enabling many theoretical plates to be achieved during the passage of a solute down the column. Diffusion will be limited if the solution is retained on a solid support, and the efficiency of the column extraction will be increased, provided that this advantage is not offset by an associated decrease in the rate of extraction. Further, an expression similar to eqn. (6) should account for the extraction of a metal by a complexing agent retained on a support, if the mechanism by which the extraction occurs is of the usual solvent extraction type, or if the complexing agent is retained more firmly in the non-aqueous phase and there is an exchange of ions at the phase interface rather than a transfer of the preformed complex from one phase to the other.

In this paper investigations are reported which have been carried out to determine the feasibility of using solutions of complexing agents retained on a solid for quantitative measurements and to test the validity of applying eqn. (6) to these systems.

The non-aqueous phase used was similar to that already reported[2] and consisted of silica gel retaining dithizone (diphenylthiocarbazone), and an organic solvent, in this case chloroform.

EXPERIMENTAL

Care was taken to ensure that apparatus and reagents were free from trace metals and oxidising agents likely to react with dithizone. Glassware was cleaned by methods described elsewhere[6] and the chloroform was AnalaR grade, redistilled once from pyrex apparatus. Laboratory distilled water was passed through a mixed-bed deioniser before use, and aqueous solutions were shaken with very dilute solutions of dithizone in chloroform, except in instances where solvent-free aqueous phases were required.

Solid phase

The solid phase was made by the method described previously[2]. Specially prepared silica gel was placed in a beaker and a solution of purified dithizone in chloroform added until a little free solution was visible at the bottom of the beaker. Surplus organic solvent was evaporated off in a current of air, until a freely running powder was obtained, and this was stored in a desiccator, over chloroform in the dark, until required for use.

Radioactive mercury solution

A known weight of irradiated mercuric oxide was dissolved in the minimum quantity of AnalaR nitric acid and diluted with water to give a solution approximately decimolar in acid. The acidity of the solution was standardised with alkali and the metal concentration checked colorimetrically using a solution of dithizone in carbon tetrachloride as reagent[7]. The radiochemical purity of the mercury was confirmed by γ-ray spectrometry.

Determination of dithizone content of the solid phase

Successive 3-ml volumes of dilute ammonia solution were used to extract the dithizone from about 0.1 g of solid phase, until the aqueous phase remained clear and all the colour had been removed from the silica gel. The combined aqueous extracts were transferred to a separating funnel, acidified, and the precipitated dithizone dissolved in carbon tetrachloride. The organic solution was made up to a known volume in a standard flask, and the optical density measured at wavelengths of 620 mμ, 515 mμ and 450 mμ. The ratio of the absorbancies at these wavelengths provided a check of the purity of the dithizone, and using a value of $34.6 \cdot 10^3$ for the extinction coefficient of dithizone in carbon tetrachloride at 620 mμ[6] the dithizone content of the solution, and hence the solid phase, was calculated. These values were confirmed by titrating the dithizone solution with a standard mercury solution.

Batch extractions

Approximately 0.1 g of the solid was accurately weighed into a 50-ml conical flask, after being allowed to stand in air for 40 min; then 20 ml of aqueous phase and 0.005 ml of active mercury solution were added. Except during experiments to determine the variation of extraction with shaking time, the flask and its contents were shaken for 1 h, on a horizontal shaker oscillating at approximately 100 c/min as it was found that the distribution ratio was not altered by a longer shaking time. After equilibration, the two phases were separated by filtration under suction through a sintered glass disc, 2 ml were pipetted into a "polytainer", and the activity was counted on a scintillation counter equipped with a well-crystal. The acidity of the aqueous phase was determined by titration, whilst the activity was compared with that of a standard, prepared from 20 ml of aqueous phase and a quantity of active mercury equal to that used in the extraction.

For each liquid–solid batch extraction an exactly similar experiment was carried out using a solid phase consisting of silica gel treated with organic solvent but no dithizone.

For liquid–liquid extraction, 20 ml of the aqueous phase was used, together with 20 ml of a solution of dithizone in chloroform, which had been presaturated with aqueous phase. Phase separation was effected by centrifugation.

RESULTS

The use of a silica gel–dithizone–chloroform solid phase for quantitative batch extractions

Silica gel which has been treated with a solution of dithizone in chloroform may be kept in an atmosphere of organic solvent, but the decrease in the dithizone concentration usually associated with the storage of dilute solutions of the reagent, also occurs when the dithizone and organic solvent are retained on silica gel. This is shown in Fig. 1. Consequently if the solid phase is to be kept for any length of time

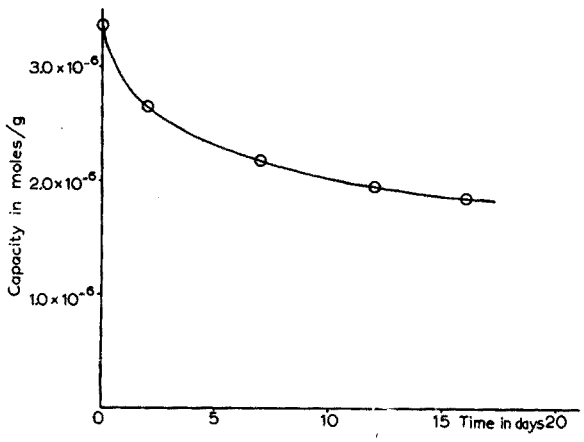

Fig. 1. Variation of the dithizone content of a silica gel–dithizone–chloroform phase with time of standing in an atmosphere of chloroform.

it should be standardised before use. The solid loses weight for the first 10 min after being removed from the atmosphere of organic solvent and exposed to air, but then achieves constant weight and can be accurately weighed out to provide the non-aqueous phase for quantitative batch extraction.

Dithizone on silica gel decomposes also upon prolonged exposure of the column material to air, and since any change in the dithizone concentration of the non-aqueous phase will be reflected in a variation of the distribution ratio of a metal partitioning between the solid and a liquid phase, it is essential to ensure that the small differences in drying time that may occur whilst weighing out samples for different extractions, do not affect the final position of the extraction equilibrium. Table I gives values for the distribution ratio of mercury between a hydrochloric acid phase

TABLE I

EFFECT OF DRYING TIME ON THE DISTRIBUTION OF MERCURY BETWEEN A 2.25 *N* HYDROCHLORIC ACID PHASE AND A DITHIZONE SILICA GEL PHASE

Drying time (min)	*D*[a]	*Drying time (min)*	*D*[a]
11	163	40	171
15	169	50	161
20	162	60	165
30	162		

[a] D = mols Hg^{+2} per kg of solid phase/mols Hg^{+2} per l of aqueous phase

and a dithizone silica gel phase, with varying drying times of the solid phase. Only slight excess of dithizone over metal was present in the system so that extraction would be sensitive to small changes in ligand concentration, and it can be seen that over a very wide range of drying times reproducible results may be obtained.

Recent investigations have shown that silica gel can act as an ion-exchanger[8]. Since any extraction of metal by silica gel retaining a complexing agent could be due either to the complexing agent or to the silica gel itself, for each batch extraction reported in this paper an exactly similar experiment was carried out using a solid phase of the same silica gel treated with organic solvent but no dithizone. In all cases no extraction was detected in the absence of dithizone.

Rate of attainment of equilibrium

In conventional liquid–liquid extractions it is frequently the practice to pre-saturate each phase with the other before equilibration in order to avoid the volume changes, on mixing, that occur if the two phases are not completely immiscible. Similarly, if an aqueous phase passing down a column of dithizone and chloroform retained on silica gel is not presaturated with organic solvent, the chloroform will tend to go into aqueous solution, and there may be associated with this a corresponding increase in the time required to achieve equilibrium for a metal partitioning from an aqueous into the silica gel phase.

A number of investigations were carried out to determine the time taken for mercury partitioning from a 5 *M* chloride phase of different acidities and a dithizone–silica gel phase, to come to equilibrium. In all cases the time required was less if the aqueous phase was presaturated with chloroform, and was usually considerably under half an hour.

Equilibrium was approached from one direction only, that of a metal-deficient non-aqueous phase.

Metal-ligand ratio

Since dithizone can apparently function as either a monobasic or a dibasic acid, reaction between the reagent and a divalent metal will be given by

$$\frac{n}{p}\mathrm{H}_p\mathrm{L}_0 + \mathrm{M}^{+n} \rightleftharpoons \mathrm{ML}_{\frac{n}{p}}^{\circ} + n\mathrm{H}^+ \qquad (9)$$

where $n = 2$ and p may have the values of either 1 or 2. Consequently if the reaction occurs in the aqueous phase of a liquid–liquid system and the species ML_n subsequently partitions into the non-aqueous phase, the dependence of the distribution ratio D upon pH and ligand acid concentration will be given by

$$D = K' \frac{[\mathrm{HL}]_0^{n/p}}{[\mathrm{H}^+]^n} \qquad (10)$$

where K' is the equilibrium constant for the reaction given in eqn. (9).

If an anion X^- is present in the aqueous phase, which is capable of forming the non-extractable species $\mathrm{MX}^{+(n-1)}$, $\mathrm{MX}_2^{+(n-2)}$ . . . $\mathrm{MX}_j^{+(n-j)}$, with the metal M^{+n}, eqn. (10) becomes

$$D = K' \frac{[\mathrm{HL}]_0^{n/p}}{[\mathrm{H}^+]^n} \{1 + K_1[\mathrm{X}^-] + K_1K_2[\mathrm{X}^-]^2 + \ldots + K_1 \ldots K_j[\mathrm{X}^-]^j\} \qquad (11)$$

where the formation constant K_j is given by

$$K_j = \frac{[MX_j^{+(n-j)}]}{[MX_{j-1}^{+(n-j+1)}][X^-]}$$

In the event of the complexing agent being retained in a solution uniformly dispersed through a solid phase, eqn. (9) would still be valid, whilst if the solution of complexing agent were retained on the surface of the individual particles, the dependence of D upon $[HL]_0$ and $[H^+]$ still would be as given by eqn. (9), but any values of K' calculated using this equation then would dependent upon particle size.

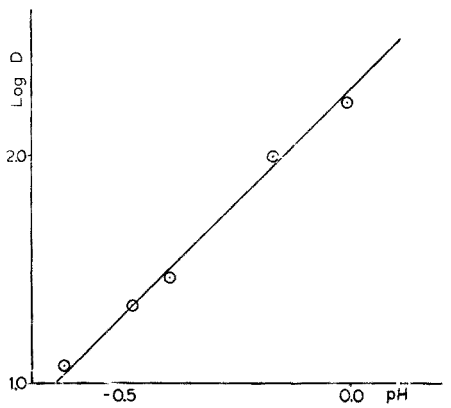

Fig. 2. Extraction of mercury from a 5 M chloride phase of different acidities by a silica gel–dithizone–chloroform phase.

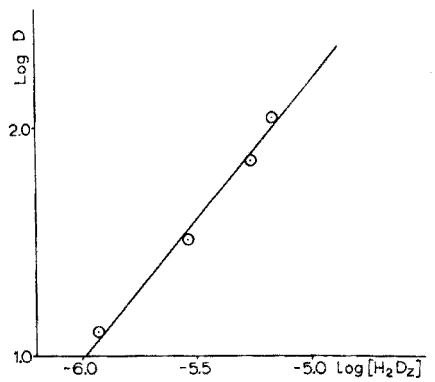

Fig. 3. Dependence of the extraction of mercury on the dithizone concentration of a silica gel–dithizone–chloroform solid phase.

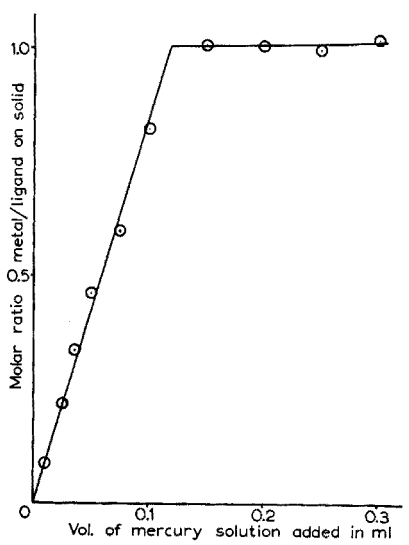

Fig. 4. Saturation of a silica gel–dithizone–chloroform phase with mercury.

The results of the batch extraction of mercury from a 5 M chloride phase of different acidities, by dithizone retained on silica gel is shown in Fig. 2, when a second power dependence of the distribution ratio upon hydrogen ion concentration is indicated. Since the concentration of dithizone on the solid phase may be altered, it is possible to investigate the variation of the distribution ratio with dithizone concentration. Provided that the total amount of mercury present in the system is small compared with the amount of dithizone, the initial and final dithizone concentrations will be little different, and accordingly D may be plotted against the initial dithizone concentration to obtain a value of n/p. A plot of the log of the distribution of mercury between a dithizone–silica gel–chloroform phase and a N hydrochloric acid phase of 5 M chloride ion concentration, against the log of the initial dithizone concentration of the solid support, was found to give a straight line of slope 1.2 (Fig. 3). The graphs drawn in Figs. 2 and 3 consequently suggest that there is a 1 : 1 metal dithizone ratio in the complex formed on the silica gel, and this was substantiated by a second series of experiments. An accurately weighed quantity of solid phase (~0.1 g) of known dithizone content was shaken with a molar hydrochloric acid phase containing increasing quantities of metal, until the metal extracted into the non-aqueous phase, determined by counting before and after equilibration, reached a maximum (Fig. 4). At this point the metal ligand ratio was 1 : 1.

Calculation of the equilibration constant for the extraction of mercury by a silica gel–dithizone–chloroform phase

Values of the equilibrium constant for the reaction between mercury and dithizone retained on silica gel, may be calculated from the extraction data plotted in Figs. 3 and 4, if an expression similar to eqn. (11) is used. Since chloride ions are present in aqueous solution, the mercury-chloride complexes $HgCl_j^{+(2-j)}$ must be considered, where j may have values from 1–4. Consequently the results quoted in Table II have been calculated using values of $K_1 = 5.5 \cdot 10^6$, $K_2 = 3.02 \cdot 10^6$, $K_3 = 8.91$ and $K_4 = 11.2$ for the stepwise stability constants of the mercury chloride complexes[9]. Included in Table II are the results derived from a series of extractions in which both the acidity and the chloride ion concentration of the aqueous phase were allowed to vary.

TABLE II

EQUILIBRIUM CONSTANTS FOR THE REACTION BETWEEN MERCURY AND DITHIZONE RETAINED ON SILICA GEL

D	$[H^+]$	$[H_2L]_0$	$\sum_0^4 K_1 - K_n[Cl]^n$	K'	D	$[H^+]$	$[H_2L]_0$	$\sum_0^4 K_1 - K_n[Cl]^n$	K'
1064	0.499	$1.42 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.96 \cdot 10^{23}$	12.9	3.0	$1.17 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.04 \cdot 10^{23}$
163.8	0.997	$1.44 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.13 \cdot 10^{23}$	6040	1.53	$1.65 \cdot 10^{-3}$	$9.62 \cdot 10^{15}$	$0.82 \cdot 10^{23}$
102.3	1.505	$1.46 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.59 \cdot 10^{23}$	1835	2.05	$1.68 \cdot 10^{-3}$	$3.05 \cdot 10^{16}$	$1.40 \cdot 10^{23}$
27.55	2.45	$1.52 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.14 \cdot 10^{23}$	234.2	2.58	$1.68 \cdot 10^{-3}$	$7.54 \cdot 10^{16}$	$0.70 \cdot 10^{23}$
21.8	3.02	$1.53 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.36 \cdot 10^{23}$	98.1	2.93	$1.69 \cdot 10^{-3}$	$1.24 \cdot 10^{17}$	$0.62 \cdot 10^{23}$
12.48	4.42	$1.54 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.66 \cdot 10^{23}$	24.9	3.54	$1.72 \cdot 10^{-3}$	$2.65 \cdot 10^{17}$	$0.48 \cdot 10^{23}$
110.5	3.0	$6.69 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.56 \cdot 10^{23}$	13.72	4.02	$1.73 \cdot 10^{-3}$	$4.42 \cdot 10^{17}$	$0.57 \cdot 10^{23}$
72.0	3.0	$5.38 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.26 \cdot 10^{23}$	5.36	4.50	$1.73 \cdot 10^{-3}$	$6.93 \cdot 10^{17}$	$0.43 \cdot 10^{23}$
71.3	3.0	$4.92 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.37 \cdot 10^{23}$	2.83	4.98	$1.73 \cdot 10^{-3}$	$1.03 \cdot 10^{18}$	$0.42 \cdot 10^{23}$
31.2	3.0	$2.94 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	$1.00 \cdot 10^{23}$			Mean value		$1.08 \pm 0.48 \cdot 10^{23}$

Concentrations are in moles/l for liquid phases and moles/kg for solid phases.

The equilibrium constant for the extraction of mercury by a solution of dithizone in chloroform

The variation in the distribution of mercury between an aqueous acid–chloride phase and a solution of dithizone in chloroform was investigated. Results indicated a 1:2 complex and equilibrium constants calculated on this assumption are given in Table III.

TABLE III

EQUILIBRIUM CONSTANTS FOR THE REACTION BETWEEN MERCURY AND A SOLUTION OF DITHIZONE IN CHLOROFORM

D	$[H^+]$	$[H_2L]_0$	$\sum_0^4 K_1 - K_n[Cl]^n$	$K' \cdot 10^{-23}$
0.442	2.50	$2.21 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	5.94
0.902	2.50	$3.18 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	5.85
1.55	2.50	$4.28 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	5.56
2.59	2.50	$5.66 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	5.31
2.62	1.69	$3.67 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	5.84
1.80	2.13	$3.67 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	6.36
1.26	2.49	$3.67 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	6.09
0.944	3.05	$3.67 \cdot 10^{-3}$	$1.05 \cdot 10^{18}$	6.84
			Mean value	5.97 ± 0.46

DISCUSSION

It is important to be able to prepare successive batches of any column material, to be used for the chromatographic separation of metals, with similar metal extraction characteristics. The solvent extraction of metals by solutions of dithizone has been the subject of much investigation[10] but the extraction of an element by the ligand might be modified by the retention of the dithizone on a solid, and this difference, in turn, could be critically dependent upon the method of preparation of the solid support. The results recorded in Table II were calculated from three separate series of experiments carried out using column material made up from different batches of silica gel, which had been prepared by the method referred to in the experimental section, but for which washing, precipitation and drying times had not been carefully controlled. It can be seen that the values calculated for K' on the assumption that a 1:1 complex is formed in the non-aqueous phase agree well, are independent of the batch of silica gel used, and are calculated from values of the free ligand acid concentration, the pH, the metal chloride complex stabilities and the chloride ion concentration only.

Combining the two forms of eqn. (11) as applied to the extraction of mercury by dithizone in a chloroform solution and retained on silica gel

$$\frac{D_1}{D_2} = \frac{K_1'}{K_2'} \frac{[HL]_{01}}{[HL]_{02}^2} \frac{[H^+]_2^2}{[H^+]_1^2} \frac{\sum_0^4 K_1 - K_n[Cl^-]_2^n}{\sum_0^4 K_1 - K_n[Cl^-]_1^n} \qquad (12)$$

where the subscripts 1 and 2 refer to the liquid–solid and the liquid–liquid extractions

respectively. For similar hydrogen and chloride ion and free ligand acid concentrations, also inserting values for K_1' and K_2' eqn. (12) reduces to

$$\frac{D_1}{D_2} \approx \frac{18.1 \cdot 10^{-2}}{[HL]_{02}}$$

Thus at a value of $[HL]_{02} = 10^{-2}$, which approaches the maximum solubility of dithizone in chloroform, the value of the distribution coefficient for the liquid–solid system is greater than 10 times that for the liquid–liquid system, and this ratio increases by a factor of 10 for each 10-fold decrease in $[HL]_0$. In practice it is rarely possible to use all the free dithizone for complex formation with a metal, since the final concentration of a metal dithizonate in the system will be limited by its solubility in the organic solvent, which is generally lower than that of dithizone itself. However, metal dithizonates may be satisfactorily retained on a silica gel–chloroform phase, in concentrations which, when given in moles/kg, are considerably larger than the solubility concentrations in moles/l of the same chelates in chloroform solution.

The extraction of mercury from a strongly acid phase by a solution of dithizone in chloroform in the presence of considerable excess of reagent over metal would be expected to occur by means of the primary rather than the secondary dithizonate, and this is supported by the experimental evidence recorded in Table III. The 1:1 metal-ligand ratio which is indicated when mercury is extracted by dithizone retained on silica gel, is consequently unexpected but this behaviour proves to be similar to that shown for the extraction of other divalent metals by dithizone retained on different support materials[11]. If the ligand is retained firmly on the silica gel, and if the mechanism by which reaction occurs is more closely akin to ion exchange than to solvent extraction, it is possible that the steric arrangements of the active groups could preclude two rather bulky organic residues combining with a relatively small metal ion. However, although X-ray crystallographic studies of the solid have shown that primary mercury(II) dithizonate is bonded through the sulphur atom[12] and infrared measurements on the complex in solution have substantiated this[13], there is still considerable doubt as to the structure of the secondary complex. This, together with the limited information available at this time, concerning the behaviour of the liquid–solid systems, makes it difficult to assess the reason for the difference in the metal-ligand stoichiometry between the liquid–liquid and liquid–solid systems, and to determine the part played by silica gel in this change.

SUMMARY

A silica gel–dithizone–chloroform phase is suitable for the quantitative batch extraction of certain metals. The extraction of mercury from a chloride phase by such a support has been investigated and the effect of varying acidity, free ligand acid concentration, and chloride ion concentration has been determined.

RÉSUMÉ

Une méthode est proposée pour l'extraction du mercure, au moyen de dithizone et chloroforme, en utilisant le silica gel comme support. Les auteurs ont également examiné l'influence de divers facteurs sur la réaction.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Extraktion von Quecksilber als Dithizonverbindung mit Chloroform unter Verwendung von Silicagel als Trägersubstanz .Der Einfluss des Säuregehaltes und der Chlor-ionenkonzentration wurde untersucht.

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STUDIES ON THE SOLVENT EXTRACTION OF SOME CADMIUM CHELATES

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INTRODUCTION

Previous cadmium extractions

Little detailed work has been done concerning the solvent extraction behavior of cadmium chelates. Although qualitative observations of the extraction behavior of cadmium with various chelating agents are available in the literature, the quantitative data necessary for a useful interpretation and utilization of these observations are in most instances undetermined.

Rather detailed studies of the solvent extraction of cadmium using dithizone and 2-(*o*-hydroxyphenyl)-benzoxazole have been reported by SCHWEITZER AND DYER[1] and DEVOE AND MEINKE[2], respectively. In addition, observations of extractions using such diverse reagents as thenoyltrifluoroacetone, isonitrosoacetophenone, 2-mercaptobenzothiazole, and other reagents have been reported.[3]

Extraction equations

Consider a system made up of an aqueous phase and a non-aqueous phase of equal volume in contact. The aqueous phase, which has been pre-equilibrated with the non-aqueous solvent, contains cadmium(II) ion as the perchlorate, hydrogen ion as the perchlorate, and is made up to an ionic strength of 0.1 with sodium perchlorate. Its

pH is adjusted by the addition of small amounts of sodium hydroxide and perchloric acid solutions. The non-aqueous phase, which has been pre-equilibrated with 0.1 *M* sodium perchlorate solution, contains a chelating agent HR with one acidic group and one neutral coordinating group.

The chelating agent HR partitions between the two phases with an organic : aqueous partition coefficient P_r and ionizes in the aqueous phase with an association constant K_r. If one assumes the extracting species to be CdR_2, then it will partition between the two phases with an organic : aqueous partition coefficient P_c and will ionize in the aqueous phase with an association constant K_c. Upon further assuming there to be no metal species other than Cd^{+2} present in significant amount in the aqueous phase and assuming there to be no metal species other than CdR_2 in the non-aqueous phase, the major extraction reaction may be written as

$$Cd^{+2} + 2HR \rightleftharpoons CdR_2 + 2H^+$$

where Cd^{+2} and H^+ are in the aqueous phase and HR and CdR_2 are predominantly in the non-aqueous phase.

By proper combination of relations plus the assumption that P_c is quite large, the organic : aqueous distribution ratio E of the metal may be expressed as follows:

$$E = \frac{P_c K_c (HR)_0^2}{P_r^2 K_r^2 (H)^2} = \frac{K (HR)_0^2}{(H)^2} \tag{1}$$

In this expression $(HR)_0$ represents the concentration of HR in the non-aqueous phase, (H) symbolizes the concentration of H^+ in the aqueous phase, and $K = P_c K_c / P_r^2 K_r^2$.

If the dominant extracting species is $CdR_2(HR)_m$, then the major extraction equation might be expressed as

$$Cd^{+2} + (m+2)HR \rightleftharpoons CdR_2(HR)_m + 2H^+ \tag{2}$$

and (1) could be altered to read[4]

$$E = \frac{P_c K_c (HR)_0^{m+2}}{P_r^{m+2} K_r (H)^2} = \frac{K (HR)_0^{m+2}}{(H)^2} \tag{3}$$

The constant P_c now represents the organic : aqueous distribution coefficient of the species $CdR_2(HR)_m$ and K_c represents its association constant. When the logarithm of relation (3) is taken, and it is remembered that equal phase volumes are being employed, the following expression may be shown to hold when $E = 1$, which is the condition at which 50% extraction of the metal has occurred

$$\log K = 2pH_{1/2} - (m+2) \log (HR)_0 \tag{4}$$

In this equation $pH_{1/2}$ represents the pH value at which 50% extraction is observed. Thus, if m, $pH_{1/2}$, and $(HR)_0$ are known for an extraction system, K can be estimated. Then if three of the four constants comprising K are found, the remaining constant can be estimated by calculation. This provides a means for estimating K_c in a number of cases.

The extraction of a metal ion from an aqueous solution into an organic solvent using a chelating agent is an increasingly useful analytical operation. The extent to which a given chelating agent can be used effectively in such an operation is deter-

mined largely by two factors, the values of $pH_{1/2}$ and P_c. If the $pH_{1/2}$ of the non-masked extraction is low, considerable variation may be effected through the use of masking agents which form water-soluble complexes.[3] This could allow selective extractions of several metals at different pH values. If the value of P_c is high, practically quantitative extractions can be effected in a one-step operation.

The present problem

In this present work, a study was made of the extraction of cadmium ion from aqueous solutions into chloroform containing a known amount of a chelating agent. Values of P_r and K_r were obtained from the literature or were determined as a part of this study. From proper extraction experiments, values of $pH_{1/2}$, P_c, and K were found. From these data, it is possible to suggest which of the eighteen chelating agents should be most effective as reagents for cadmium extractions.

EXPERIMENTAL PROCEDURES

The chemicals, apparatus, and general procedures were essentially the same as described in previous works[1,5]. 10-ml portions of the aqueous phase were stirred with 10-ml portions of the chloroform phase for 12 h at 30° ± 0.5°. In all cases the original cadmium concentration was approximately $10^{-5.1}$ M and was radioactively labelled with ^{115m}Cd to facilitate measurement of the extraction. All aqueous phases were maintained at constant ionic strength of 0.1 by the addition of sodium perchlorate. At least 20 individual determinations were made in order to characterize each of the systems listed in Table I.

TABLE I

DATA AND CALCULATED QUANTITIES FOR CADMIUM EXTRACTIONS

System	*Reagent*	*Reagent concn.*	$pH_{1/2}$	$\log P_c$	$\log P_r$	$\log K_r$
1	2-mercaptobenzothiazole	$10^{-1}M$	3.9	4.1	2.2	7.8
2	5,7-dichlorooxine	10^{-2}	4.6	3.8	(3.9)[e]	(7.4)[e]
3	oxine	10^{-1}	5.2	4.0	2.6	9.7
4	isonitrosoacetophenone	10^{-1}	5.6	1.6	2.2	7.0
5	5,7-dibromooxine	10^{-2}	6.1	3.5	(4.2)[e]	(7.3)[e]
6	thenoyltrifluoroacetone	10^{-1}	6.7	1.5	2.5	(6.2)[d]
7	dibenzoylmethane	10^{-1}	9.7	1.1	(5.2)[e]	(9.2)[e]
8	benzoylacetone	10^{-1}	9.8	1.7	(3.7)[f]	(8.7)[f]
9	cinnamic acid	10^{-1}	[a]	2.1	—	—
10	salicylaldoxime	10^{-1}	[a]	—	2.1	7.4
11	2-methyloxine	10^{-2}	[a]	—	—	—
12	acetylacetone	10^{-1}	[a]	—	—	—
13	quinine	10^{-1}	[a]	—	3.2	—
14	*o*-methoxylbenzoic acid	10^{-1}	[b]	—	—	—
15	salicylic acid	10^{-1}	[b]	—	—	—
16	N-phenylbenzohydroxamic acid	10^{-1}	[b]	—	—	—
17	3,5-dinitrobenzoic acid	10^{-3}	[b]	—	—	—
18	anthranilic acid	10^{-1}	[b]	—	—	—

[a] Irregular curves obtained; see text.
[b] No extraction in pH range 2.0 to 12.0.
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Determinations of the values of P_r and K_r followed the procedure as outlined by SCHWEITZER AND MOTTERN.[6] Values of P_c were found by equilibrating a 20-ml. portion of chloroform containing the cadmium chelate with 1 l of 10^{-1} M sodium perchlorate solution at a proper pH value. After equilibration, aliquots of each phase were evaporated to dryness, counted, and the P_c value was calculated. Each value represents the average of at least three determinations.

RESULTS

Table I summarizes the results of this study along with some values obtained from the literature. All values enclosed in parentheses have been derived from previous works. No attempt is made to provide P_r and K_r values for those systems which showed irregular or no extraction (systems 10–18).

Curves of per cent metal extracted into the organic phase *versus* the final pH of the aqueous phase for systems 1–8 gave the theoretically-predicted sigmoid pattern shown by regular systems of this type,[7] having a slope of approximately 115% units per pH unit at the $pH_{1/2}$. However, systems 7 and 8 approached a maximum at about 90% metal extracted instead of the regular 100%.

System 9 gave an approximately linear curve having a slope of 17% per pH unit between a pH of 6.0 (5% extraction) and one of 11.0 (92% extraction). System 10 gave extraction behavior which may be characterized by the following points: pH of 6.7 (1% extracted), 7.3 (1%), 7.4 (3%), 7.7 (16%), 8.2 (18%), 8.6 (21%), 9.1 (17%), 10.0 (2%). System 11 also gave an irregular curve best characterized by the following points: pH of 6.3 (7% extracted), 6.7 (23%), 7.2 (28%), 7.4 (27%), 8.2 (26%), 9.2 (42%), 11.6 (44%). Systems 12 and 13 exhibited non-reproducible extraction behavior. The remainder of the systems, 14–18, showed no extraction in the pH range 2.0–12.0.

DISCUSSION

From the results of this study, the potential usefulness of several of the reagents studied is apparent. For example, 2-mercaptobenzothiazole, by virtue of the high P_c and the low $pH_{1/2}$, is an excellent reagent. The same is true for 5,7-dichlorooxine, oxine, and, to a lesser extent, 5,7-dibromooxine. The low values of P_c for the cadmium chelates of isonitrosoacetophenone and thenoyltrifluoroacetone indicate that the extractions with these reagents would not be as quantitative as might be desired.

The other reagents, by virtue of either high $pH_{1/2}$ values or low P_c values or no extraction, could not be employed to extract cadmium effectively. On the other hand, these reagents might be used to separate one or more metals from cadmium if the extraction were more favorable with respect to these other metals.

In these experiments, the exact nature of the extracting species in each case has not been determined. Consequently, the value of m cannot be assigned with any degree of assurance. From the data presented in this study, however, equations 3 and 4 can be used to calculate possible values of K and K_c assuming various values for m. This is done as follows: Choosing from Table I system 3, oxine, P_r is $10^{2.6}$, K_r is $10^{9.7}$, P_c is $10^{4.0}$, $pH_{1/2}$ is 5.2, and $(HR)_0$ is 10^{-1} M. If the extracting species is CdR_2, then n is 2 and m is 0. Thus equations 3 and 4 may be used to give K equal to $10^{-8.4}$ and K_c equal to $10^{12.2}$. If the species is $CdR_2 \cdot HR$, then values of K equal to $10^{-7.4}$ and K_c equal to $10^{15.8}$ result. If the species is $CdR_2 \cdot 2HR$, K turns out to be $10^{-6.4}$ and K_c

to be $10^{18.4}$. HELLWEGE AND SCHWEITZER[8] have found in the case of cadmium oxinate that the extracting species is $CdR_2 \cdot 2HR$, thus the last values in the previous paragraph are the applicable ones. In no other case, however, is there unequivocal knowledge of the character of the extracting species. Thus calculations of K and K_e must await such determinations.

SUMMARY

Eighteen different chelating agents have been investigated as possible extractants for radiolabelled $10^{-5.1}$ M cadmium from aqueous solutions into chloroform. The experimentally-determined extraction data have been analyzed theoretically by measurement of metal chelate and chelating agent association constants and distribution constants.

RÉSUMÉ

Les auteurs ont effectué une recherche sur l'extraction par le chloroforme de quelques chélates de cadmium en solution aqueuse.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Extrahierbarkeit von Cadmiumchelaten mit Chloroform aus wässrigen Lösungen.

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CHELATING PROPERTIES OF BIS(8-HYDROXY-2-METHYL-5-QUINOLYL)METHANE

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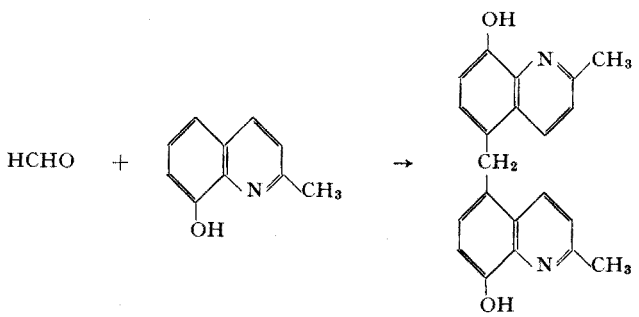
In continuing investigations of chelating agents containing two 8-quinolinol functions per molecule[1], we have prepared the title compound (I) by acid condensation of formaldehyde and 8-hydroxyquinaldine.



I

As expected from the presence of methyl groups in the 2-positions[2] I does not precipitate aluminum but does react with most of the other ions forming chelates with 8-quinolinol. The colors and pH conditions of precipitation of these chelates are closely similar to 8-hydroxyquinaldine chelates. A continuous variations study of the green color formed by I and ferric ion in acid solution indicated a 1:1 ratio of reagent to metal in this soluble complex. Analysis of the copper chelate was acceptable for the 2:1 ratio of reagent to metal expected if only one of the chelating functions in the molecule was used. However, metal analyses of dried samples of the zinc, nickel, and ferric chelates were high for the 2:1 ratio expected with zinc and nickel or for the 3:1 ratio expected with iron, and the metal content increased as the ratio of reagent to metal was decreased in the preparation of these samples.

It is well-known that reagents like I should be capable of forming chelate polymers in which the metal links one unit to the next. Such polymers from bis(8-hydroxy-5-quinolyl)methane appear to have been prepared[3], although our own investigations of this reagent[1] indicated that only normal chelates with one chelating function used in each reagent molecule were obtained in dilute aqueous solutions. However, under these conditions the reaction would no doubt be terminated by precipitation of the chelates.

Since a 1:1 mole ratio of I to metal would be expected for a chelate polymer of substantial chain length, it is conceivable that our high analytical results can be attributed to a partial polymer formation. However, the extraordinary thermal stability supposedly characteristic of these chelate polymers was not apparent.

In addition to I there were also prepared by similar reactions bis(8-hydroxy-3-methyl-5-quinolyl)methane (II) and bis(8-hydroxy-3-chloro-5-quinolyl)methane (III). An attempt to obtain bis(8-hydroxy-4-methyl-5-quinolyl)methane from 8-hydroxylepidine gave no product. The ultraviolet absorption spectra of these compounds are roughly similar to those of the corresponding 8-quinolinols but with approximately doubled molar absorbancies and a considerable shift of the long wavelength maximum toward the visible (Table I).

TABLE I

ANALYSES AND ULTRAVIOLET SPECTRA OF BIS(8-HYDROXY-5-QUINOLYL)METHANES

Compound	*Formula*	*m.p. °C*	*%N*		*Solvent*	*Max.(log ε)*
			Calculated	*Found*		
I	$C_{21}H_{18}N_2O_2$	191–2	8.49	8.44	EtOH	249(5.02),328(3.94)
					EtOH–HCl	263(5.18),315(3.79), 375(3.87)
II	$C_{21}H_{18}N_2O_2$	252–4	8.49	8.19	EtOH–HCl	263(4.94),313(3.37), 384(3.63)
III	$C_{19}H_{12}N_2O_2Cl_2$	260d	7.55	7.82	EtOH–HCl	270(4.72),319(3.59) 360(3.60)

The ionization of I in 20% ethanol as a function of acidity resembled the behavior of bis(8-hydroxy-5-quinolyl)methane, but the values of pK_1 and pK_2 were 4.9 and 10.3 respectively, demonstrating the slightly greater basicity imparted by the methyl substituents.

Quantitative bromination of I gave a dibromo derivative.

EXPERIMENTAL

Preparation of compounds

The condensation of 8-hydroxyquinaldine with formaldehyde in sulfuric acid by the method of ZINNER AND FIEDLER[4] for 8-quinolinol gave a 55% yield of I, recrystallized as the dihydrochloride from dilute hydrochloric acid; neutralization with dilute base and recrystallization from isopropanol gave the free base, melting at 191–2°, in the form of long (3–5 mm) anisotropic rods showing oblique extinction (see Table I for analysis). The infrared spectrum (KBr pellet) had principal bands at 2.93 (hydroxyl), 6.24, 6.35, 6.63, 6.80, 7.15, 7.55, 8.00, 8.45, 9.33, 9.72, 10.15, 11.05, 12.04, 12.65, 12.85, 13.20, and 14.03 μ.

Preparations of II and III were similar (see Table I).

Bromination of I in acid solution with standard bromate–bromide gave quantitative direct potentiometric end-points, but unsatisfactory results if excess bromate was back-titrated as in the familiar 8-quinolinol method. A prepared sample of the dibrominated product, m.p. 235.5–6.5°, gave the following analysis: calculated for $C_{21}H_{16}Br_2N_2O_2$: N, 5.74; found: N, 5.27.

It was also possible to obtain I in 40% yield by the reaction of 5-hydroxymethyl-8-

hydroxyquinaldine[5] with 8-hydroxyquinaldine in acetic–sulfuric acid solution following the same procedure used by ZINNER AND FIEDLER for the preparation of bis(8-hydroxy-5-quinolyl)methane.

Chelation studies

Chelate compounds of I with copper, zinc, nickel, and ferric ions were prepared by standard methods[1], washed throughly with 50% isopropanol and air-dried before analysis. Analyses for metal were performed by ignition to the oxides. Calculated results for 2 : 1 ratios of I to copper, nickel and zinc were respectively 8.80, 8.18 and 9.0% metal; found results were respectively 8.62, 10.50, and 16.43%. The calculated iron % for a 3 : 1 ratio of reagent to metal was 5.4%; found, 7.5 %.

The method of continuous variations applied to the green color of I and ferric ion at pH 1.9 and at 600 mμ gave a 1 : 1 complex formula. Attempts to find a soluble aluminum complex of I by the continuous variations method indicated no complex was formed. All spectra were recorded with a Beckman DK-2 spectrophotometer.

ACKNOWLEDGEMENT

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SUMMARY

A new chelating reagent, bis(8-hydroxy-2-methyl-5-quinolyl)methane, has been prepared and characterized. It does not react with aluminum but does chelate with many other metals. Analytical data did not permit a decision on the possibility that some of these chelates are polymeric.

RÉSUMÉ

Les auteurs ont préparé et examiné un nouveau réactif pouvant former des chélates: le bis-(hydroxy-8-méthyl-2-quinolyl-5)méthane. Ce composé ne réagit pas avec l'aluminium, mais il forme des chélates avec de nombreux autres métaux.

ZUSAMMENFASSUNG

Beschreibung der Darstellung von Bis-(8-hydroxy-2-methyl-5-chinolyl)-methan und Untersuchung seiner Eignung als chelat-bildendes Reagenz: Die Verbindung reagiert nicht mit Aluminium, aber bildet Chelate mit zahlreichen anderen Metallen.

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THE METAL COMPLEXES OF SOME AZO AND AZOMETHINE DYESTUFFS

PART I. SPECTRA IN WATER, AND IN DIOXAN/WATER IN THE WAVELENGTH RANGE 320–600 mμ

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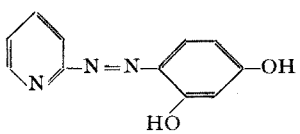
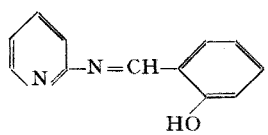
The development of 4-(2-pyridylazo)-resorcinol(I) as a reagent for the colorimetric determination of cobalt(II), lead(II), and uranium(VI) has been previously reported[1] and to explain its high sensitivity a study of the structural properties of this reagent and of the metal complexes has been made. In order to obtain some measure of the part played by each of the reactive groups (the pyridine nitrogen, the *o*-hydroxyl group, and the azo group), compounds (II), (III) and (IV), in which each of these groups except the hydroxyl group has been replaced by a non-coordinating group, have been investigated.



(I)



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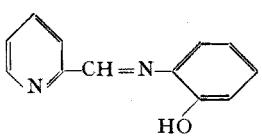

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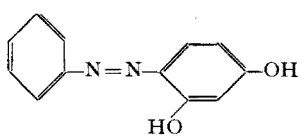


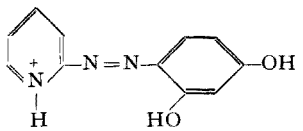
(IV)

4-(2-Pyridylazo)-resorcinol and the metal complexes it forms are sufficiently soluble in water to permit spectral measurements in this medium, whereas the compounds (II), (III), and (IV), and their metal complexes, are insoluble in water. Measurements were therefore made in both water and 1 : 1 *v/v* dioxan-water for (I), the ionic strength (μ) being maintained at 0.1 by addition of the appropriate quantity of sodium perchlorate, and in 1 : 1 *v/v* dioxan-water for compounds (II), (III), and (IV).

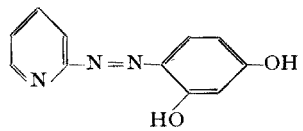
MEASUREMENTS IN AQUEOUS SOLUTION

The visible spectrum of 4-(2-pyridylazo)-resorcinol was obtained at twenty-one in-

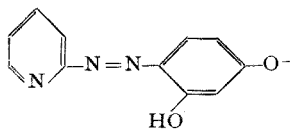
crements of pH between 1.0 and 13.0, and 4 chromophoric species of the reagent were identified.



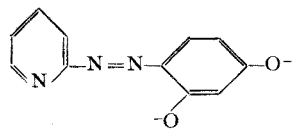
A



B=I



C



D

The dominant form is the mono-ionic species C, which has λ_{max} 415 mμ, with a molar extinction coefficient $\varepsilon = 25{,}900$, in all solutions in the pH range 5.98–12.50. The protonated form A has λ_{max} 395 mμ at pH values of 1.32, 1.72 and 2.44 ($\varepsilon = 15{,}500$). The free base form B has λ_{max} 383 mμ ($\varepsilon = 15{,}700$) at pH 3.60, whilst form D has λ_{max} 485 mμ, ($\varepsilon = 17{,}300$) at all pH values above 12.58. Confirmation that the reagent was in fact in these chromophoric forms was obtained by potentiometric titration, from which the average number of hydrogen ions bound per ligand could be calculated.

The first hydroxyl ionisation causes a shift in peak wavelength of 32 mμ, whilst the second results in a shift of 70 mμ. This seems to confirm the view of SNAVELY[2] that in azo-resorcinol dyestuffs the *p*-hydroxyl group ionises first. The ionisation of this hydroxyl group would be expected to produce less disruption of the chromophoric arrangement than would that of the *o*-hydroxyl group, for the latter would require rupture of the hydrogen-bonded ring formed by the *o*-hydroxyl group and the azo-nitrogen nearest the heterocycle.

By use of the graphical method of SCHWARZENBACH *et al.*[3], the dissociation constants were found to be as follows:

$$pK_{NH}\,(\log {}^{C}K_{3}^{H}) = 2.66 \pm 0.06;\ pK_{OH}^{1}\,(\log {}^{C}K_{2}^{H}) = 5.48 \pm 0.03;\ pK_{OH}^{2}\,(\log {}^{C}K_{1}^{H}) = 12.31 \pm 0.03.$$

Use was made of these values in computation of the stability constants of the metal complexes (see Part II[4]).

The complexes of 4-(2-pyridylazo)-resorcinol with cobalt(II), lead(II), and uranium-(VI) have been shown previously[1] to have peak wavelengths at 510 mμ, 520 mμ, and 530 mμ respectively. The spectra of the complexes with copper(II) and nickel(II) have now been determined. The copper(II) complex has peak wavelength at 505 mμ, the optical density at this wavelength increasing steadily with pH over the range 4.8–10.0. The band is relatively narrow, there being minimal absorption at wavelengths greater than 580 mμ. The nickel(II) complex has a rather different spectrum. Up to pH 6.0 absorption is relatively small, and is spread almost evenly in a broad band over the range 550–750 mμ. Above pH 6.0 absorption in the region 450–550 mμ

rises very rapidly until pH 8.0, when it begins to fall again. Thus at a wavelength of 475 mμ optical density is 0 at pH 4.8, 0.200 at pH 6.0, 0.810 at pH 7.0, 2.00 at pH 8.0, and 1.80 at pH 9.0. The actual peak is at 490 mμ and pH 8.0. There are interesting correlations of this behaviour with the results obtained potentiometrically for the nickel(II) complex (see Part II of this series[4]).

The formulae of the complexes were determined at these peak wavelengths by the continuous variations method of JOB[5]. In two separate determinations at pH 8, the plot for the cobalt(II) complex showed a sharp break at a ratio of 3.0 : 1 for ligand : cobalt(II). Similar determinations for copper(II) at pH 10.0 gave a ratio of 2.00 : 1, for nickel(II) at pH 8.0 gave 3 : 1, for lead(II) pH 10.0 gave 1.95 : 1, and for uranium-(VI) at pH 8 gave 2.0 : 1. By potentiometric titration it was shown that complexes containing a ratio greater than 2 : 1 were not formed; it therefore seems that the high mole ratio determined spectrophotometrically derives from an excess of ligand being required for the complete colorimetric reaction, possibly by co-ordination through the pyridine nitrogen of the heterocyclic ring which would invoke no corresponding release of hydrogen ions as would co-ordination through the hydroxyl groups. Such behaviour has been noted before: thus, for the reaction between copper(II) and bis-cyclohexanone-oxalyl-dihydrazone, PETERSON AND BOLLIER[6] found a mole-ratio of 8 : 1. The value of 2 : 1 for the lead(II) complex does not agree with that found by KRISTIANSEN *et al.*[7], who obtained a maximum at a 1 : 1 ratio. However, a 2 : 1 ratio has been confirmed by potentiometric titration, and also by other work in our laboratories. The 2 : 1 ratio for the uranium(VI) complex is in accordance with the value found by CHENG[8] and GILL *et al.*[9], for the very similar compound 1-(2-pyridylazo)-2-naphthol.

MEASUREMENTS IN 50 : 50 DIOXAN/WATER

(*a*) *Visible spectra of parent ligands*

Except with benzeneazoresorcinol (IV), all measurements were made at an ionic strength (μ) of 0.1; precipitation of (IV) occurred if μ was raised greatly above zero. The pH meter used was calibrated for 1 : 1 dioxan/water mixtures at $\mu = 0.1$, and the measured values of pH were very nearly correct, (see Part II[4]).

The visible spectra of 4-(2-pyridylazo)-resorcinol were determined at thirteen values of pH from 1.0 to 13.0, and the chromophoric species were identified as follows:

Protonated form (A):	420 mμ; ε = 14,750; pH 1.06, 1.52
Free base form (B):	392 mμ; ε = 15,240; pH 3.19, 4.35, 5.56
Mono-ionic form (C):	414 mμ; ε = 23,100; pH 7.56–13.56
Di-ionic form (D):	502 mμ, ε = 17,800; pH 12.96, 13.56.

The values of ε are of the same order as for aqueous solution, and the mono-ionic species (C) is again the dominant form. Further, the shift in λ_{max} for the first hydroxyl ionisation (22 mμ) is again much less than that for the second (88 mμ). Apart from the two extreme forms, the ligand absorbs at almost the same peak wavelengths in aqueous and mixed solvents.

Values for the dissociation constants were again determined graphically[3] as follows:

pK_{NH} (log ${}^{C}K_{3}^{H}$) = 2.35 ± 0.05, pK_{OH}^{1} (log ${}^{C}K_{2}^{H}$) = 7.01 ± 0.05, pK_{OH}^{2} (log ${}^{C}K_{1}^{H}$) = 13.00 ± 0.05.

The depression of pK_{NH} values, and the elevation of pK_{OH} values on the change

from water to dioxan/water has been observed by IRVING AND ROSSOTTI[10] for 8-hydroxyquinoline and derivatives.

The visible spectrum of benzeneazoresorcinol (IV) was determined at ten values of pH between 3.51 and 13.90 ($\mu \rightarrow 0$), and the peaks observed were assigned as follows:

Free base form IVB, 385 mμ: ε = 19,900; pH 3.51–7.58
Mono-ionic form IVC, 432 mμ: ε = 35,500; pH 8.68–12.63
Di-ionic form IVD, 440 mμ: ε = 34,000; pH 13.42; 13.90

The visible spectra of ligands (I) and (IV) are seen to have little in common. The shift in λ_{max} for the first ionisation (47 mμ) is much greater in (IV) than in the pyridine analogue (I) (22 mμ), but for the second ionisation it is very much less (8 mμ, 88 mμ). This would seem to indicate a much smaller degree of hydrogen-bonding in the benzene compound. With both compounds the mono-ionic species has the greatest value of ε. pK values were determined[3] as follows:

$$pK^{1}_{OH}\ (\log {}^{C}K_{2}{}^{H}) = 8.30 \pm 0.03,\ pK^{2}_{OH}\ (\log {}^{C}K_{1}{}^{H}) = 13.60 \pm 0.10$$

These values are both more alkaline than those of 4-(2-pyridylazo)-resorcinol.

The measurement of the visible spectrum of salicylidene-2-amino-pyridine (II) was rendered difficult by instability of absorbance with time, the readings decreasing to less than half the initial value over a period of 2 h. Thus, at λ = 385 mμ, and pH = 9.60 the results given in Table I were obtained:

TABLE I

DECREASE IN OPTICAL DENSITY WITH TIME OF SALICYLIDENE-2-AMINOPYRIDINE IN 1 : 1 DIOXAN/WATER AT pH = 9.60 AND λ = 385 mμ

t (min)	*O. D.*
0	.409
5	.385
10	.369
15	.353
20	.340
25	.327
30	.314
35	.304
40	.293
45	.283
60	.257
76	.233
101	.199
120	.176

Only the ionised form (IID) was found to have a measurable visible spectrum, the pH of the five solutions measured ranging from 7.52 to 12.34. Solutions were allowed to stand for 4 h before measurement; by this time the optical density was constant. The peak wavelength of the ionised form was found to be 380 mμ, the approximate value of ε being 3125. This is very much less than for either of the azo dyestuffs, and is a good indication of the strength of the —N : N— chromophore. No calculation of pK_{OH} was attempted from these data since the decrease in optical density with time placed quantitative measurements in doubt. A preliminary investigation of the ultra-

violet spectrum at pH 7.07 showed that the free base form had a broad peak at 300 mμ; thus the shift in λ_{max} for the *o*-hydroxyl ionisation is approximately 80 mμ, which compares with 88 mμ for 4-(2-pyridylazo)-resorcinol.

The instability of optical density with time also caused difficulty in the measurement of the visible spectrum of 2-(*o*-hydroxyphenyl-imino-methyl)-pyridine. Thus, after a period of 2.5 h the optical density at $\lambda = 380$ mμ and pH 9.6 had increased from 0.173 to 0.678. Measurements were taken at 10 increments of pH between 1.30 and 13.06, solutions being allowed to stand for 4 h before the spectrum was determined. The range of concentrations of ligand required to obtain readable optical density values varied considerably. In the most acid solutions (pH 1.30, 2.48) and in the alkaline range (pH 6.39–13.56), the final molarity was $1.992 \cdot 10^{-4}$. At pH 3.76 it was $0.996 \cdot 10^{-4}$ *M*, and at pH 4.88 it was $0.498 \cdot 10^{-4}$ *M*. Peaks could only be observed in the visible region in five of the solutions studied. These are listed in Table II.

TABLE II

PEAK WAVELENGTHS IN THE SPECTRA OF LIGAND(III) IN THE RANGE 320–500 mμ

pH	*max(mμ)*	ε
1.30	430	873
2.48	410	1657
4.88	350	14060
4.88	420	7330
6.39	440	703
7.66	440	2068

There were no peaks in this wavelength region at pH 3.76, 10.66, 11.39 and 13.06. The observed peaks could not be assigned to a particular chromophoric species with any certainty; by potentiometric titration it was shown that two protons were added per molecule of ligand, the pK_{NH} values being 4.45 and 3.05, and this undoubtedly accounts for some of the observed shifts in maximum wavelengths and in molar absorbance.

(*b*) *Visible spectra of metal complexes*

The visible spectra of the complexes of 4-(2-pyridylazo)-resorcinol with copper(II), nickel(II), cobalt(II), lead(II) and uranium(VI) were determined at values of pH ranging from 3.50 to 10.60 and the peak wavelengths were found as follows:

Copper(II): 510 mμ: all values of pH between 3.50 and 10.90
Nickel(II): 500 mμ: pH $\geqslant$ 9.71
Cobalt(II): 510 mμ: pH $\geqslant$ 8.28
Lead(II): 515 mμ: (very weak even at pH 9.88)
Uranium(VI): 490 mμ: pH $\geqslant$ 9.81

These results show that except for uranium(VI) there is no significant shift in the λ_{max} of the complexes on change from water to mixed solvent. The shift with uranium(VI) is 30 mμ to a lower wavelength.

With benzeneazoresorcinol, the metal complexes absorbed at an almost identical peak wavelength as the ligand itself. Thus at pH 6.35, where potentiometric titration indicated that the 2 : 1 complex was fully formed, the copper(II) complex had a peak at 380 mμ compared with 385 mμ for the ligand. The role of the pyridine nitrogen of

4-(2-pyridylazo)-resorcinol in the colorimetric reaction with metal ions is immediately apparent from these results. There is no significant shift in λ_{max} on chelation by the benzene analogue, a fact which can only be attributed to the removal of the heterocyclic nitrogen in the *o*-position.

Because of the difficulty of obtaining a satisfactory estimate of the visible spectra of the imines (II) and (III), a rather less detailed examination of the spectra of their metal complexes was carried out.

With salicylidene-2-aminopyridine (II), only the copper(II) complex was studied; it was found that the complex had a peak wavelength of 395 mμ at pH values of, or above, 8.50. This represents a shift of 15 mμ from the peak wavelength of the ligand at this pH. This is considerably less than the shift of 100 mμ for the copper complex of 4-(2-pyridylazo)-resorcinol, yet the co-ordinating system is the same as in (I) except that the azo nitrogen nearest the heterocycle is replaced by a —CH= group. It is apparent, therefore, that the removal of this nitrogen has a profound effect on the colour reaction with metal ions, and it seems clear that in 4-(2-pyridylazo)-resorcinol the azo nitrogen farthest from the heterocycle must play a greater part in the chromophoric reaction than its neighbour.

This was conclusively shown by the visible spectra of the metal complexes of 2-(*o*-hydroxy-phenyl-imino-methyl)-pyridine, (III). This ligand gave highly sensitive red-coloured complexes very similar to those with (I). Thus the main peak of the ligand at 350 mμ at pH 4.88 was shifted to 453 mμ at this pH with copper(II), to 457 mμ with nickel(II), to 450 mμ with cobalt(II), and to 445 mμ with uranium(VI). The sensitivity of the reaction was in the order: copper(II) > uranium(VI) > nickel(II) > cobalt(II). Solutions with lead were turbid. The only difference from 4-(2-pyridylazo)-resorcinol is that, except for copper(II), the colour reaction is not instantaneous, requiring 15 min for full colour development. There seems no doubt, however, that these results demonstrate that in (I) the chromophoric reaction is due to coordination by the pyridine nitrogen, the azo nitrogen farthest from the heterocycle, and the *o*-hydroxyl group. The extreme sensitivity of the colour reaction of this ligand with metal ions is therefore explained by the combination of a *pseudo*-phenanthroline system and an *o-o'*-disubstituted azo dyestuff.

It follows from this that the roles of the azo nitrogens in chelation of metal ions are by no means equal, and that bonds of the type $\underset{\downarrow}{\overbrace{\text{—N : N—}}}$ often found in the literature are misleading. This view was confirmed by determination of the stability constants of the metal complexes of these four ligands (see Part II[4]).

EXPERIMENTAL

Preparation of ligands

The disodium salt of 4-(2-pyridylazo)-resorcinol was prepared as previously described[1]. The free base form was also isolated and characterized. To a saturated solution of the disodium salt in water, dilute hydrochloric acid (0.5 *M*) was added slowly, with good stirring. The precipitated free base form of (I) was filtered, washed well with water, recrystallised from methanol, and dried in a vacuum desiccator. It was an amorphous orange-brown solid, m.p. 182° (Found: C, 61.5; H, 4.1; N, 19.7: $C_{11}H_9N_3O_2$ requires C, 61.4; H, 4.2; N, 19.5%).

Salicylidene-2-aminopyridine was prepared by a Schiff condensation of 2-amino-

pyridine and salicylaldehyde in boiling ethanol. It formed bright yellow plates, m.p. 67.5° (Literature values[11–13], 65°, 66°–67°, 69°) (Found: C, 72.4; H, 5.1; N, 14.1. Calc. for $C_{12}H_{10}N_2O$: C, 72.7; H, 5.1; N, 14.1%).

2-(*o*-Hydroxy-phenyl-imino-methyl)-pyridine was prepared by a similar condensation of pyridine-2-aldehyde with *o*-aminophenol, the latter having been purified by sublimation and the aldehyde by distillation. *o*-Aminophenol (8.7 g) was dissolved in the minimum of ethanol and pyridine-2-aldehyde (9.0 g, 9.0 ml) was added with good stirring. On evaporation of excess of ethanol, a dark-brown resinous mass was obtained. Extraction of this with ether afforded a bright yellow solution, from which was deposited a crop of yellow-orange needle-like crystals, m.p. 107.5° (Found: C, 72.7; H, 5.2; N, 14.2%) [It should be noted that this compound has been used before by MUTO[14] but no details of preparation or melting point were given.]

Materials

All the reagents used in preparation of CLARK AND LUBS buffer solutions[15] were AnalaR grade. Carbonate-free sodium hydroxide was prepared by the method of DAVIES AND NANCOLLAS[16]. Sodium perchlorate, used for maintaining constant ionic strength, was a technical grade product recrystallised thrice from small quantities of water.

All solutions of metal salts were prepared from AnalaR sulphates, except for lead(II) for which AnalaR lead nitrate was used.

Dioxan was AnalaR grade.

Preparation of solutions

The extremely high sensitivity of 4-(2-pyridylazo)-resorcinol necessitated the use of very dilute solutions of metal ions. At the dilutions employed (μg/ml level) adsorption of ions on glass vessels was appreciable, and such dilute solutions could not be stored without deterioration. The final optical solutions were therefore prepared either from freshly prepared solutions, or, in the case of lead, from a more concentrated solution, volumes of which were delivered from an "Agla" micrometer syringe.

Measurement of pH

pH values were measured with a "Cambridge" bench-type pH-meter fitted with a dip-type calomel electrode and a "Cambridge" yellow-cap glass electrode.

Measurement of visible spectra

All measurements were made using a "Unicam" SP. 500 spectrophotometer, fitted with 1 cm silica cells. Ligand solutions were measured against blank solutions containing all components except the ligand, and solutions of the complexes against blank solutions containing all components except the metal ion.

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SUMMARY

The visible spectra of the highly sensitive colorimetric reagent 4-(2-pyridylazo)-resorcinol (I), and of the coloured complexes formed with copper(II), nickel(II), cobalt(II), lead(II), and uranium(VI) were obtained in water and in aqueous dioxan. The structures of these complexes were determined by spectrophotometric methods, and chelation by (I) established as essentially terdentate. Comparison is made with the visible spectra of salicylidene-2-aminopyridine (II), 2-(*o*-hydroxyphenyl-imino-methyl)-pyridine (III), and benzeneazoresorcinol (IV), and of the metal complexes of (II), (III), and (IV). The red coloration obtained with 4-(2-pyridylazo)-resorcinol is explained by the presence of a pseudo-phenanthroline system and an *o-o'*-disubstituted azo system, the active groups in chelation being the pyridine nitrogen atom, the azo nitrogen farthest from the heterocycle, and the *o*-hydroxyl group.

RÉSUMÉ

Les spectres dans le visible du 4-(2-pyridylazo)-résorcinol et de ses complexes avec le cuivre, le nickel, le cobalt, le plomb et l'uranium ont été effectués. La structure de ces complexes a ainsi pu être déterminée. Une comparaison a été faite avec d'autres composés: salicylidène-2-aminopyridine, 2-(*o*-hydroxy-phényl-imino-méthyl)-pyridine et le benzèneazorésorcinol.

ZUSAMMENFASSUNG

Die Spektren im sichtbaren Gebiet von 4-(2-pyridylazo)-resorcin, sowie dessen Komplexe mit Kupfer-II, Nickel-I, Kobalt-II, Blei-II und Uran-VI wurden aufgenommen und die Struktur der Komplexe durch spektrophotometrische Methoden bestimmt. Sie werden verglichen mit den Spektren von Salicyliden-2-amino-pyridin, 2-(*o*-hydroxy-phenyl-imino-methyl)-pyridin und Benz-azo-resorcin und deren Komplexe mit den erwähnten Metallen.

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CHLORPROMAZINE HYDROCHLORIDE AS AN ANALYTICAL REAGENT

PART III. A NEW INDICATOR FOR TITRATIONS WITH VERY DILUTE CERIC SULPHATE SOLUTIONS

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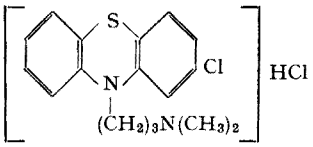
Ceric sulphate has long been recognised as a convenient reagent for the volumetric determination of iron(II) and arsenic(III). Ferroin and N-phenylanthranilic acid are the two most commonly used indicators for such titrations. Other indicators that have been recommended are substituted phenanthrolines[1,2], amino derivatives of diphenylamine[3], methylene blue[4], triphenylmethane dyes[5], 2,2'-dipyridyl[6], ruthenium 2,2'-dipyridyl[7] and Rhodamine 6G[8]. More recently the use of crystal violet[9] and copper phthalocyanine 4,4',4'',4'''-tetrasulphonic acid[10] has been proposed but these are not likely to supplant ferroin.

However, the titration of μg quantities of reducing substances with very dilute ceric sulphate solutions has been severely limited by the lack of an indicator with a small or no blank correction. With 0.1 *N* ceric sulphate, 0.02 ml is generally deducted from the titre for one drop of the ferroin indicator used; similar corrections are made for 1 ml of the dipyridyl ferrous perchlorate indicator and for 0.5 ml of the triphenylmethane indicators[11].

ELLIS[12], KIRK AND TOMPKINS[13], and SALOMAN *et al.*[14] have recommended the use of ammonium hexanitratocerate in perchloric acid for μg titrations, and nitroferroin as the suitable indicator .The blank correction for a 0.00025 *M* nitroferroin indicator was claimed to be about 0.1 ml of 0.001 *N* ceric sulphate solution[14], but the application of ammonium hexanitratocerate as a titrant is limited by its relative instability[15]. KIRK has suggested an ultramicro technique for the determination of small quantities of iron(II) using 0.01 *N* ceric sulphate and ferroin indicator[16]. This method is, however, fraught with technical difficulties and the indicator correction required is of the same order as the volume of titrant consumed in a determination.

Recently KOLTHOFF AND BHATIA[17] have reported an amperometric titration of very dilute iron(II) solutions in which ceric sulphate is used as titrant. The accuracy and precision of the method are good but special equipment is required, which makes the method unattractive for occasional use.

Chlorpromazine hydrochloride, whose structure is shown below,



is a commonly used tranquilizer. Its oxidation product has an intensely red colour and is stable in acid media. From kinetic studies CAVANAUGH[18] has concluded that the red coloured product is a precursor of the sulphoxide. From a study of its electronic spin, FORREST *et al.*[19] have suggested it to be a free radical and from titrimetric evidence, DUŠINSKY AND LIŠKOVA[20] have proposed a semiquinonoidal structure for the free radical.

Because of the ease with which chlorpromazine hydrochloride is oxidised to the red coloured product we have used this reagent for the detection of certain inorganic ions[21] and for the determination of μg quantities of gold[22]. The present paper describes its use as an indicator for titration with very dilute ceric sulphate solutions in the determination of iron(II), arsenic(III), ascorbic acid and hydroquinone, and for the colorimetric determination of cerium(IV) and arsenic(III).

EXPERIMENTAL

0.1 N Ceric sulphate

This stock solution was prepared according to VOGEL[23]. More dilute solutions were prepared by dilution with 2 *N* sulphuric acid.

Standardisation of 0.001 N and 0.0005 N ceric sulphate solution with ferrous ammonium sulphate

About 2–3 mg of A.R. ferrous ammonium sulphate (Merck) were weighed accurately into a 25-ml conical flask and dissolved in 3–4 ml of 2 *N* sulphuric acid; 1 ml of 20% phosphoric acid was added, followed by one drop of 1% aqueous chlorpromazine hydrochloride solution and one drop of 0.01% aqueous methylene blue solution. This was then titrated with the ceric solution until the colour changed from pale blue to violet. The end-point was taken when the violet colour was permanent for not less than 1 min. A blank titration was carried out with the same amounts of indicators. This value was found to be 0.08 to 0.10 ml of 0.001 *N* ceric solution. Iron(II) did not appear to have any catalytic effect on the oxidation of the indicator.

Titrimetric determination of iron(II), ascorbic acid and hydroquinone

The standard procedure was as follows. The solution containing a known amount of solute is run into a 25-ml conical flask; 1 ml of 20% phosphoric acid and 2 ml of 2 *N* sulphuric acid are added, followed by one drop of 1% chlorpromazine hydrochloride solution and one drop of 0.01% methylene blue solution. This is titrated with 0.001 *N* or 0.0005 *N* ceric sulphate until the appearance of a violet colour which indicates the end-point. 1 ml of 0.0005 *N* ceric sulphate is equivalent to 44 μg ascorbic acid, 28 μg iron or 27.5 μg hydroquinone. Results are given in Tables I, II and III.

TABLE I

TITRATION OF FERROUS AMMONIUM SULPHATE

Titrant added[a] (ml)	Iron (II)		Difference (μg)
	Found (μg)	Added (μg)	
0.350*	9.8	10.7	—0.9
0.800*	22.4	21.5	+0.9
1.550*	43.4	43.0	+0.4
3.000*	84.0	86.0	—2.0
4.550*	127.4	129.0	—1.6
7.750*	217.0	215.0	+2.0
0.495	27.7	27.9	—0.2
0.995	55.7	55.9	—0.2
1.250	70.0	69.9	+0.1
2.150	120.4	119.6	+0.8
2.590	145.0	144.3	+0.7
2.990	167.4	167.8	—0.4
4.135	231.6	231.1	+0.5
7.675	429.8	431.7	—1.9
9.780	547.7	547.3	+0.4
11.250	630.0	629.0	+1.0

[a] Titrations were carried out with 0.001 *N* ceric sulphate solution, except those marked with * which were done with 0.0005 *N* ceric solutions.

TABLE II

TITRATION OF ASCORBIC ACID WITH 0.001 *N* CERIC SULPHATE SOLUTION

Titrant added (ml)	Ascorbic acid		Difference (μg)
	Found (μg)	Added (μg)	
0.500	44.0	45.0	—1.0
0.755	66.4	66.7	—0.3
1.135	99.9	100.1	—0.2
2.520	221.8	222.2	—0.4
3.415	300.5	300.1	+0.4
5.040	443.5	444.4	—0.9

TABLE III

TITRATION OF HYDROQUINONE WITH 0.001 *N* CERIC SULPHATE SOLUTION

Titrant added (ml)	Hydroquinone		Difference (μg)
	Found (μg)	Added (μg)	
0.425	23.4	23.4	—
0.895	49.2	49.4	—0.2
1.410	77.6	78.1	—0.5
2.965	163.1	164.6	—1.5
5.690	313.0	312.7	+0.3
5.985	329.2	329.2	—

Titrimetric determination of arsenic (III)

A standard arsenious oxide solution was prepared by dissolving a convenient quantity in 1 *N* sodium hydroxide, acidifying with 2 *N* sulphuric acid and diluting to volume.

The solution to be titrated and containing about 10–100 μg of arsenious oxide is run into a 50-ml conical flask. To this is added 1 ml of potassium iodide solution (3 μg of KI per ml), 1 ml of 20% phosphoric acid and 5.0 ml of 0.001 *N* ceric sulphate solution. After 30 min, 5.0 ml of 0.001 *N* ferrous solution are added. The excess ferrous solution is then titrated with 0.001 *N* ceric solution using one drop of 1% aqueous chlorpromazine hydrochloride solution and one drop of 0.01% methylene blue as indicator. 1 ml 0.001 *N* ceric sulphate solution is equivalent to 37.5 μg As(III). Table IV shows the accuracy of this method.

TABLE IV

TITRATION OF ARSENIC(III) WITH 0.001 *N* CERIC SULPHATE SOLUTION

Titrant added (ml)	*As(III)*		*Difference (µg)*
	Found (µg)	*Added (µg)*	
0.467	17.5	17.2	+0.3
0.939	35.2	34.5	+0.7
1.400	52.5	51.7	+0.8
1.850	69.4	69.0	+0.4
2.295	86.1	86.2	—0.1
2.740	102.8	103.5	—0.7
3.165	118.7	120.8	—2.1
3.965	148.7	151.2	—2.5

Colorimetric determination of cerium(IV)

Reagents: (1) 0.0001 *N* ceric sulphate solution was prepared by dilution of standard 0.001 *N* solution with *N* sulphuric acid. (2) Aqueous chlorpromazine hydrochloride solution, 50 mg/ml.

Procedure. Different volumes of standard ceric sulphate solution are measured into 25-ml volumetric flasks followed by 10 ml of 50% phosphoric acid (v/v) and 3 ml of chlorpromazine hydrochloride solution. The solutions are diluted to volume with water, thus making the phosphoric acid concentration 20% and the chlorpromazine hydrochloride concentration 6 mg per ml. After 30 min the absorbances of these solutions at 530 mμ are measured with a Hilger spectrophotometer and cells of 1 cm light path. The calibration curve for concentrations of 1 to 20 μg ceric ions per ml of the final solution is linear, showing that Beer's law is obeyed for these concentrations. The following ions, Fe(III), Ag, Cu, Hg, UO_2^{+2}, Ca, Ba, K, Na and Mg do not interfere. The phosphoric acid forms a complex with iron(III), thus preventing the latter from oxidizing the reagent. This method is useful for the determination of μg quantities of ceric ions.

Colorimetric determination of arsenic (III)

The reagents used were the same as those described for the determination of cerium.

Procedure. Aliquots of 1, 2, 3, 4 and 5 ml of a standard arsenious oxide solution are pipetted into five 25-ml volumetric flasks. A sixth flask is used for a simultaneous blank determination. One ml of potassium iodide solution (3 μg KI per ml), 10 ml of 50% phosphoric acid and 3 ml of 0.001 *N* ceric sulphate solution are then added successively to each flask. After 30 min 3 ml of chlorpromazine hydrochloride solution

are added and the solutions are diluted to the mark with distilled water. The solutions are shaken thoroughly and after a further 30 min, their absorbances at 530 mμ are measured against distilled water. The amounts of arsenious oxide present are directly proportional to the difference in the reading between the blank and the sample as shown in Table V.

TABLE V

CALIBRATION READINGS FOR THE COLORIMETRIC DETERMINATION OF ARSENIC(III)

Amounts of As_2O_3 (μg)	*Reduction in optical density at 530 mμ*	
20	0.142	0.153
40	0.288	0.270
60	0.430	0.440
80	0.568	0.575
100	0.690	0.710
120	0.822	0.831

DISCUSSION

Titrimetric determination of iron(II), arsenic(III), ascorbic acid and hydroquinone

Chlorpromazine hydrochloride alone may be used as indicator for the above titrations without the addition of methylene blue; but the end-point is not so sharp, particularly when the final volume exceeds 10 ml. The indicator cannot be used for the reverse titration of ceric sulphate with iron(II) or ascorbic acid solutions.

In the titration of iron(II), phosphoric acid is added to form a complex with the iron(III) formed which would otherwise oxidise the indicator. Iron(II) can be titrated in the presence of arsenic(III) when this indicator is used. In the titration of arsenic(III), the amount of potassium iodide should not exceed the recommended concentration, because larger amounts interfere and the determination becomes complicated by blank corrections.

The oxidation potential of chlorpromazine hydrochloride is 0.70 V. This would suggest that the reagent could also be used as an indicator for titration with potassium dichromate. However, preliminary experiments have shown that although satisfactory colour changes could be observed during the titration, the results obtained for both iron and ascorbic acid were erratic.

This indicator cannot be used in titrations with ceric sulphate solutions stronger than 0.01 *N*. The end-point is difficult to detect because the coloured free radical of chlorpromazine is easily converted to the colourless sulphoxide compound by excess of ceric sulphate solution.

Colorimetric determination of cerium(IV) and arsenic(III)

Ceric ions oxidise chlorpromazine to a red coloured product which can be used for the colorimetric determination of cerium. The optimum concentration in the final solution with regard to phosphoric acid and chlorpromazine hydrochloride are 20% and 6 mg per ml respectively. The reagent has been used for the colorimetric determination of μg quantities of gold[22] and the effects of acid, reagent concentration and the stability of the colour have been studied in detail. Beer's law is found to be obeyed for solutions containing 1 to 20 μg of cerium per ml.

The proposed method for the colorimetric determination of arsenic(III) is an indirect one. The arsenic(III) is oxidised by a fixed amount of standard ceric sulphate solution the excess of which is then determined colorimetrically. In the absence of other reducing substances the reduction of the colour of the fixed amount of ceric sulphate solution is directly proportional to the quantities of arsenic(III) present. This method could be used for the colorimetric determination of microquantities of other reducing substances.

ACKNOWLEDGEMENT

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SUMMARY

Chlorpromazine hydrochloride is proposed as an indicator for the microtitration of iron(II), arsenic(III), ascorbic acid and hydroquinone with 0.0005–0.001 *N* ceric sulphate; the indicator blanks are small. The colorimetric determinations of μg quantities of cerium(IV) and arsenic(III) using the same reagent are also described.

RÉSUMÉ

Le chlorhydrate de chloropromazine est proposé comme indicateur pour le microsodage du fer(II), de l'arsenic(III), de l'acide ascorbique et de l'hydroquinone, par titrage au moyen de sulfate cérique 0.0005–0.001 *N*. Ce réactif peut également être utilisé pour le dosage colorimétrique de microquantités de cérium(IV) et d'arsenic(III).

ZUSAMMENFASSUNG

Zur Mikrotitration von Eisen-(II), Arsen-(III), Ascorbinsäure und Hydrochinon mit 0.0005–0.001 *N* Cer-(IV)-sulfatlösung wird Chloropromazinhydrochlorid als Indikator empfohlen. Der Indikator kann auch zur colorimetrischen Bestimmung von Cer-(IV) und Arsen-(III) verwendet werden.

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STUDIES ON ADSORPTION INDICATORS

PART I. TITRATION OF IODIDE IN PRESENCE OF CHLORIDE. MECHANISM OF THE COLOUR CHANGES DURING ARGENTOMETRIC TITRATIONS WITH CONGO RED AS ADSORPTION INDICATOR

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MEHROTRA[1] has described the use of congo red as an adsorption indicator in argentometric titrations. The colour changes from blue to red on the coagulated precipitate at the end-point in the titration of halides and thiocyanate with silver ions when the pH is maintained at 3–5. The reverse colour change occurs on titration of silver solution.

In the present studies, it has been observed that the titration of the iodide with silver ion is possible even at pH 5–5.5, whereas in this pH range chloride cannot be titrated. This furnishes a method for the titration of iodide in presence of chloride.

The colour change from blue to red at the end-point of the titration of halide with silver ion, cannot be explained[2] by a change in the acidity of the suspension because it takes place even at a constant pH value of 4. If the silver nitrate solution affects the pH of the suspension at all, it would tend to make an unbuffered suspension slightly more acidic owing to hydrolysis, and hence any colour change caused by pH alone should turn the indicator blue rather than red. But the colour change on the surface of the precipitate is the opposite of what would be expected from the acidity of the solution.

A similar behaviour has been reported by SCHULEK AND PUNGOR[3], when silver is titrated with iodide in presence of *p*-ethoxychrysoidine as adsorption indicator. During the titration, the initial red colour of the solution becomes yellow, and at the end-point, the colour changes to intense raspberry red. This colour change cannot be explained by existing theories of adsorption indicators. SCHULEK AND PUNGOR[4] titrated iodide with silver solution and *vice versa* in dilute solutions and recorded the changes in pH values. With an increase or decrease of pH in the solution an opposite colour change occurred on the precipitate, which indicates that the precipitate gains or loses protons during the process.

Congo red contains both acidic groups (—SO_3H) and basic amino groups and shows a colour change from blue to red in the pH range 3–5. Thus, in presence of acid it gives blue cations, and in alkaline solution red anions are produced. At the end-point of the titration of halide with silver ion, the dye cations become anions owing to the reversal of the sign of the charge on the surface of the precipitate. In the reverse titrations, dye cations are formed. Accordingly, it was expected that at the end-point of the titra-

tion a sudden change of pH would occur. Hence, the experiments of SCHULEK AND PUNGOR were repeated with congo red as adsorption indicator. The results of these experiments are given in Tables I, II and III. In all cases 10 drops of an aqueous 0.2% congo red solution were used. It can be seen that the pH change at the end-point is largest in the iodide titration and smallest in the chloride titration.

TABLE I

pH CHANGES IN TITRATION OF 0.001 *M* KI WITH 0.01 *M* $AgNO_3$

Vol. of 0.001 M KI(ml)	*0.01 M $AgNO_3$ % equivalent*	*pH changes*			
		I	*II*	*III*	*IV*
50	0	4.60	4.36	5.34	5.44
50	20	4.66	4.42	5.43	5.53
50	40	4.78	4.49	5.54	5.64
50	60	4.84	4.56	5.62	5.78
50	80	4.96	4.60	5.69	5.82
50	90	4.98	4.62	5.72	5.85
50	95	4.98	4.62	5.72	5.86
50	100	4.74	4.46	5.54	5.64
50	105	4.73	4.46	5.54	5.63
50	110	4.73	4.46	5.54	5.63
50	120	4.73	4.46	5.54	5.63
50	140	4.73	4.46	5.54	5.63
50	160	4.73	4.46	5.54	5.63

TABLE II

pH CHANGES IN TITRATION OF 0.001 *M* KBr OR KSCN WITH 0.01 *M* $AgNO_3$

Vol. of 0.001 M soln. (ml)	*0.01 M $AgNO_3$ % equivalent*	*pH changes*			
		KBr		*KSCN*	
		I	*II*	*I*	*II*
50	0	4.61	4.34	4.60	4.35
50	20	4.66	4.38	4.64	4.38
50	40	4.75	4.43	4.72	4.42
50	60	4.80	4.48	4.78	4.46
50	80	4.86	4.53	4.83	4.51
50	90	4.88	4.55	4.85	4.54
50	95	4.89	4.55	4.85	4.54
50	100	4.75	4.45	4.76	4.47
50	105	4.74	4.45	4.76	4.47
50	110	4.74	4.45	4.76	4.47
50	120	4.74	4.45	4.78	4.47
50	140	4.77	4.45	4.79	4.48
50	160	4.78	4.45	4.82	4.48

It is interesting to observe that the pH change at the end-point occurs in the iodide titration even when the titration is started at a pH of more than 5 (Table I) whereas no pH change is observed in the titration of chloride under similar conditions (Table III). Furthermore, when a mixture of iodide and chloride is titrated at pH 5–5.5, the

pH change occurs just after the addition of an amount of silver nitrate equivalent to the iodide (Table IV).

Congo red is very strongly adsorbed on the silver halide precipitate. At pH 3–5, in presence of excess silver nitrate, the colour of the precipitate is red; it changes to blue on the addition of excess halide. The dye remains adsorbed on the surface of the

TABLE III

pH CHANGES IN TITRATION OF 0.001 *M* KCl WITH 0.01 *M* $AgNO_3$

Vol. of 0.001 M KCl (ml)	*0.01 M $AgNO_3$ % equivalent*	*pH changes*			
		I	*II*	*III*	*IV*
50	0	4.62	4.36	5.36	5.42
50	20	4.66	4.38	5.36	5.43
50	40	4.71	4.41	5.36	5.44
50	60	4.76	4.45	5.39	5.44
50	80	4.79	4.47	5.39	5.46
50	90	4.80	4.48	5.39	5.46
50	95	4.80	4.48	5.41	5.46
50	100	4.75	4.44	5.41	5.47
50	105	4.75	4.44	5.41	5.48
50	110	4.75	4.44	5.41	5.49
50	120	4.75	4.44	5.41	5.49
50	140	4.76	4.44	5.41	5.49
50	160	4.78	4.42	5.41	5.49

TABLE IV

pH CHANGES IN TITRATION OF A MIXTURE OF HALIDES WITH 0.01 *M* $AgNO_3$

Vol. and conc. of halide mixture	*0.01 M $AgNO_3$ % iodide-equivalent*	*pH changes*	
		I	*II*
	0	5.42	5.36
	20	5.48	5.43
	40	5.56	5.50
	60	5.66	5.56
	80	5.72	5.62
5 ml of 0.01 *M* KI + 5 ml of 0.01 *M* KCl diluted to 100 ml	90	5.77	5.64
	95	5.78	5.66
	100	5.78	5.66
	101	5.68	5.58
	105	5.68	5.58
	110	5.68	5.58
	120	5.68	5.58
	140	5.69	5.60
	160	5.69	5.62

precipitate and is not desorbed even on addition of dilute nitric acid or ammonia although the precipitate changes colour to blue or pink respectively. This observation is difficult to explain on FAJANS' theory[5] or on KOLTHOFF's theory[6] of adsorption indicators.

MEHROTRA[7] has emphasized the chemical nature of the adsorption of the dye ions on the surface of the silver halide precipitate. Therefore, it was interesting to find out

whether such compounds could be isolated. An attempt was made to prepare the silver compound with congo red; the compound has been isolated and its properties studied.

EXPERIMENTAL

Titration of iodide in presence of chloride

As already mentioned, the titration of iodide in presence of chloride with silver ions can be carried out accurately with congo red as indicator (Table V). For every 10 ml of 0.1 *M* halide mixture, 2–3 ml of 0.001 *N* nitric acid and 2–3 drops of indicator (aqueous 0.2% solution of congo red) are added. As the titrant is added, the particles

TABLE V

TITRATION OF IODIDE IN PRESENCE OF CHLORIDE

Vol. of 0.1 M KI (ml)	*Vol. of 0.1 M KCl (ml)*	*Vol. of 0.001 N HNO_3 (ml)*	*Drops of indicator*	*Vol. of 0.1 M $AgNO_3$ required (ml)*	*Transition at the end-point*
10	5	8–9	4	15.0–15.02	Blue → pink violet[a]
5	5	2–3	2–3	4.99–5.01	Greenish blue → pink[b]
16	4	5–6	4	16.0–16.03	Greenish blue → pink[b]
4	16	5–6	3	4.01–4.03	Greenish blue → pink[b]
2	18	5–6	2–3	2.01–2.03	Greenish blue → pink[b]

[a] Coagulation occurs before the end-point and the colour changes on the coagulated particles.
[b] Colour change occurs in the suspension phase and is sharp and reversible.

become greenish blue in colour, and just after an amount equivalent to the iodide has been added, the colour changes to pink or pink violet. The colour change is sharp and reversible; addition of one drop of potassium iodide solution changes it to greenish blue whereas excess of chloride does not affect the colour. The colour change occurs in the suspension phase and no coagulation takes place. Even a small amount of iodide in presence of large quantities of chloride can be titrated with reasonable accuracy. Results are high to the extent of 1% when the concentration of iodide is less than 10% of the halide mixture; for higher concentrations of iodide, the error does not exceed 0.5%.

Purification of congo red

The congo red (B.D.H. adsorption indicator) was first freed from the chloride; about 5 g of congo red was dissolved in 1 l of warm water, and the filtered solution was treated with 100 ml of *N* nitric acid and boiled. The blue form of the dye was precipitated. This was filtered and washed with 0.01 *N* nitric acid solution until the filtrate was free from the chloride ions. Finally, it was washed with water and then dried at 120°. Thus the acidic dye was obtained. This is insoluble in water and alcohol.

Preparation of the silver compound

About 0.2 g of the acidic dye was suspended in 100 ml of water and 5–6 drops of ammonium hydroxide solution were added to give a definite smell of ammonia. The insoluble blue dye changed to the soluble red dye and on slight heating dissolved completely to give a red solution. The solution was boiled to expel ammonia, and diluted to nearly 100 ml. To this was added 0–10 ml of 0.01 *N* nitric acid solution so that the pH was above 3, and 40 ml of 0.1 *M* silver nitrate solution was then added. A pink-violet

coloured precipitate was formed; this was filtered, washed with water and dried at 120° (Table VI).

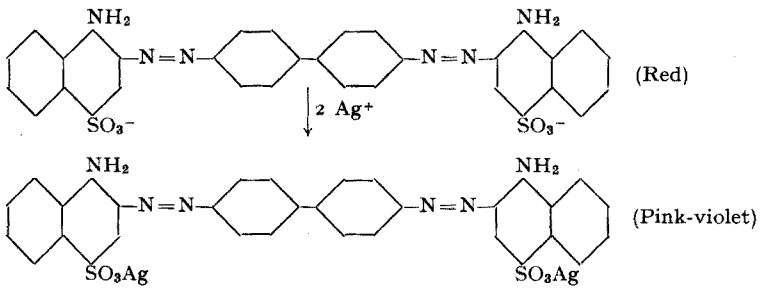


TABLE VI

PREPARATION OF SILVER COMPOUND WITH CONGO RED

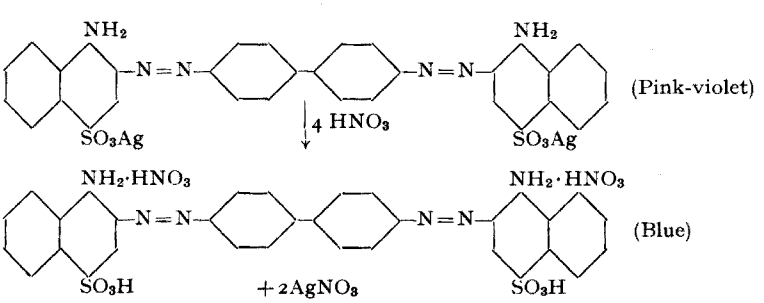
Sample No.	*Amount of the acidic dye (blue) g*	*Vol. and strength of nitric acid added after boiling off ammonia completely*	*Vol. of 0.1 M $AgNO_3$ added (ml)*	*Vol. of water with which the precipitate is washed (ml)*	*Yield of the compound (g)*	*%Ag*
1	0.2050	0	40	50	0.2512	25.6
2	0.2034	2 ml of 0.01 *N*	40	70	0.2484	25.3
3	0.2086	5 ml of 0.01 *N*	40	100	0.2432	24.9
4	0.1994	7 ml of 0.01 *N*	40	60	0.2394	24.1
5	0.1986	10 ml of 0.01 *N*	40	80	0.2364	23.5
6	0.2022	10 ml of *N*	40	50	0.2048	2.3
7	0.2168	20 ml of *N*	40	100	0.2174	0.8

Silver in the compound was determined by igniting a known weight of the compound in a weighed silica crucible and weighing the metallic silver residue. The ash was repeatedly treated with a drop of concentrated nitric acid and ignited so that carbonaceous matter was completely oxidised and volatilised. The compound was found to contain 23.5–25.6% Ag.

Properties of the compound

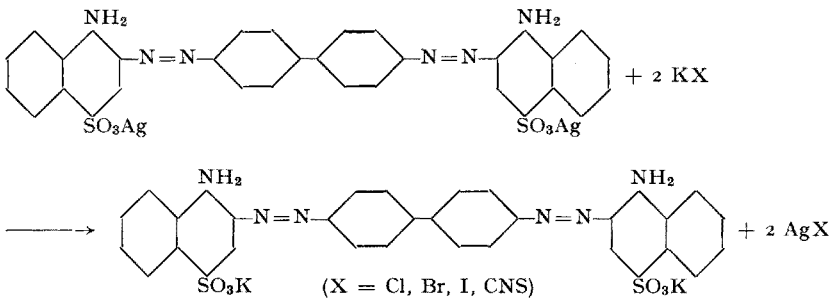
The freshly precipitated compound is pink-violet in colour and is partly soluble in water, producing a faintly pink solution. The dried compound is less soluble in water. It does not melt but decomposes on ignition to give metallic silver.

With dilute nitric acid the compound changes to the blue dye. This form is less soluble than the silver compound, hence on the addition of dilute nitric acid the silver ions are displaced by hydrogen ions. The compound is stable only above pH 3; it tends to change to the blue dye if the pH is lower than 3:



The compound dissolves in ammonium hydroxide to form a red solution. Probably silver ions form a complex with ammonia and the soluble ammonium salt of the dye is formed.

When the freshly precipitated compound is suspended in water and treated with a halide or thiocyanate solution, the pink violet colour changes into deep red suspension. This may be explained according to the following equation



When the reaction is carried out in neutral medium, the solution obtained is red in colour because the dye would be anionic at this pH. But if the reaction is carried out at pH 3, then a blue suspension is obtained because the dye produced is then cationic (blue). The reaction takes place with halide solution as dilute as 0.01 *M*.

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SUMMARY

Congo red is a suitable indicator for the titration of iodide in presence of chloride with silver solution at pH 5–5.5. The behaviour of congo red as an adsorption indicator is described in detail. The silver compound of congo red has been isolated and its properties investigated.

RÉSUMÉ

Les auteurs ont effectué une étude sur le rouge Congo comme indicateur d'adsorption. Il peut être utilisé lors du dosage des iodures, en présence de chlorures, au moyen d'une solution d'argent, au pH 5–5.5. Le composé argent-rouge Congo a été séparé et examiné.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Eignung von Kongorot als Adsorptionsindikator bei der Titration von Jodid in Gegenwart von Chlorid mit Silbernitratlösung. Die Silberverbindung mit Kongorot wurde isoliert und untersucht.

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Short Communication

Spot test examination of materials for aromatic compounds based on sulfonation

It is very desirable in qualitative organic analysis to have available tests which are based on different chemical reactions and are of various sensitivities, when it is necessary to detect functional groups, or characteristic types of compounds, or individual organic compounds. The response to such different tests will enhance the reliability of the conclusions. This reasoning will apply also to so-called preliminary tests whose revelations regarding the absence or presence of compounds possessing certain functional groups rest on the outcome of suitable exploratory procedures. In fact, there are times when adequate insight can be secured only through preliminary tests and the intensity of the response to them. This is the case for example when the problem is to determine the presence or absence of aromatic compounds. There are available very sensitive spot reactions in this area and they are reliable within certain ranges[1]. The new procedure described here is not very sensitive but nevertheless it deserves attention because of its clear chemical basis and also because it is applicable to a number of aromatics which do not respond to the tests used hitherto.

The test rests on the fact that aromatic hydrocarbons and heterocyclic nuclei can be sulfonated by concentrated sulfuric acid[2], and on the additional fact that aromatically bound SO_3H groups are reductively cleaved with production of nickel sulfide when warmed with caustic alkali and Raney alloy (50% Ni, 50% Al)[3]. This selective reduction results from the fact that Raney alloy and caustic alkali react to give Raney nickel, which owes its reactivity to its content of nickel hydride:

$$ArSO_3H + 6\ Ni_2H \rightarrow ArH + NiS + NaOH + 2\ H_2O + 11\ Ni$$

The occurrence of this redox reaction can be detected through the evolution of hydrogen sulfide by the resulting nickel sulfide when the system is made acidic. The hydrogen sulfide is revealed by the blackening of lead acetate paper. Since the detection of aromatic sulfonic acids and their derivatives is very sensitive[4] it is possible to detect even a slight sulfonation of aromatic compounds accomplished under mild conditions, and consequently to determine the presence of such compounds. In this connection it should be noted that substituents in aromatic rings may impede or even completely prevent sulfonation by concentrated sulfuric acid. This selectivity of sulfonation proved to be a notable factor in the compounds tested in the present study.

This new test is not impaired by the presence of aliphatic compounds. They can be "kjeldahled" by hot concentrated sulfuric acid. Any aliphatic sulfonic acids resulting from this treatment will be resistant to Raney nickel and caustic alkali.

Procedure I (Non-volatile and non-sublimable aromatics)

A small quantity of the solid or a drop of its solution in alcohol, ether, etc. is placed in a micro test tube. The solvent is driven off if need be and 1 drop of conc. sulfuric

acid is introduced. The mixture is kept for 30 min in an oven at 140° and then made alkaline with concentrated alkali solution. Several cg of Raney alloy are added and the reaction system is warmed for 5 min in a boiling water bath. After the contents of the test tube have cooled, conc. hydrochloric acid is added, and the mouth of the test tube is covered with a piece of lead acetate paper and the tube is then returned to the water bath. A positive response is indicated by the development of a black or brown stain on the reagent paper. The warming with alkali and acid should be postponed until the initial stormy evolution of hydrogen has subsided. Otherwise, there is danger of that the reaction mixture may foam over.

Procedure II (Low-boiling or sublimable aromatics)

The test material or 1 drop of its solution is placed in a micro test tube with one drop of conc. sulfuric acid and the open end sealed by fusion. After 30 min at 140°, the constricted end of the test tube is cut off. The remainder of the operation is as described in Procedure I, after a brief warming to drive off any sulfur dioxide that may have been produced.

Procedures I and II were tested with 0.5 mg amounts of the following compounds, whose reactions can be placed in three classes:

Positive response: anthracene, benzene, 7,8-benzoflavone, benzophenone, benzil, diphenyl, 1,4-diphenylbenzene, hydroquinone, naphthalene, 1-naphthol, 2-naphthol, phenanthrene, pyrocatechol, pyrogallol, toluene.

Weaker response: alizarin, azobenzene, benzoic acid, carbazole, cinnamic acid, curcumin, diphenylamine, isoquinoline, 1-nitroso-2-naphthol, quinaldine, quinine, quinoline, phenanthranequinone, *o*-phenylphenol, tryptophane, tyrosine.

No response: anthraquinone, caffein, chloranil, D.D.T., hexachlorobenzene, pentachlorphenol, phenolphthalein, phthalic acid, resorcinol, tribromoaniline.

The following limits of identification give an idea of the sensitivity of the test: 15 μg naphthalene; 15 μg diphenyl; 10 μg benzene; 15 μg phenanthrene; 10 μg 1,4-diphenylbenzene.

ACKNOWLEDGEMENT

Professor RALPH E. OESPER of the University of Cincinnati is thanked for preparing the translation of this communication.

Laboratorio da Produção Mineral, F. FEIGL
Ministério das Minas e Energia, V. GENTIL
Rio de Janeiro (Brazil)

1 F. FEIGL, *Spot Tests in Organic Analysis*, 6th ed., Elsevier, Amsterdam, 1960, Chap. 3.
2 R. B. WAGNER AND H. D. ZOOK, *Synthetic Organic Chemistry*, John Wiley and Sons, New York, 1953, p. 811.
3 F. FEIGL, *Angew. Chem.*, 73 (1961) 113.
4 F. FEIGL, *Anal. Chem.*, 33 (1961) 1118.

Received January 18th, 1962

Book Reviews

Dosages colorimétriques des éléments minéraux, Principes et méthodes, de G. Charlot, Deuxième édition entièrement refondue, Masson & Cie., Paris, 1961. Pages 380, avec 72 figures, 45 N.F.

Une nouvelle édition de cet ouvrage vient de paraître; elle a été complètement refondue car cet auteur tient à ce que tous les livres qu'il publie soient à l'extrême pointe du progrès.

Dans la partie intitulée "Généralités" sont exposés les principes et méthodes de la colorimétrie visuelle et photoélectrique qui comprennent les lois fondamentales, l'appareillage, sans détails superflus, les titrations photométriques et spectrophotométriques, les méthodes de dosages simultanés et la méthode différentielle. Les causes d'erreurs, la sensibilité font l'objet d'une étude spéciale. Enfin, un certain nombre de chapitres sont consacrés aux méthodes de séparations et singulièrement celles de traces dont l'importance ne cesse de croître.

La deuxième partie traite du dosage des principaux éléments (65). Pour chacun d'entre eux, l'auteur donne les méthodes de séparations de traces, les caractéristiques analytiques; il décrit succinctement quelques méthodes de dosages spécialement choisies et donne les références y relatives.

On peut toujours critiquer un choix qui est forcément arbitraire, surtout lorsque la méthode qu'on a mise au point n'en fait pas partie. Pourtant, en ce qui concerne les éléments que nous avons étudiés, cobalt, nickel, plomb et zinc, nous pouvons certifier que les méthodes sélectionnées l'ont été de façon fort judicieuse.

Signalons encore que les références données concernent non seulement les méthodes proprement dites, mais aussi l'application de celles-ci aux dosages de l'élément étudié dans les aciers, les alliages, les métaux, les milieux biologiques, par exemple.

Un livre que sera très précieux pour tous ceux qui utilisent les méthodes colorimétriques et ils sont très nombreux. Ils pourront très rapidement se documenter et choisir la méthode qui convient le mieux aux problèmes qu'ils ont à résoudre. Grâce à l'esprit de synthèse qui a présidé à l'élaboration de cet ouvrage, le néophyte saisira rapidement les bases fondamentales d'une des méthodes les plus importantes de la chimie analytique moderne.

D. MONNIER (Genève)

Anal. Chim. Acta, 26 (1962) 597

The Analysis of Titanium, Zirconium and their Alloys, by W. T. ELWELL AND D. F. WOOD. John Wiley & Sons, Ltd., London, 1961, xi + 198 pp., 53s.

The monograph entitled *Analysis of Titanium and its Alloys*, a privately printed publication from the Metals Division of Imperial Chemical Industries, Ltd., ran to three editions between 1956 and 1959. The material has now been brought up to date and

extended to cover the analysis of zirconium and its alloys, and the results are made available to a wider public in this commercial production.

Essentially the book is a laboratory manual for the complete analysis of these metals and their alloys. Thus for titanium and its alloys, determinations of 25 elements and of water are described, as well as spectrographic and spot-test methods of identification. For zirconium and its alloys, methods of determination for 29 elements and spectrographic procedures for hafnium, rare earths and other elements are given. In all cases, the experimental detail is profuse. The procedures are those which have been developed by the I.C.I. Metals Division or have been thoroughly checked in their research laboratories; there is therefore no doubt about their reliability for the purposes mentioned. A value for the reproducibility of results at the expected level of concentration is given for all the methods.

There is very little discursive material in the book as a result of the authors' laudable desire not to repeat information which is already available in the literature. It is indeed the analysis, and not the analytical chemistry, of titanium, zirconium and their alloys which is described, and anyone faced with a problem in such analyses will find the answer here in a precise and reliable procedural format.

R. BELCHER (Birmingham)

Anal. Chim. Acta, 26 (1962) 597–598

Announcement

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Post Graduate Summer School

A Post Graduate Summer School on *"Separation Methods in Inorganic Chemistry"* will be held in Rome, Italy, from September 17th to 27th, 1962. The lecturers will include E. BLASIUS (Berlin), J. P. EBEL (Strasbourg), K. A. KRAUS (Oak Ridge), M. LEDERER (Rome), F. H. POLLARD (Bristol), R. J. P. WILLIAMS (Oxford). The topics dealt with will be Ion Exchange, Partition Chromatography, Solvent Extraction, Paper Electrophoresis, etc.

A limited number of rooms at student hotels is available for foreign participants. Applications and inquiries should be addressed to Dr. M. LEDERER, Istituto di Chimica dell'Università, Piazzale delle Scienze 5, Roma, Italy.

Anal. Chim. Acta, 26 (1962) 598

ANALYTICA CHIMICA ACTA VOL. 26 (1962)

AUTHOR INDEX

ANALYTICA CHIMICA ACTA VOL. 26 (1962)

SUBJECT INDEX

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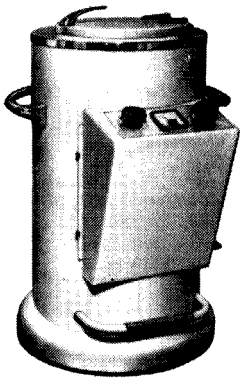

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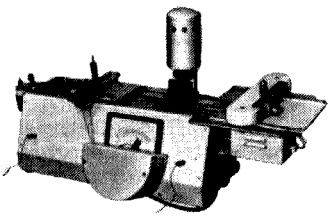

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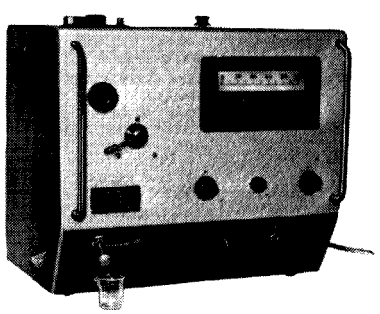

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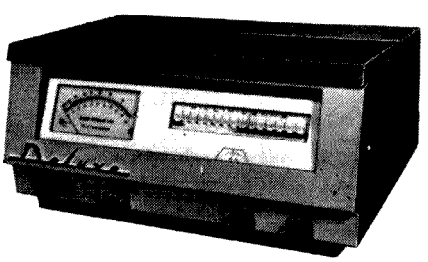

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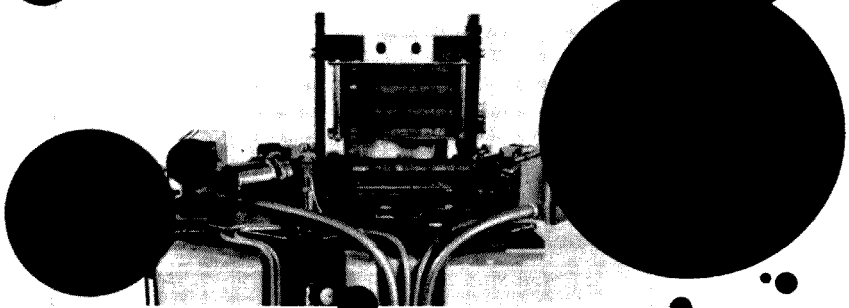

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by

J. H. BEYNON

Research Physicist, Imperial Chemical Industries, Manchester (England)

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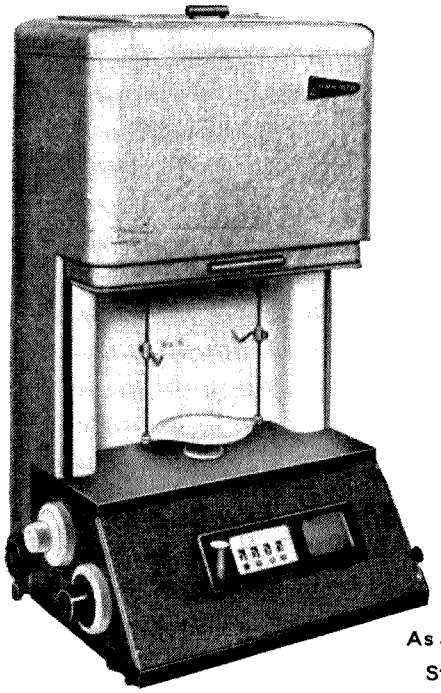

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