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Part I. Synthesis and Spectroscopic Examination of Reagents and Some Chelates

2-(2-Pyridylazo)-1-naphthol (*o*-α-PAN), 2-(2-pyridylazo)phenol (*o*-PAP) and 4-(2-pyridylazo)phenol (*p*-PAP) have been prepared. They and 1-(2-pyridylazo)-2-naphthol (*o*-β-PAN) and their chelates with various transition metals have been examined and characterised by infrared spectroscopy and mass and nuclear magnetic resonance spectrometry. The purity and structures of the reagents have been established and it was confirmed that they are terdentate ligands.

D. BETTERIDGE and D. JOHN

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Analyst, **1973, 98**, 377–389.

Pyridylazonaphthols (PANs) and Pyridylazophenols (PAPs) as Analytical Reagents

Part II. Spectrophotometric and Solvent-extraction Studies of Complex Formations

The reactions between 2-(2-pyridylazo)-1-naphthol (*o*-α-PAN), 1-(2-pyridylazo)-2-naphthol (*o*-β-PAN) and 2-(2-pyridylazo)phenol (*o*-PAP) with manganese(II), zinc(II) and lanthanum(III) and 4-(2-pyridylazo)phenol (*p*-PAP) with cobalt(II), nickel(II) and copper(II) have been studied. The spectrophotometric procedure based on linear extrapolation, as used by Sommer, has been critically evaluated. The results from the spectrophotometric method have been used to predict the optimum conditions for solvent extraction. It is shown that this procedure is a valuable approach for systems in which hydroxy-complexes are common.

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Chemistry Department, University College of Swansea, Swansea, Glamorgan, SA2 8PP.

Analyst, **1973, 98**, 390–411.

Determination of Chloride in Aqueous Soil Extracts and Water Samples by Means of a Chloride-selective Electrode

The chloride contents of water samples and soil extracts have been determined with an Orion chloride-selective electrode. The chloride content, at levels up to 100 mg l^{-1}, is determined in a solution that is 0·5 M with respect to ammonium nitrate and 0·03 M with respect to nitric acid.

Comparison of this method with a colorimetric AutoAnalyzer method showed no significant difference between the results obtained, but for water samples low in chloride (less than 3 mg l^{-1}) the colorimetric method was more accurate.

A. R. SELMER-OLSEN

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Analyst, **1973, 98**, 412–415.

Precise Coulometric Determination of Acids in Cells Without Liquid Junction
Part III. Determination of the Silver Error by Amperostatic Anodic Stripping

The plating and stripping of silver on platinum electrodes have been examined in the context of the determination of the silver error, which arises from the solubility of silver bromide when the deposition of bromide on a silver anode is used as the auxiliary reaction in the coulometric assay of acids. In order to calibrate the stripping method, it is necessary to plate known amounts of silver quantitatively on to platinum-gauze electrodes. Low recoveries are obtained when the platinum is not fully reduced. The oxidation and reduction of platinum electrode surfaces have been briefly examined, and it is demonstrated that oxide forms on an electrode when its potential is allowed to rise beyond 0·8 V, the termination potential in silver stripping. For calibration purposes, plating and stripping in a 0·1 M solution of silver nitrate in 0·1 M perchloric acid was first investigated. Amperostatic and potentiostatic reduction of the platinum electrode are shown to be ineffective, but chemical reduction leads to excellent plating and recoveries, provided great care is taken completely to remove all traces of reductant. Calibration being satisfactory, stripping in 0·1 M perchloric acid, as in an actual acidimetric assay, has been examined and shown to give excellent recoveries. The anodic stripping curves show an extended second wave, which is identified as arising from reduction of oxygen to hydrogen peroxide at the auxiliary stripping electrode, particularly when the latter becomes plated with silver. The hydrogen peroxide is oxidised at the stripping electrode, and the process is cyclic.

E. BISHOP and M. RILEY
Chemistry Department, University of Exeter, Stocker Road, Exeter, EX4 4QD.
Analyst, 1973, **98**, 416–425.

Precise Coulometric Determination of Acids in Cells Without Liquid Junction
Part IV. The Assay of Primary Standard Sulphamic Acid

The precise (1 to 2 p.p.m.) location of the end-point in the pre-titration of the supporting electrolyte and in the titration of sulphamic acid has been examined, and d.c. differential electrolytic potentiometry gives excellent results. The methods and simple apparatus previously described in Parts I, II and III are applied to the assay of primary standard sulphamic acid previously collaboratively assayed by mass titrimetry, and give results with an accuracy and precision of 100 p.p.m., and a 95 per cent. confidence level of 0·02 per cent., but with a positive bias of 0·014 per cent., the reasons for which are canvassed. The method is of high merit; it is simple, fast and direct, and is capable of further refinement.

E. BISHOP and M. RILEY
Chemistry Department, University of Exeter, Stocker Road, Exeter, EX4 4QD.
Analyst, 1973, **98**, 426–431.

A Quantitative Tunable Element-selective Detector for Gas Chromatography

A detector based on the atomic-emission spectra that result when organic compounds are decomposed in a low-pressure, microwave-sustained helium plasma is described. All of the non-metallic elements normally found in organic compounds can be sensitively and selectively detected in a linearly proportional and quantitative manner by means of conventional diffraction grating spectrometer equipment. A controlled amount of a scavenger gas is used to prevent carbon deposition inside the plasma tube. The chromatographic column outflow is split between the element-selective detector and a non-selective flame-ionisation detector. The latter acts as a reference for interpreting element-selective detector results and assists with the determination of atomic ratios and the empirical formulae of organic compounds.

W. R. McLEAN, D. L. STANTON and G. E. PENKETH
Imperial Chemical Industries Limited, Petrochemicals Division, Billingham, Teesside, TS23 1JB.
Analyst, 1973, **98**, 432–442.

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THE ANALYST

Pyridylazonaphthols (PANs) and Pyridylazophenols (PAPs) as Analytical Reagents

Part I.* Synthesis and Spectroscopic Examination of Reagents and Some Chelates

BY D. BETTERIDGE AND D. JOHN†

(Chemistry Department, University College of Swansea, Swansea, Glamorgan, SA2 8PP)

2-(2-Pyridylazo)-1-naphthol (*o*-α-PAN), 2-(2-pyridylazo)phenol (*o*-PAP) and 4-(2-pyridylazo)phenol (*p*-PAP) have been prepared. They and 1-(2-pyridylazo)-2-naphthol (*o*-β-PAN) and their chelates with various transition metals have been examined and characterised by infrared spectroscopy and mass and nuclear magnetic resonance spectrometry. The purity and structures of the reagents have been established and it was confirmed that they are terdentate ligands.

A REVIEW by Anderson and Nickless[1] has shown that analysts have not been slow to realise the importance of 1-(2-pyridylazo)-2-naphthol (*o*-β-PAN). Since Cheng and Bray's original work,[2] there have been many developments with respect to both the use of *o*-β-PAN and the development of related reagents. These reagents react with many cations to form intensely coloured complexes that are eminently suitable for spectrophotometric determinations, chelatometric end-point detection and solvent extraction. The sensitivities are comparable with those obtained with dithizone (diphenylthiocarbazone), and the versatility is comparable with that of 8-hydroxyquinoline. The great advantage of *o*-β-PAN is that its solutions and also solutions of its complexes are unusually stable for such a sensitive reagent. Reagent solutions can be kept for several months without change in the absorbance (Galik,[3] and D. Betteridge, unpublished work), which should make *o*-β-PAN well suited for use in automated determinations. The disadvantage of using PAN-type compounds at present is that their solution chemistry is very complex. Slight alterations of conditions, when modifying a published procedure, can result in irreproducible results or even in no results being obtained. For example, Galik[3] has shown that copper is not extracted from a sulphate medium at pH 4 although it is extracted with other common anions from the bulk of the electrolyte. It has also been found that care has to be taken when extracting manganese, although a useful procedure for determining manganese in high-purity zirconium, etc., has been published.[4] We shall show later that this care is necessary because of the formation of a hydroxy species, of the form MnR_2OH, which is very dependent upon pH. These difficulties can be easily overcome if the basic chemistry of the system being used is understood. Accordingly, we have undertaken the study of four related compounds and their reactions with metal ions. Two prime considerations have been borne in mind: the chemistry of the system considered should be examined in considerable detail, and the information obtained and the methods used to obtain it should be of value to analysts. The reagents examined are insoluble in water and they form water-insoluble complexes that can often be extracted. Hence the work of Sommer and co-workers[5–9] on water-soluble complexes of 4-(2-pyridylazo)resorcinol (PAR) and 4-(2-thiazolylazo)resorcinol (TAR) is to some extent paralleled and the possibilities of solvent extraction are considered more fully. The reagents are 1-(2-pyridylazo)-2-naphthol (*o*-β-PAN), 2-(2-pyridylazo)-1-naphthol (*o*-α-PAN), 2-(2-pyridylazo)phenol (*o*-PAP) and 4-(2-pyridylazo)phenol (*p*-PAP).

This paper deals with the nature of the reagents and some chelates. Subsequent papers in this series will deal with methods for investigating the equilibria of complex formation and analytical procedures.

* For Part II of this series, see p. 390.

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Experimental

Reagents—

PAN-type compounds have been synthesised by the Chichibabin[10] reaction of coupling 2-pyridyldiazotate with an appropriate naphthol or phenol under an inert atmosphere. Low yields and ill defined products usually result. Pollard, Nickless and Anderson,[11] Anderson and Nickless[12] and Anderson[13] have shown that the coupling of 2-hydrazinopyridine, synthesised by the procedure of Fargher and Furness,[14] with a suitable quinone results in relatively pure products of definite composition being produced in over-all yields of 40 to 60 per cent. We confirm these findings with the reservation that 2-hydrazinopyridine and *o*-quinones are usually unstable so that some experimental skill is required in order to obtain the desired results. The final purification stages were very difficult, and the products were subjected to repeated recrystallisation and, when appropriate, sublimation until the microanalyses and mass spectrum indicated that the compound was pure or that further attempts at purification would be valueless.

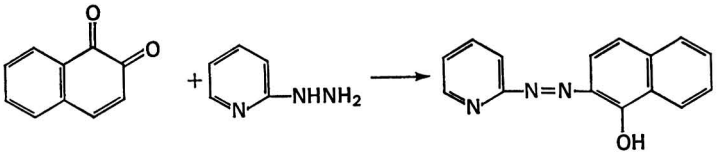
2-(2-*Pyridylazo*)*phenol* (o-*PAP*)—Aqueous solutions of 2-hydrazinopyridine and 1,2-benzoquinone acidified with perchloric acid were allowed to react together to give *o*-PAP. The 1,2-benzoquinone was prepared by reaction of catechol in anhydrous diethyl ether with tetrachloro-*o*-quinone, which had been synthesised by chlorination of catechol. The 1,2-benzoquinone is unstable and was used immediately. 2-Hydrazinopyridine was prepared by allowing hydrazine hydrate and 2-chloropyridine to react together.[14] The solid first isolated was *o*-PAP perchlorate, m.p. 170 °C. Successive recrystallisations of this perchlorate salt from aqueous ethanolic mixtures gave deep red, granular crystals that melted at 128 °C. The lower melting-point indicated that these granular crystals were no longer the salt, but pure *o*-PAP, which was verified by microanalysis, thin-layer chromatography and infrared spectroscopy. The microanalytical results were as follows—

	C	H	N
Calculated for $C_{11}H_9N_3O.HClO_4$, per cent.	44·1	3·4	14·0
Calculated for $C_{11}H_9N_3O$, per cent.	66·0	4·5	21·0
Found, per cent.	65·7	5·2	20·5

4-(2-*Pyridylazo*)*phenol* (p-*PAP*)—Commercially available 1,4-benzoquinone was purified by recrystallisation from light petroleum of boiling range 40 to 60 °C and allowed to react with a solution of 2-hydrazinopyridine in perchloric acid. The product was washed with water, dissolved in methanol - formic acid (10 + 6) and ammonia was added to re-precipitate the *p*-PAP. The microanalytical results were as follows—

	C	H	N
Calculated for $C_{11}H_9N_3O$, per cent.	66·0	4·5	21·0
Found, per cent.	66·0	4·6	21·6

2-(2-*Pyridylazo*)-1-*naphthol* (o-α-*PAN*)—This reagent was prepared by the reaction of 1,2-naphthoquinone with 2-hydrazinopyridine under acidic conditions—



In order to obtain a pure sample of 1,2-naphthoquinone, it was synthesised by oxidising 1,2-aminonaphthol hydrochloride with iron(III) chloride.[15] The crude, commercially available 1,2-aminonaphthol hydrochloride was purified as described by Conant and Corson.[16] Crude *o*-α-PAN was precipitated by neutralising the ice-cold acidic reaction mixture with ammonia, but repeated recrystallisations failed to yield a pure product. Purification was effected by sublimation at 122 °C. Mass-spectrometric analysis indicated that there was a slight impurity (about 1 per cent.) of a compound similar to *o*-α-PAN but with a higher relative molecular mass (28 a.m.u.). The microanalytical results were as follows—

	C	H	N
Calculated for $C_{15}H_{11}N_3O$, per cent.	72·3	4·4	16·9
Found, per cent.	72·1	4·4	16·5

1-(2-*Pyridylazo*)-2-*naphthol* (o-β-*PAN*)—Impure *o*-β-PAN was obtained commercially and purified by repeated recrystallisations from aqueous ethanol (m.p. 140 °C). The microanalytical results were as follows—

	C	H	N
Calculated for $C_{15}H_{11}N_3O$, per cent.	72·3	4·4	16·9
Found, per cent.	72·5	4·3	16·5

4-(2-*Pyridylazo*)-1-*naphthol* (o-α-*PAN*)—This compound was prepared by reaction of 2-hydrazinopyridine with 1,4-naphthoquinone. It could not be purified by the methods outlined above as it formed tars on recrystallisaton and exploded rather than sublimed. No further work was carried out on it.

MASS SPECTRA—

The mass spectra of reagents and chelates were obtained on an A.E.I. MS9 double-focusing mass spectrometer.

INFRARED SPECTRA—

The infrared spectra of the solid reagents and chelates were obtained from caesium iodide pressed discs with a Perkin-Elmer 225 grating infrared spectrometer. The caesium iodide was spectroscopically pure.

NUCLEAR MAGNETIC RESONANCE SPECTRA—

Nuclear magnetic resonance spectra were obtained with a Varian 100 H.A. spectrometer.

Spectra of reagents—Saturated solutions of *o*-α-PAN, *o*-β-PAN and *o*-PAP in deuterated chloroform were concentrated enough for spectra to be measured, but it was necessary to use dimethyl sulphoxide as a solvent for *p*-PAP.

Spectra of chelates—Equal volumes (5 ml) of a solution of the reagent (60 mg) in carbon tetrachloride and a buffered aqueous solution of a metal ion (30 mg) were equilibrated. The organic phase was removed and dried over molecular sieves. Other experiments showed that under these conditions of excess of the metal ion at a suitable pH, all of the organic reagent in the organic phase would be converted into the chelate.

RESULTS AND DISCUSSION

A detailed study of the mass, infrared and nuclear magnetic resonance spectra of the reagents and of some chelates of common transition metals was carried out with several objects in mind—

to confirm that no errors of identification had been made;
to see if the marked difference between *o*-α-PAN and *o*-β-PAN could be explained;
to check the generally held views on bonding in the chelates;
to provide a reference for the chelates of less common metals to be examined later, which chelates may be anomalous.

MASS SPECTRA—

A detailed discussion of the mass spectra of the reagents and of their chelates with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) has been presented elsewhere.[17]

The two steps in the main fragmentation pattern of the reagents are loss of azo-nitrogen with the fusion of the pyridine and phenol or naphthol groups, and rupture of the compound formed with the release of pyridine and phenol or naphthol fragments. Alternatively, the pyridine group was lost first and the azo-nitrogen second. The 1:2 chelates, typically, lost first a whole ligand molecule and then the 1:1 complex that remained fragmented to give a metal - pyridine complex and a diazophenol or naphthol group.

It was found that *o*- and *p*-hydroxyl groups could be detected with certainty so that the identification of the reagents was confirmed. It was also found that the spectra of the chelates provided information that was of value in the interpretation of the results of solution studies. It was possible to check the stoicheiometry of the chelates but not to ascertain their structure.

INFRARED SPECTROSCOPY—

In contrast to mass spectrometry, infrared spectroscopy is well established as a means of investigation of chelate compounds.[18,19]

INFRARED SPECTRA OF REAGENTS—

The infrared spectra of the complex molecules are extremely complicated and the extensive overlap of bands makes detailed interpretation very difficult. The assignments for the spectrum of pyridine are well established,[20–22] as are those for α-naphthol, β-naphthol and phenol.[23–25] Examination of the spectra of these individual compounds shows that there are several absorption bands in similar regions. This effect can be anticipated owing to the expected similarity of the ring vibrations and the C–H stretching and bending frequencies of the compounds. It is this type of similarity that leads to the extensive overlapping of bands in the reagent spectra and to the corresponding complexity.

Spectrum of 2-(2-*pyridylazo*)-1-*naphthol* (o-α-*PAN*)—The principal bands and their assignments are shown in Table I.

TABLE I

INFRARED SPECTRUM OF *o*-α-PAN

Peak/cm^{-1}	Intensity*	Assignment
3050	m	Aromatic C–H stretch
1620 to 1400	s (multiplet)	N=N, C=N, C=C stretch
1400 to 110	s (multiplet)	C–O stretch, O–H deformation, pyridine C–H deformation
990	s	Pyridine C–H deformation
900 to 400	s (multiplet)	C–H in-plane deformations
400 to 200	m (multiplet)	C–H out-of-plane deformations

* m, bands of medium intensity; and s, bands of strong intensity.

The spectrum consists principally of aromatic C–H and C=C absorptions, together with CO, OH and CN absorptions. Many of the bands that arise from these absorptions will inevitably overlap and give rise to the high degree of complexity observed.

The well defined band at 3050 cm^{-1} is characteristic of aromatic C–H stretching frequencies [Fig. 1(*a*)]. Coupled with this band are the expected aromatic C=C ring vibration frequencies at about 1590, 1500 and 1450 cm^{-1}. The shoulder at 1580 cm^{-1} could be assigned to the presence of conjugated rings, and is often taken as an indication of such a system. The spectral range from 1620 to 1400 cm^{-1} is further complicated by the presence of the C=C and C=N stretching frequencies of the pyridine ring. According to Bassignana and Cogrossi,[26]

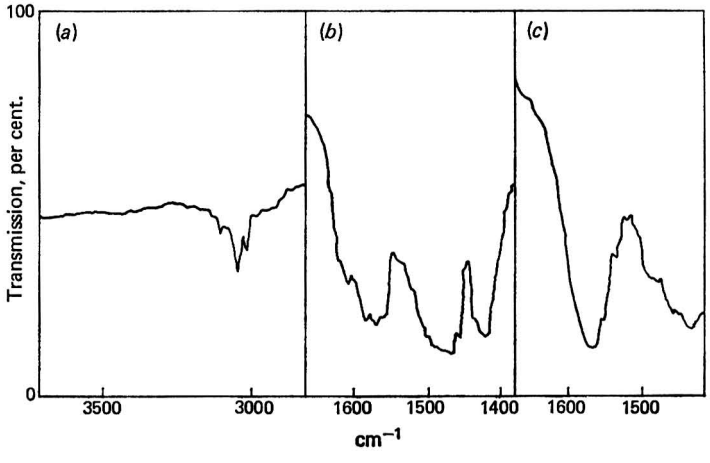
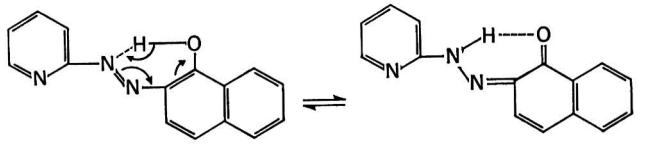


Fig. 1. Infrared spectra: (*a*) aromatic C–H stretching for *o*-α-PAN; (*b*) 1600 to 1400 cm^{-1} region for *o*-α-PAN; and (*c*) 1600 to 1400 cm^{-1} region for *p*-PAP

the N=N stretching frequency could also be observed in the region of 1410 ± 30 cm^{-1}. Because of the complexity of this region, positive identification of the band, which is usually of medium intensity, is extremely difficult. Another interesting feature of this region of the spectrum is the occurrence of a well defined shoulder peak at 1610 cm^{-1}, which is also observed in the spectrum of *o*-β-PAN [Fig. 1(*b*)]. In view of the known tautomerism of *o*-hydroxyazo compounds, it is possible to assign this band to the presence of the C=O stretching frequency of the hydrazo form, *i.e.*—



Azo Hydrazo

Although the free carbonyl band is to be expected in the 1700 cm^{-1} region, such a shift is often observed in hydrogen-bonded systems. Examination of the spectra of *o*-PAP and *p*-PAP shows that there is no absorption of any kind at this wavelength [Fig. 1(*c*)]. This result is in keeping with Hadzi's observation that *o*-hydroxyazophenols are true azo compounds and that naphthols exist as tautomers.[27]

The strong bands observed in the region of 1100 to 1300 cm^{-1} are probably due to the C–O stretching and O–H deformation frequencies. Complications in this region are the expected ring vibrations and C–H deformations of the pyridine ring at about 1200 cm^{-1}. At lower frequencies, in the range 1000 to 500 cm^{-1}, are a large number of strong absorptions that can be attributed to the C–H deformations of both the pyridine and naphthol rings. The presence of two strong bands at 990 and 705 cm^{-1} is indicative of the presence of the pyridine ring. Most of the other bands overlap to such an extent that assignment would be extremely speculative. The remaining region of the spectrum below 500 cm^{-1} consists mainly of the C–H out-of-plane deformations.

A notable absence from the spectrum is a band in the region of 3500 cm^{-1} corresponding to an O–H stretching frequency. It is known that in the presence of strong intramolecular hydrogen bonding this band would become broad and very weak. The absence of this band would therefore suggest that α-PAN has a strong intramolecular hydrogen bond and this is also suggested by the nuclear magnetic resonance spectrum (see below).

Spectrum of 1-(2-*pyridylazo*)-2-*naphthol* (o-β-PAN)—As expected, the spectrum of *o*-β-PAN is very similar in nature and complexity to that of *o*-α-PAN. The identification of individual bands is again difficult because of the high degree of overlap, but the aromatic stretching frequency at 3060 cm^{-1} is well defined. The presence of extensive intramolecular hydrogen bonding is again evident, due to the absence of a band in the 3500 cm^{-1} region, corresponding to the hydroxyl stretching mode.

Because of the similarity of the spectra of *o*-α-PAN and *o*-β-PAN, a table of frequencies and their assignments for *o*-β-PAN can be considered to be identical with that for *o*-α-PAN (Table I).

Spectrum of 2-(2-*pyridylazo*)*phenol* (o-*PAP*)—The principal absorption bands and their assignments are listed in Table II.

TABLE II

INFRARED SPECTRUM OF *o*-PAP

Peak/cm^{-1}	Intensity*	Assignment
3020	m	Aromatic C–H stretch
1600 to 1400	s (multiplet)	C=C, C=N, N=N stretch
1300 to 110	s (multiplet)	C–O stretch, O–H deformation, pyridine C–H deformation
980	s	Pyridine C–H deformation
900 to 500	s (multiplet)	C–H in-plane deformations
450 to 200	s (multiplet)	C–H out-of-plane deformations

* m, bands of medium intensity; and s, bands of strong intensity.

Many of the absorption bands that arise from the phenol ring will be similar to those of the α- and β-naphthol rings, so that this spectrum is similar to those of *o*-α-PAN and *o*-β-PAN. The aromatic C–H stretching frequency band at 3020 cm^{-1} is well defined. The aromatic C=C ring vibrations are observed in the region 1600 to 1400 cm^{-1}, which region is again complicated owing to the presence of C=N and N=N bands. The remaining regions of the spectrum are also similar to those of *o*-α-PAN and *o*-β-PAN, and consist of bands that arise from C–O, O–H and C–H stretching and deformation modes.

The presence of strong intramolecular hydrogen bonding is indicated by the absence of absorption in the region of 3500 cm^{-1}. In this respect, *o*-PAP is again similar to *o*-α-PAN and *o*-β-PAN, and interpretation is also supported by nuclear magnetic resonance studies.

Spectrum of 4-(2-*pyridylazo*)*phenol* (o-*PAP*)—Below 2400 cm^{-1}, this spectrum is virtually identical with that of *o*-PAP, but above this frequency there is a big difference. In the region of 3400 to 2400 cm^{-1} there is an extremely broad, very strong absorption band (Fig. 2). This band must be due, in part, to aromatic C–H stretching absorptions, but is so large that some other contributions must be involved. It seems likely that the broadening is caused by intermolecular hydrogen bonds formed by polymeric association of the reagent. This type of association is known to give rise to very broad, concentration-dependent bands in the 3-μm region. Such a change from intramolecular to intermolecular bonding can also be inferred from nuclear magnetic resonance spectra.

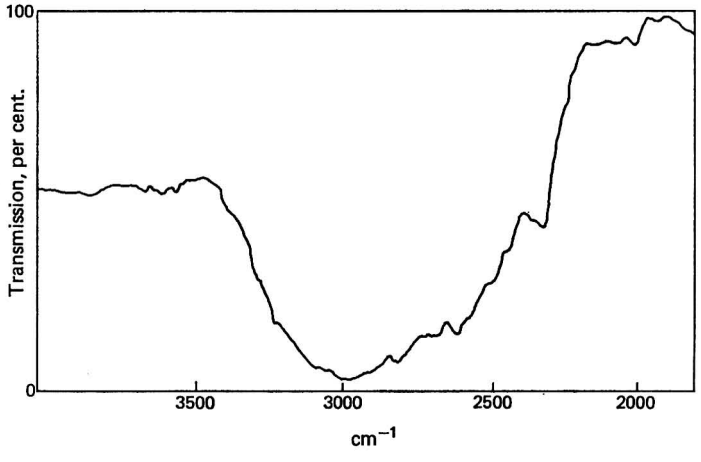


Fig. 2. Intermolecular hydrogen-bond absorption for *p*-PAP

Attempts to investigate the presence of this intermolecular bonding more closely were made by obtaining reagent spectra for saturated solutions in chloroform. The only absorption observed was a well defined band at 3020 cm^{-1} that corresponded to aromatic C–H stretching. The broad band previously observed in the spectral region of 3400 to 2400 cm^{-1} was no longer observed. Because of the limited solubility of the reagent in this solvent, spectra were obtained for saturated solutions in acetone. These solutions were prepared by using spectroscopically pure acetone dried over molecular sieves. The spectra were very similar to those obtained for chloroform solutions, but an additional broad, very weak band in the region of 3600 cm^{-1} was also observed. Although acetone was used as a blank solution, this band can be assigned to the hydroxyl stretching frequency only tentatively because of the ease with which acetone picks up moisture. The solutions in both chloroform and acetone were very dilute, and the disappearance of the broad absorption band is consistent with the presence of intermolecular bonds that would be broken on dilution. Although these results tend to confirm the presence of intermolecular bonding, conclusive proof would involve a complete concentration-dependent study. Unfortunately, the relative insolubility of the reagent in non-polar, non-hydroxylic solvents would seem to preclude this.

INFRARED SPECTRA OF THE CHELATE COMPOUNDS—

The spectra of the chelates of each reagent are similar and resemble each other more closely than the spectrum of the parent reagent. The general similarity of all the chelate spectra suggests that each metal has a similar effect on the vibrations of the ligand. For convenience, the spectra are divided into four regions, which are discussed separately.

4000 *to* 2800 cm^{-1} *region*—A common feature in the spectra of all the chelates, and of each reagent, is the presence of a well defined band in the region of 3050 cm^{-1}. That this band is stable in position in the spectra of both ligands and chelates indicates that it is due solely to aromatic C–H stretching.

2800 *to* 1600 cm^{-1} *region*—This region is largely featureless in all the spectra studied.

1600 *to* 900 cm^{-1} *region*—This skeletal region possesses a large number of broad, very strong bands in the spectra of both chelates and ligands. It is to be expected that several of the ligand absorption bands that occur in this region will undergo shifts on chelation. Identification of these shifts, normally to lower frequencies, is very difficult because of the large degree of overlapping of bands. A number of workers have found[28,29] that one of the more prominent shifts observed in this region has been that of the C–O stretching frequency from about 1200 cm^{-1} to about 1100 cm^{-1}. Although in the present spectra the positive identification of this shift is difficult, a broadening effect near 1100 cm^{-1} in each spectrum suggests that such a shift has occurred.

One of the major features of this region is the appearance of a broad, very strong band at about 1340 cm^{-1} in the spectrum of each chelate investigated (see Table III).

TABLE III

POSITION OF CHELATE –N=N– FREQUENCY* (cm^{-1})

Metal	*o*-α-PAN	*o*-β-PAN	*o*-PAP
Ni	1330 (b, s)	1335 (b, s)	1345 (fs, s)
Zn	1355 (b, s)	1335 (b, s)	1350 (fs, s)
Mn	1330 (b, s)	1330 (b, s)	—

* b, broad; s, strong; and fs, fairly sharp.

It has been suggested by Ueno,[30] in his study of the chelate compounds of *o*-hydroxyazobenzene, that this band is due to the shift to lower frequencies of the azo stretching band.

950 *to* 200 cm^{-1} *region*—It is in this region, and in particular the medium to far infrared region, that the metal - oxygen and metal - nitrogen frequencies are likely to be found. These bands are usually well defined, but it is possible that they may be overlapped by other strong absorptions such as those resulting from the C–H deformations of the pyridine or enol ring.

METAL - NITROGEN INFRARED FREQUENCIES—

The general region expected for metal - nitrogen vibrations is the spectral region from 300 to 150 cm^{-1}.[31,32] Bands found in this region of the spectra of chelates, and which are not present in the ligand spectra and cannot be assigned to any form of shift, are considered to be metal - nitrogen stretching vibrations. The frequencies are summarised in Table IV.

TABLE IV

METAL - NITROGEN FREQUENCIES* (cm^{-1})

	o-α-PAN	*o*-β-PAN	*o*-PAP
Ni	245 (sh, w); 225 (sh)	244 (sh, s); 222 (sh, s)	243 (s, sh); 226 (sh)
Zn	243 (m); 228 (sh, m)	247 (sh, w); 220 (vs, sh)	243 (sh, m); 223 (sh, w)
Mn	240 (sh, m)	244 (m); 219 (vs, sh)	243 (sh, m); 222 (m)

* sh, sharp; w, weak; m, medium; s, strong; and vs, very strong.

METAL - OXYGEN INFRARED FREQUENCIES—

Metal - oxygen stretching frequencies occur between 1000 and 250 cm^{-1}. The highest frequencies are associated with double bonds, while those in the region of 400 to 600 cm^{-1} are associated with single bonds. The lowest frequencies, below 300 cm^{-1}, arise either with heavy oxide ligands or with co-ordinated oxy-anions. In the present study, two distinct regions of metal - ligand absorptions were observed.

600 *to* 650 *cm*$^{-1}$ *region*—Lecomte[33] suggested that the absorptions may be due solely to metal - oxygen stretching vibrations. However, it has since been shown that this suggestion is an over-simplification, and that the metal - oxygen stretching is probably coupled with ring or C–H deformations (J. M. Williams and D. Betteridge, unpublished work). The bands observed in this range are shown in Table V, but for *o*-PAP chelates they may be superimposed with shifted pyridine C–H deformations.

TABLE V

METAL - OXYGEN FREQUENCIES* IN THE 600 TO 650 cm^{-1} REGION

	o-α-PAN	*o*-β-PAN	*o*-PAP
Ni	622 (sh, s)	622 (w)	638 (sh, s)
Zn	615 (sh, s)	630 (sh, m)	640 (s)
Mn	625 (sh, s)	626 (w)	636 (sh, s)

* sh, sharp; w, weak; m, medium; and s, strong.

400 *to* 500 *cm*$^{-1}$ *region*—The absorption bands observed in this region are generally accepted as being solely metal - oxygen stretching frequencies. They are listed in Table VI.

TABLE VI

METAL - OXYGEN FREQUENCIES* IN THE 400 TO 450 cm^{-1} REGION

	o-α-PAN	*o*-β-PAN	*o*-PAP
Ni	430 (w)	442 (m); 429 (m)	485 (sh, m)
Zn	423 (w)	437 (sh, s)	478 (sh, m)
Mn	420 (w)	438 (sh, s)	—

* sh, sharp; w, weak; m, medium; and s, strong.

Several attempts have been made to correlate metal - ligand frequencies with stability constants or electronegativities. Such a correlation has little value because too few chelates have been examined.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY—

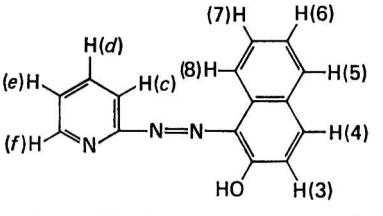
Nuclear magnetic resonance spectroscopy has been applied to the study of chelate compounds on only a relatively few occasions.[34–36] The technique is handicapped by the difficulty of obtaining resolvable spectra for those chelates which contain a paramagnetic or ferromagnetic central metal atom. Mass spectrometry and infrared spectroscopy have been found to be more versatile, as these techniques permit the ready investigation of both reagents and chelates.

The spectra are complex and those obtained on a 60-MHz instrument could not be resolved.

NUCLEAR MAGNETIC RESONANCE SPECTRA OF LIGANDS—

1-(2-*Pyridylazo*)-2-*naphthol* (o-β-*PAN*)—The proton signals obtained in the spectrum and their tau (τ) values and assignments are shown in Table VII.

For convenience of discussion the protons are labelled as follows—



The hydroxyl proton in *o*-β-naphthol is observed at τ 3·90. The corresponding peak with *o*-β-PAN is observed at τ −5·70. (The positions of these hydroxyl protons were verified by deuterium oxide exchange.) This large shift can be attributed to strong hydrogen bonding in the reagent molecule. Generally, it is accepted that the greater the extent of hydrogen bonding, the greater is the "hydrogen-bond shift."[37] The hydrogen bonding was proved to be intramolecular, as no signal shift occurred on dilution of the solvent.

TABLE VII

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF *o*-β-PAN

τ	Peak	Integration	Assignment
1·59	Complex multiplet	2	*f*, *c* (lower is *f*, upper is *c*)
2·17	Complex multiplet	2	*e*, 8
2·35, 2·45	Doublet	1	4
2·58	Multiplet	3	5, 6, 7
2·93	Multiplet	1	*d*
3·30, 3·40	Doublet	1	3
−5·70	Broad multiplet	1	OH

Apart from the hydroxyl proton signal, all other proton signals are observed in the range τ 1·0 to 4·0 (Fig. 3). The resulting complex spectrum is expected, as signals for aromatic and heteroaromatic protons are usually observed in this range. In order to assign the signals in this range successfully, a scale-expanded spectrum was provided. The interpretation is summarised as follows.

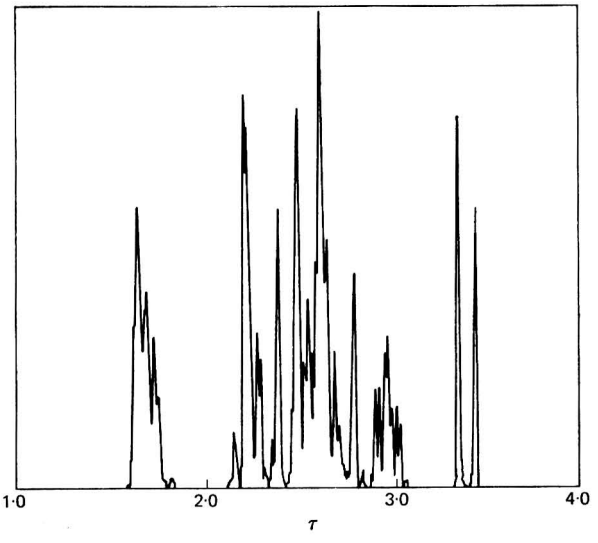


Fig. 3. Nuclear magnetic resonance spectrum of *o*-β-PAN

The maximum effect of the electron-donating properties of the naphthol hydroxyl group is observed for proton 3, which is in an *ortho* position. The position of proton 3 does not permit any long-range coupling, and as there is only one adjacent proton then the expected signal would be a distinct upfield doublet. Such a doublet is observed at τ 3·30 to 3·40, which also integrates for only one proton. The *ortho* coupling constant for protons 3 and 4 was found to be 10 Hz. In order to locate proton 4, it was therefore required to find a doublet signal with a splitting of 10 Hz. Ideally, this doublet should be a mirror image of doublet 3, but because of the position of proton 4 some long-range coupling from proton 5 would be expected. Such a doublet is observed at τ 2·35 to 2·45.

The complex multiplet at an average τ value of 2·93 corresponds to the proton *d*, which is the γ-pyridine proton. The complex pattern occurs owing to the two *ortho* couplings of protons *e* and *c* and the *meta* coupling of proton *f*. The multiplet observed in the region of τ 1·60 integrates for two protons. These protons are the α-pyridine proton *f*, and the β-pyridine proton *c*. The low field position of these protons is typical of α-pyridine protons,[38] and is due to the effect of the pyridyl nitrogen atom. The low field position of proton *c* is a result of the proximity of the azo group which, like the pyridyl nitrogen, causes de-shielding effects. The only other pyridine proton to be accounted for is *e*, which is hidden under the multiplet in the region of τ 2·17.

The four remaining naphthol protons, 5, 6, 7 and 8, can be assigned as follows: three of them, 5, 6 and 7, are located in the multiplet at τ 2·58, while the other is further downfield at τ 2·17 owing to the effect of the azo group.

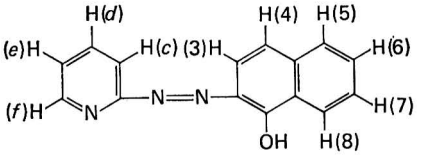
2-(2-*Pyridylazo*)-1-*naphthol* (o-α-*PAN*)—The features of the spectrum are summarised in Table VIII.

TABLE VIII

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF *o*-α-PAN

τ	Peak	Integration	Assignment
1·57	Singlet (much fine structure)	1	*f*
1·64	Singlet (much fine structure)	1	*c*
2·20 to 2·65	Complex multiplet	5	*e*, 5, 6, 7, 8
2·98	Multiplet	1	*d*
2·95 to 3·05	Doublet	1	3
3·07 to 3·17	Doublet	1	4
−5·22	Broad multiplet (weak)	1	OH

The protons are labelled as follows—



For α-naphthol, the hydroxyl proton was observed at τ 3·65, whereas for *o*-α-PAN the signal is observed at τ −5·22. This is a clear indication that hydrogen bonding occurs, and that the hydrogen-bond shift is comparable with, but slightly less than, that observed for *o*-β-PAN. An interesting feature of this signal is that it is much less pronounced than the corresponding signal for *o*-β-PAN, which may be due to a combination of relaxation, exchange and structural effects.[39]

The pyridyl and naphthol protons of *o*-α-PAN are in an environment similar to that in which they occur in *o*-β-PAN. As a consequence, the signals are observed at approximately the same positions, the variations being slight.

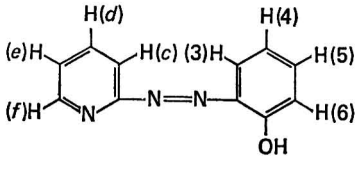
2-(2-*Pyridylazo*)*phenol* (o-*PAP*)—The signals of the spectrum obtained for this compound are listed in Table IX.

TABLE IX

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF *o*-PAP

τ	Peak	Integration	Assignment
1·26 to 1·30	Doublet with much splitting	1	*f*
1·94 to 2·00	Doublet (fine structure)	1	*c*
2·07 to 2·20	Multiplet	2	*e*, 3
2·50 to 2·70	Multiplet	2	*d*, 5
2·82 to 3·00	Multiplet	2	4, 6
−2·86	Broad singlet	1	OH

The protons are labelled as follows—



The intramolecular hydrogen bonding expected to be present in this reagent is confirmed by the large hydrogen-bond shift of the hydroxyl proton to τ −2·86.

A significant feature of this spectrum is that the signal of the pyridine proton *f* is well removed from the others. It occurs as a doublet at τ 1·26 to 1·30 with much fine structure due to *ortho*, *meta* and *para* coupling of the protons *e*, *d* and *c*, respectively. Another feature of the spectrum is the decreased de-shielding of proton *c*, which is located as a doublet at τ 1·94 to 2·00. This decreased de-shielding is due to the increased aromaticity of the phenol ring and the consequent loss of bond fixation. The increased aromaticity is further reflected in the position of proton 3. This proton, which is in conjugation with the azo group, is in a similar environment to proton *c* and the corresponding signal is contained in the multiplet in the range τ 2·07 to 2·20. It is likely that the signal for proton 3 contributes to the central largest peak at τ 2·14. The remainder of this multiplet, which integrates for two protons, consists of the triplet of the pyridine proton *e*. The remaining γ-pyridine proton *d* is observed as the usual multiplet in the range τ 2·50 to 2·70. Also contained in this multiplet is the phenol proton 5, in which the triplet peaks have coupling constants matched by protons 4 and 6.

The electron-donating effect of the phenol hydroxyl group should be noticeable at both the *o*- and *p*-positions of the phenol ring. As a result, both protons 4 and 6 should be shielded, the effect being greatest for proton 6. This proton occurs as a doublet at τ 2·91 to 2·99, the coupling constant being 8 Hz, which is matched for proton 5. This doublet is part of a multiplet, the remainder of which is the expected triplet of proton 4.

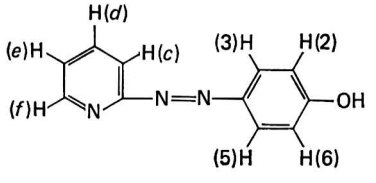
4-(2-*Pyridylazo*)*phenol* (p-*PAP*)—The signals observed in the spectrum are summarised in Table X.

TABLE X

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF *p*-PAP

τ	Peak	Integration	Assignment
2·95 to 3·04	Doublet	2	2, 6
2·07 to 2·16	Doublet	2	3, 5
1·91 to 2·56	Multiplet	3	*c*, *d*, *e*
1·30 to 1·35	Highly split doublet	1	*f*
−0·46	Singlet	1	OH

The protons are labelled as follows—



The spectrum of this reagent is less complicated than those of the reagents already discussed because of the equivalence of the phenol protons (Fig. 4). The very strong upfield doublet at τ 2·95 and 3·04 integrates for two protons, and can be assigned to protons 2 and 6. These protons are *ortho* to the hydroxyl group, and are equivalent, thus giving rise to identical signals. These two protons are split by the two equivalent protons 3 and 5, which are located by the powerful doublet at τ 2·07 to 2·16. This doublet is the mirror image of the first doublet and has the same splitting of 9 Hz.

The pyridyl protons have the usual type of signals in the expected regions. Proton *f* has the downfield multiplet expected. The other pyridine protons, *e*, *d* and *c*, are located in the highly complex series of signals in the range τ 1·9 to 2·6.

One of the noticeable features of the spectrum is the occurrence of a sharp singlet signal at τ −0·46, which can be assigned to the hydroxyl proton (Fig. 4). The position and shape of this signal suggests that the introduction of a *para*-hydroxyl group leads to a decrease in hydrogen bonding. This evidence, coupled with the results of the infrared studies, indicates that the decreased hydrogen-bond shift is due to the presence of intermolecular hydrogen bonding, in contrast with the intramolecular bonding in the other reagents.

NUCLEAR MAGNETIC RESONANCE SPECTRA OF CHELATES—

The spectra of the nickel(II) and zinc(II) chelates of *o*-α-PAN, *o*-β-PAN and *o*-PAP have been obtained. These spectra were found to be very different from those of the parent

ligands. The spectra of the nickel chelates were very poor, with small, ill defined signal peaks. The spectra of the zinc chelates were much clearer, with strong, well defined signals. Unlike the mass and infrared spectra, similar patterns were not observed with the different metals, but the three zinc spectra were very similar, as were the nickel spectra.

Detailed interpretation of these spectra is exceedingly complicated, as the review of the nuclear magnetic resonance characteristics of paramagnetic molecules by Eaton and Phillips[35] clearly indicates, and was not attempted.

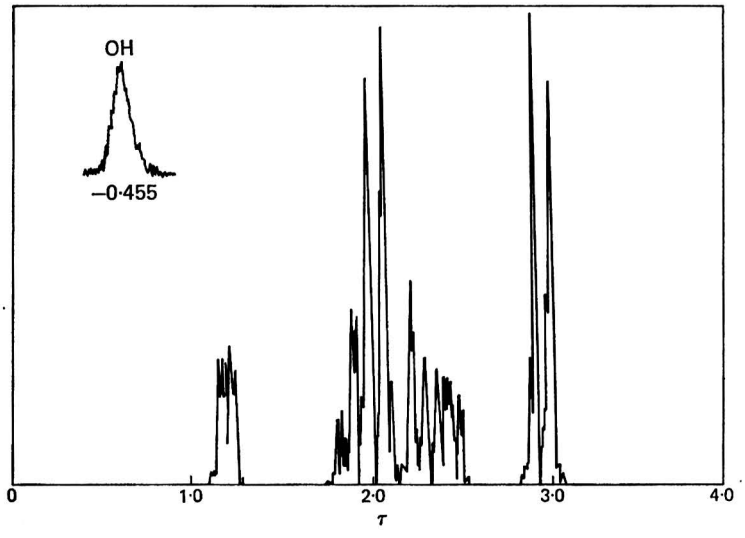


Fig. 4. Nuclear magnetic resonance spectrum of *p*-PAP

General conclusions

The foregoing discussions show that these three spectroscopic techniques can contribute greatly to the understanding of the chemistry of chelates. In addition, the methods can be used to confirm many of the conclusions obtained from solution studies, and as such are useful complementary techniques. It seems that mass spectrometry and infrared spectroscopy are the most useful, as nuclear magnetic resonance spectrometry is somewhat restricted.

It is clear that the compounds have now been correctly defined and that the compound previously reported[40] as 4-(2-pyridylazo)-1-naphthol (*p*-α-PAN) is in fact 2-(2-pyridylazo)-1-naphthol. However, these techniques do not provide a ready explanation for the large difference in pK values between *o*-α-PAN and *o*-β-PAN, which led to the initial mis-identification. The infrared and nuclear magnetic resonance spectra both indicate strong intramolecular hydrogen bonding of comparable strength. It is clear from the infrared spectra that the reagents act as terdentate ligands so that the basic stereochemistry of the chelates is fixed. There are, however, eight basic geometrical isomers of the reagent, depending on whether the ring systems are *cis* or *trans* to the diazo-nitrogen group and the relative positions of the pyridine-nitrogen and the hydroxyl group. With the aid of models (Prentice-Hall Framework Molecular Models), it is possible to envisage that two of these eight positions, by virtue of hydrogen bonding, will be much more favoured than the others, but that one might result in a stronger hydrogen bond than the other. It is therefore possible that the difference in the pK values is explained by the geometrical configuration of the reagent. The spectroscopic techniques applied do not give any information about this possibility, which will have to be checked by an X-ray determination or by a full equilibrium study in order to isolate the relative contributions of the enthalpy and entropy terms to the free energy change.

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Pyridylazonaphthols (PANs) and Pyridylazophenols (PAPs) as Analytical Reagents

Part II.* Spectrophotometric and Solvent-extraction Studies of Complex Formations

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The reactions between 2-(2-pyridylazo)-1-naphthol (*o*-α-PAN), 1-(2-pyridylazo)-2-naphthol (*o*-β-PAN) and 2-(2-pyridylazo)phenol (*o*-PAP) with manganese(II), zinc(II) and lanthanum(III) and 4-(2-pyridylazo)phenol (*p*-PAP) with cobalt(II), nickel(II) and copper(II) have been studied. The spectrophotometric procedure based on linear extrapolation, as used by Sommer, has been critically evaluated. The results from the spectrophotometric method have been used to predict the optimum conditions for solvent extraction. It is shown that this procedure is a valuable approach for systems in which hydroxy-complexes are common.

SEVERAL studies have shown that *o*-β-PAN is very useful for the extraction of many cations.[1–3] However, the extraction systems are often more complex than some of the early work suggests, and at present few detailed solvent-extraction studies have been made. Preliminary studies showed that 2-(2-pyridylazo)-1-naphthol (*o*-α-PAN) is often more advantageous than 1-(2-pyridylazo)-2-naphthol (*o*-β-PAN) and that 2-(2-pyridylazo)phenol (*o*-PAP) and 4-(2-pyridylazo)phenol (*p*-PAP) also form extractable complexes. The conventional method of determining equilibrium constants from solvent-extraction experiments is time consuming. It is possible, in principle, to determine the complex formation constants by other means, to determine the partition coefficient of the reagent and complex experimentally and to use the values obtained to predict the extraction graphs. One practical difficulty is that the constants that are obtained from solvent-extraction data relate to the aqueous phase saturated with the organic solvent and as, almost by definition, the complex is only sparingly soluble in water, the equilibrium constants must be determined in some other medium, *e.g.*, 1 + 1 dioxan - water, so that they cannot be used directly for predicting extraction equilibria. Spectrophotometric methods can partially overcome this difficulty because solutions can be used that are so dilute that the complex can be maintained with such a small proportion of organic constituent that the values of the equilibrium constants are close enough to those obtained by solvent-extraction procedures to be interchanged. However, most spectrophotometric methods are based on Job's method, which can result in misleading or erroneous results, or both,[4] and the study of a system over a wide range of conditions with these methods is extremely tedious.

Recently, Sommer and co-workers[5–11] have demonstrated that spectrophotometric procedures based upon linear extrapolation, when used with care, can be used most advantageously to study the complex equilibria of systems based on compounds analogous to the compounds discussed below. A practical advantage of their approach is that it is based upon the analysis of pH - absorbance curves so that no superfluous information is gathered and basic data are interpreted fully.

In this paper, we assess this procedure by analysing several systems, for some of which results are already available for comparison, and show how it can be used for predicting extraction curves with an accuracy that is acceptable to the analyst.

EXPERIMENTAL

REAGENTS—

Salts and solvents of analytical-reagent grade purity or better were used throughout.

* For Part I of this series, see p. 377. Parts III and IV will appear in the July issue.

† Present address: BP Chemicals (U.K.) Ltd., Llandarcy, Swansea.

1-(2-*Pyridylazo*)-2-*naphthol* (o-β-*PAN*).
2-(2-*Pyridylazo*)-1-*naphthol* (o-α-*PAN*).
2-(2-*Pyridylazo*)*phenol* (o-*PAP*).
4-(2-*Pyridylazo*)*phenol* (p-*PAP*).

The above four reagent solutions were prepared and purified as described in Part I. Solutions in absolute or aqueous ethanol were prepared for spectrophotometric studies and in carbon tetrachloride or chloroform for solvent extraction. The concentrations are given in the procedures. The solutions were taken to be standard and the validity of this assumption was checked occasionally by spectrophotometric titration of a standardised metal-ion solution.

Metal-ion solutions—Solutions of manganese(II), zinc(II), nickel(II), cobalt(II) and lanthanum(II) were prepared and standardised titrimetrically with EDTA by standard procedures.

Buffer solutions—Standard chloride, phthalate, phosphate, borate and hydroxide buffer solutions to cover the pH range from 0 to 12 were used.

Sodium perchlorate—Solid sodium perchlorate was used in order to maintain an ionic strength of $0{\cdot}10 \pm 0{\cdot}01$.

Radioisotopes—Manganese-54 and zinc-65 were obtained from the Radiochemical Centre, Amersham. They were diluted and mixed with carrier manganese(II) and zinc(II) so that solutions of known concentration and radioactivity were obtained.

APPARATUS—

pH meter—Radiometer, Model M4C.

Spectrophotometers—Unicam SP500, SP600 and SP800 and Cary, Model 16, instruments were used as appropriate. Absorbance values used for the calculation of equilibrium constants were obtained on fixed-wavelength instruments. One-centimetre cells were used.

Radioactivity—A 1-inch well sodium chloride (thallium-activated) crystal connected to a photomultiplier and a 1DL 1700 scaler was used to measure the radioactivity. Samples of constant volume were taken so as to ensure constant geometry and sufficient counts were taken so as to ensure a statistical error of not more than 1 per cent. on all except the very low count-rates, when an error of 10 per cent. was accepted.

Computer—An IBM 1600 computer was used for the calculation of constants based on the spectrophotometric data and the statistical analyses of them. The standard program for linear regression in two variables 1620/6.0.27 from the 1620 General Program Library was used.

PROCEDURES—

Spectrophotometric determination of acid-dissociation constants—A 10-ml aliquot of a solution of o-α-PAN (1×10^{-4} M) in absolute ethanol or o-PAP ($2{\cdot}5 \times 10^{-4}$ M) or p-PAP ($1{\cdot}25 \times 10^{-4}$ M) in 12·5 per cent. aqueous ethanol was placed in a 25-ml calibrated flask and sufficient solid sodium perchlorate to maintain an ionic strength of $0{\cdot}10 \pm 0{\cdot}01$ was added. The solution was then made up to the mark with buffer solution. The solution was mixed well, the spectrum recorded and the absorbance and pH were measured. A pH - absorbance curve was plotted for each of the reagents at suitable wavelengths and the pK_a values were calculated from the inflection point as determined from a graph of the differential $\Delta A/\Delta$pH against pH. The pK_a values were also calculated from the same pH - absorbance curve by the procedure described below.

Spectrophotometric determination of formation constants—pH - absorbance curves were obtained with both the metal ion and the reagent in excess. The general procedure was to place 10 ml of ethanolic solution, 10 ml of metal-ion solution and 5 ml of buffer in a 25-ml calibrated flask that contained sufficient solid sodium perchlorate to maintain the ionic strength of the final solution at $0{\cdot}10 \pm 0{\cdot}01$. These solutions were mixed thoroughly and the colour was allowed to develop to a maximum (a few minutes). The absorbance remained constant for the period of the measurement and showed little change after 24 hours. The spectra were recorded, the absorbances were determined at suitable wavelengths and the pH values were measured. The measurements were carried out at room temperature. The method of continuous variations[12] and the mole-ratio method[13] were also applied to some systems.

Solvent extraction and determination of acid-dissociation constants—The reagent solutions were made up in carbon tetrachloride (for o-α-PAN, o-β-PAN and o-PAP) or chloroform (for p-PAP) to concentrations of $1{\cdot}0 \times 10^{-2}$, $1{\cdot}0 \times 10^{-2}$, $2{\cdot}0 \times 10^{-3}$ and $5{\cdot}0 \times 10^{-4}$ M,

respectively (*p*-PAP is insufficiently soluble in carbon tetrachloride for the distribution ratio to be measured accurately). A 5-ml aliquot of reagent solution was placed in a vial and 60 ml of buffered aqueous phase of ionic strength $0{\cdot}10 \pm 0{\cdot}01$ were added. The solutions were shaken overnight in a box shaker that was maintained thermostatically at 24 ± 1 °C. The phases were allowed to separate and the absorbance of the organic phase was measured with the Unicam SP600 instrument and that of the aqueous phase, after adjustment of the pH to zero with concentrated hydrochloric acid, with the Cary 16 instrument. Calibration graphs were used to convert the absorbance values into concentration values.

The distribution ratio of the reagent, D, was calculated from

$$D = (C_T - C_w)V_w/C_wV_o$$

for $D > 1$, or

$$D = C_oV_w/C_wV_o$$

for $D < 1$, where C_T is the total concentration of the reagent, C_o and C_w are the concentrations of the reagent in the organic and aqueous phase, respectively, and V_o and V_w are the volumes of the organic and aqueous phase, respectively.

Log D was plotted against pH and the partition coefficient of the reagent, K_{DR}, and acid-dissociation constants, K_{a_1} and K_{a_2}, were calculated from[14]

$$D = K_{DR}\{[H]/K_{a_1} + 1 + K_{a_2}/[H]\}$$

Solvent extraction of metal ions—Reagent solutions were $5{\cdot}0 \times 10^{-3}$ M in carbon tetrachloride. Stock metal-ion solutions of 5×10^{-3} M were diluted to a suitable concentration when the extraction was followed spectrophotometrically. When the extraction was followed radiochemically, a solution that was as dilute as the specific activity of the isotope would allow was used and a 0·2 M solution of sodium perchlorate was prepared. Equal volumes of organic and aqueous phase were used, the latter consisting of 2 ml of metal-ion solution, 2 ml of buffer solution and 4 ml of sodium perchlorate solution. The solutions were placed in a vial and shaken overnight, the layers were separated and the radioactivity of each phase was measured. The total activity in the two phases was computed and if it was less than 80 per cent. of the total activity in the vial, the results were discarded.

RESULTS AND DISCUSSION

The following symbols are used—

HR, H_2R^+, R^-		the neutral, protonated and ionised forms of the reagent, respectively
$[C_x]$		the total analytical concentration of species x
ϵ_x		the molar absorptivity of species x
A		the total absorbance
D		$\lvert M\rvert_o/\lvert M\rvert_w$, the distribution ratio
K_{DR}, K_{DX}	=	$[HR]_o/[HR]_w$ or $[MR_n]_o/[MR_n]_w$, the partition coefficient of the reagent and extractable complex, respectively
K_{a_1}	=	$[HR][H^+]/[H_2R^+]$, the first acid-dissociation constant
K_{a_2}	=	$[R^-][H^+]/[HR]$, the second acid-dissociation constant
K_{MR}	=	$[MR]/[M][R]$
K_{MR_2}	=	$[MR_2]/[M][R^-]^2$, the over-all formation constant of MR_2
$^*K_{MR_2}$	=	$[MR_2][H^+]^2/[M][HR]^2$
$K_{MR_2(OH)}$	=	$[MR_2OH]/[MR_2][OH]$
α_x	=	$[H_{n-x}R]/\sum_{x=o}^{x=n}[H_{n-x}R]$
β	=	$[M]/C_{M_{Tot}}$
f	=	the fractional extent of completion of the reaction as written.

Charges are omitted unless possible ambiguity would arise from their absence.

REAGENT EQUILIBRIA IN THE ABSENCE OF METAL IONS

SPECTROPHOTOMETRIC STUDIES—

Principles of graphical analysis of absorbance versus *pH curves*—This method was re-examined by Sommer[5] in 1964 and has since been applied to the study of a number of reagents.[6,7] The principles involved are summarised below.

The method involves a detailed algebraic study of the equilibria of the reagent, and in the present study these are taken to be:

$$HR \overset{K_{a_2}}{\rightleftharpoons} R^- + H^+ \quad \text{(Equilibrium 1)}$$

$$H_2R^+ \overset{K_{a_1}}{\rightleftharpoons} HR + H^+ \quad \text{(Equilibrium 2)}$$

On the initial assumption that these equilibria represent the true reagent equilibria, a series of linear algebraic transformations can be derived. Experimental values of absorbance and pH are introduced into these transformations, which then provide values of the acid-dissociation constants, K_{a_1} and K_{a_2}, and also molar absorptivity values of individual reagent species. An observed lack of linearity in these transformations indicates that the assumed equilibria are incorrect.

In Equilibrium 1, if it is assumed that only the neutral (HR) and anionic (R^-) forms of the reagent are present, it follows that the total reagent concentration, C_R, is given by

$$\begin{aligned} C_R &= [HR] + [R] \\ &= [R]\left\{\frac{[H]}{K_{a_2}} + 1\right\} \quad .. \quad .. \quad .. \quad .. \quad (1) \end{aligned}$$

The total absorbance, A, is given by

$$\begin{aligned} A &= \epsilon_{HR}[HR] + \epsilon_R[R^-] \\ &= [R]\left\{\epsilon_{HR}\frac{[H]}{K_{a_2}} + \epsilon_R\right\} \quad .. \quad .. \quad .. \quad .. \quad (2) \end{aligned}$$

Substitute for [R] from equation (1) and re-arrange to give

$$\frac{[H]}{K_{a_2}} + 1 = \frac{C_R}{A}\left\{\epsilon_{HR}\frac{[H]}{K_{a_2}} + \epsilon_R\right\}$$

Multiply throughout by $1/\epsilon_R$ and re-arrange to give

$$\frac{C_R}{A} = \frac{1}{\epsilon_R} + \frac{[H](A - \epsilon_{HR}C_R)}{K_{a_2}\epsilon_R A} \quad .. \quad .. \quad .. \quad .. \quad (I)$$

A graph of C_R/A *versus* $[H]A$ is usually a straight line of intercept $1/\epsilon_R$, as $A \gg \epsilon_{HR}C_R$. Values of the acid-dissociation constant, K_{a_2}, can be obtained by calculation by using corresponding values of absorbance and pH.

Alternatively, it can be argued that

$$C_R = [H]\left\{1 + \frac{K_{a_2}}{[H]}\right\} \quad .. \quad .. \quad .. \quad .. \quad (1a)$$

and

$$A = [HR]\left[\epsilon_{HR} + \frac{\epsilon_R K_{a_2}}{[H]}\right] \quad .. \quad .. \quad .. \quad .. \quad (2a)$$

which give

$$\frac{K_{a_2}}{[H]} + 1 = \frac{C_R}{A}\left[\epsilon_{HR} + \frac{C_R K_{a_2}}{[H]}\right]$$

This equation, on multiplication by $1/\epsilon_{HR}$ and subsequent re-arrangement, gives

$$\frac{C_R}{A} = \frac{1}{\epsilon_{HR}} + \frac{K_{a_2}(A - C_R\epsilon_R)}{\epsilon_{HR}} \cdot \frac{1}{A[H]} \quad .. \quad .. \quad .. \quad (IA)$$

Equation (IA) should also yield a straight line when C_R/A is plotted against $1/A[H]$. The intercept of this line represents the reciprocal of the molar absorptivity, ϵ_{HR}. Values of K_{a_2} can be calculated from corresponding values of absorbance and pH.

Alternatively, a value of ϵ_R, which can be found from other experiments, can be substituted and C_R/A plotted against $(A - C_R\epsilon_R)/A[H]$. A similar procedure can be adopted to solve graphically all of the subsequent transformations, where the linearity is not obvious.

These equations are therefore derived simply from consideration of mass balance and equilibrium constants, with the one important algebraic manipulation being effected by the multiplet $1/\epsilon_{HR}$ or $1/\epsilon_{R}$.

In equilibrium 2, if it is assumed that $[R^-]$ is negligible compared with $[H_2R]$ and [HR], then

$$C_R = [HR] + [H_2R]$$

and

$$A = \epsilon_{HR}[HR] + \epsilon_{H_2R}[H_2R]$$

By using these equations and proceeding in the same manner as before, it can be shown that

$$\frac{C_R}{A} = \frac{1}{\epsilon_{H_2R}} + \frac{K_{a_1}(A - \epsilon_{HR}C_R)}{\epsilon_{H_2R}} \cdot \frac{1}{A[H]} \quad .. \quad .. \quad .. \quad \text{(II)}$$

and

$$\frac{C_R}{A} = \frac{1}{\epsilon_{HR}} + \frac{(A - \epsilon_{H_2R}C_R)}{K_{a_1}\epsilon_{HR}} \cdot \frac{[H]}{A} \quad .. \quad .. \quad .. \quad .. \quad \text{(IIA)}$$

For equation (II), the graph of C_R/A *versus* $1/A[H]$ should be a straight line. Similarly, the graph of C_R/A *versus* $[H]/A$ for equation (IIA) should be linear. Values of the first acid-dissociation constant, K_{a_1}, and of the molar absorptivities, ϵ_{HR} and ϵ_{H_2R}, can be calculated from these equations.

Absorbance curves and results of calculations—The absorbance *versus* pH curves are shown in Fig. 1. The wavelength of maximum absorption for the various species and isosbestic points are given in Table I. The results obtained for each transformation are summarised in Table II. The transformations are represented as straight-line equations of the form $y = mx + c$, where $y = C_R/A$ and $x = 1/A[H]$ or $[H]/A$ multiplied by a power factor to keep x and y mainly within the range 0·1 to 10.

The values obtained are in good agreement with those obtained from the inflection point of the pH - absorbance curve. It is slightly advantageous that the molar absorptivity is calculated simultaneously and that a check on the nature of the equilibrium is provided. If two protons were to be released simultaneously, for example, the observed transformations would be curved or extremely ill defined. The least-squares analysis permits the precision of the result to be calculated. It was found that because the method is based on an extrapolation, it is very sensitive to the choice of points used for the calculation. Inevitably, at one end of the part of the pH - absorbance curve that is being used for analysis, the basic assumption that one species is of negligible concentration compared with the others becomes less valid. A point from this part of the curve will therefore be "bad" and because it will be at the end of the transformation it can exert a disproportionate effect on the least-squares analysis. Several checks are possible: (*i*) the point may be so "bad" that it falls outside the 95 per cent. confidence limits and can be rejected; (*ii*) the point can be discarded and the analysis carried out again, and if the result is then the same the point can be accepted and if it is markedly different it can be rejected; and (*iii*) a different transformation can be used and the results compared. Rejection by the second of these procedures is not entirely satisfactory and care was taken to reject not more than one result and to confirm, by examination of the experimental pH - absorbance curves, that this result was a marginal value. Checks of (*i*) and (*iii*) were always carried out. A practical disadvantage of the method, therefore, is that a larger number of "good" experimental points must be obtained than is necessary for the simpler spectrophotometric procedures.

SOLVENT-EXTRACTION STUDIES—

The experimental curves of log D *versus* pH were very similar to that already published for *o*-α-PAN.[14] All of the curves indicated that a protonated species of reagent was formed under acidic conditions and an anionic species under alkaline conditions. The pK values obtained are given in Table III. The logarithm of the partition coefficients for *o*-α-PAN, *o*-β-PAN, *o*-PAP and *p*-PAP are 5·20, 5·00, 3·75 and 2·53, respectively. It was found that although the partition coefficients for *o*-α-PAN and *o*-β-PAN were an order of magnitude greater than those reported earlier, the acid-dissociation constants were in reasonable agreement. This agreement is surprising, as the values of the partition coefficients are used in the calculation of the acid-dissociation constants. With such high partition coefficients, the

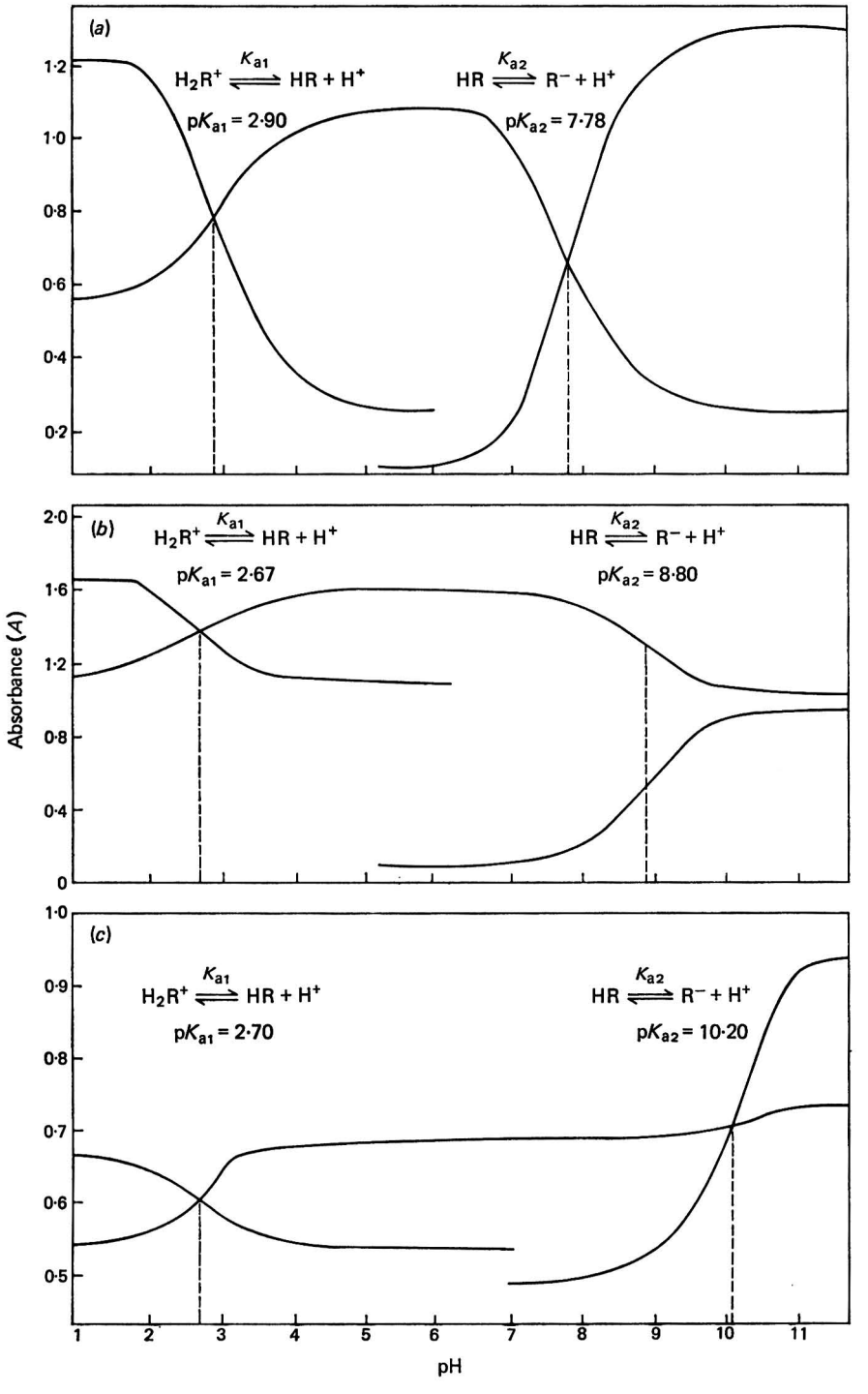

Fig. 1. Absorbance *versus* pH graphs: (*a*) $5{\cdot}0 \times 10^{-5}$ M *p*-PAP in 5 per cent. aqueous ethanol; (*b*) $1{\cdot}0 \times 10^{-4}$ M *o*-PAP in 5 per cent. aqueous ethanol; and (*c*) $4{\cdot}0 \times 10^{-5}$ M *o*-α-PAN in 40 per cent. aqueous ethanol

TABLE I

ABSORBANCE MAXIMA, MOLAR ABSORPTIVITIES AND ISOSBESTIC POINTS

	H_2R^+		HR		R^-		Isosbestic point	
Reagent	λ_1/nm	ϵ	λ_2/nm	ϵ	λ_3/nm	ϵ	$H_2R \leftrightharpoons HR^+ + H^+$	$HR \leftrightharpoons R^- + H^+$
p-PAP	402	$2{\cdot}38 \times 10^4$	358	$1{\cdot}89 \times 10^4$	442	$2{\cdot}10 \times 10^4$	373	382
o-PAP	352	$1{\cdot}62 \times 10^4$	328	$1{\cdot}56 \times 10^4$	480	$9{\cdot}16 \times 10^3$	337	410
o-α-PAN	365	$1{\cdot}63 \times 10^4$	486	$1{\cdot}62 \times 10^4$	520	$2{\cdot}08 \times 10^4$	476	—

TABLE II

MOLAR ABSORPTIVITIES AND ACID-DISSOCIATION CONSTANTS OF REAGENTS FROM LEAST-SQUARES FIT OF TRANSFORMATIONS (I), (IA), (II) AND (IIA)

Transformation	Reagent	$y = mx + c$	Correlation coefficient	Standard error of		Molar absorptivity	Acid-dissociation constant
				slope, m	estimate		
						ϵ_R	pK_{a_2}
I	*p*-PAP	$y = 0{\cdot}101x + 4{\cdot}756$	0·992	0·0046	0·183	$2{\cdot}10 \times 10^4$	$7{\cdot}66 \pm 0{\cdot}02$
	o-PAP	$y = 0{\cdot}023x + 1{\cdot}093$	0·990	0·0010	0·057	$9{\cdot}16 \times 10^3$	$8{\cdot}77 \pm 0{\cdot}02$
	o-α-PAN	$y = 0{\cdot}081x + 4{\cdot}808$	0·988	0·0045	0·048	$2{\cdot}08 \times 10^4$	$10{\cdot}17 \pm 0{\cdot}02$
						ϵ_{HR}	pK_{a_2}
IA	*p*-PAP	$y = 0{\cdot}264x + 5{\cdot}056$	0·979	0·0192	0·198	$1{\cdot}98 \times 10^4$	$7{\cdot}78 \pm 0{\cdot}02$
	o-PAP	$y = 0{\cdot}018x + 6{\cdot}638$	0·975	0·0014	0·091	$1{\cdot}51 \times 10^4$	$8{\cdot}92 \pm 0{\cdot}04$
	o-α-PAN	—	—	—	—	—	—
						ϵ_{H_2R}	pK_{a_1}
II	*p*-PAP	$y = 0{\cdot}183x + 4{\cdot}203$	0·980	0·0142	0·057	$2{\cdot}38 \times 10^4$	$3{\cdot}00 \pm 0{\cdot}03$
	o-PAP	$y = 0{\cdot}030x + 6{\cdot}189$	0·992	0·0015	0·054	$1{\cdot}62 \times 10^4$	$2{\cdot}72 \pm 0{\cdot}06$
	o-α-PAN	$y = 0{\cdot}055x + 6{\cdot}154$	0·993	0·0020	0·018	$1{\cdot}63 \times 10^4$	$2{\cdot}73 \pm 0{\cdot}03$
						ϵ_{HR}	pK_{a_1}
IIA	*p*-PAP	$y = 0{\cdot}044x + 5{\cdot}561$	0·978	0·0033	0·150	$1{\cdot}80 \times 10^4$	$2{\cdot}94 \pm 0{\cdot}07$
	o-PAP	$y = 0{\cdot}041x + 6{\cdot}621$	0·989	0·0020	0·035	$1{\cdot}51 \times 10^4$	$2{\cdot}64 \pm 0{\cdot}05$
	o-α-PAN	$y = 0{\cdot}099x + 6{\cdot}182$	0·990	0·0049	0·023	$1{\cdot}62 \times 10^4$	$2{\cdot}60 \pm 0{\cdot}05$

No calculations were carried out for *o*-α-PAN by using transformation (IIA) because of the proximity of the $\lambda_{max.}$ values of the reagent species HR and R^-.

presence of a small amount (*e.g.*, 0·1 per cent.) of a coloured impurity that is less extractable than the reagent can profoundly affect the experimentally determined value of the partition coefficient, but would scarcely affect the log *D versus* pH curve when the value of the distribution ratio is less than 100. This effect would result in the experimentally determined pK_{a_1} value being greater than and the pK_{a_2} value being less than the true values. As there is an internal consistency in both sets of studies, which should prevent miscalculation, we can offer no explanation for the discrepancy unless there is some slight difference between the samples of reagent-grade carbon tetrachloride used in the two studies. The values obtained in this study were used throughout this work.

TABLE III

ACID-DISSOCIATION CONSTANTS AT AN IONIC STRENGTH OF 0·10

Reagent	Method*	Medium	pK_{a_1}	pK_{a_2}	Reference
o-β-PAN	Sp.	20% aqueous dioxan	1·9	12·2	15
	Pot.	50% aqueous dioxan	<2	12·3	16
	S.E.	—	2·9	11·5	17
	S.E.	Chloroform - water	2·9	11·2	18
o-α-PAN	Pot.	50% aqueous dioxan	2·54	10·74	14
	Sp.	Water	3·0	9·1	14
	S.E.	Water - carbon tetrachloride	3·1	9·5	14
	S.E.	Water - carbon tetrachloride	2·90	9·63	This work
	Sp.	50% aqueous methanol	2·29	10·00	19
	Sp.	40% aqueous ethanol	2·67	10·17	This work, graphical
	Sp.	40% aqueous ethanol	2·70	10·23	This work, conventional
o-PAP	Sp.	50% aqueous methanol	1·85	9·42	20
	Sp.	5% aqueous ethanol	2·68	8·84	This work, graphical
	Sp.	5% aqueous ethanol	2·68	8·79	This work, conventional
	S.E.	Water - carbon tetrachloride	2·68	8·68	This work
p-PAP	Sp.	50% aqueous methanol	2·47	8·29	20
	Sp.	5% aqueous ethanol	2·97	7·72	This work, graphical
	Sp.	5% aqueous ethanol	2·86	7·76	This work, conventional
	S.E.	Water - carbon tetrachloride	3·58	7·55	This work

* Sp. = spectrophotometric; Pot. = potentiometric; S.E. = solvent extraction.

COMPLEX FORMATION EQUILIBRIA

SPECTROPHOTOMETRIC STUDIES—

The graphical method that is used for the determination of acid-dissociation constants can be applied in the study of the formation of complexes.

The method consists in first postulating the chelation reaction and the species formed over a particular pH range, then algebraically deriving transformations that would necessarily be followed if the postulates were correct. Typically, these transformations are straight lines, and false assumptions are readily detected by the presence of curvature or random scatter when experimental values are substituted into the transformations. All parts of the simple absorbance - pH curve can be subjected to such analysis, so that the various conditions of chelation can be deduced over a wide pH range. Normally, absorbance - pH curves are obtained in the presence of excess of reagent and excess of metal ions, so that the absorbance can be expressed generally as

$$A = f(\mathrm{pH})_{C_M,C_R}$$

$$A = f(C_M)_{\mathrm{pH},C_R}$$

and

$$A = f(C_R)_{\mathrm{pH},C_M}$$

Sommer and co-workers have summarised a large number of basic equations for a variety of chelation reactions in the presence of various concentrations of reagent and metal ions, and have since applied the method successfully to different systems. These systems include the reactions of 4-(2-thiazolylazo)resorcinol (TAR) and 4-(2-pyridylazo)resorcinol (PAR) with thallium and uranyl ions.[8–10] The reactions of copper(II), lead(II), cadmium(II), zinc(II) and bismuth(III) with TAR and of the lanthanides with PAR have also been reported.[6,11]

We have applied the method to the reactions of zinc(II), manganese(II), cobalt(II), nickel(II), lanthanum(III), copper(II) and titanium(IV) with *o*-α-PAN, *o*-β-PAN, *o*-PAP and *p*-PAP and compared the results when possible with those obtained by different methods. Most of the findings are given below but some will be dealt with in subsequent papers.

GRAPHICAL ANALYSIS OF ABSORBANCE CURVES—

The general approach can be illustrated by the derivation of a few basic equations. One common reaction is chelate formation when the reagent is predominantly in the neutral form. The reaction can be represented as

$$M + 2HR \overset{{}^{*}K_{MR_2}}{\rightleftharpoons} MR_2 + 2H \quad .. \quad .. \quad .. \quad .. \quad (3)$$

This reaction can be carried out with either metal ions or the reagent in excess and the unreacted reagent may or may not contribute to the absorbance at the wavelength of maximum absorbance of the chelate. The effects of these variations are considered below.

In the presence of excess of metal ions—In this instance, $[M] = C_M$, the total metal-ion concentration, and if it is assumed that ϵ_{HR} is negligible at the wavelength being used, then

$$A = \epsilon_{MR_2}[MR_2] \quad .. \quad .. \quad .. \quad .. \quad (4)$$

Furthermore, if it is assumed that the concentration of the intermediate chelate species, MR, is negligible, then

$$C_R = [HR] + 2[MR_2] \quad .. \quad .. \quad .. \quad .. \quad (5)$$

Re-arrange equation (5) and substitute for $[MR_2]$:

$$[HR] = \frac{C_R\epsilon_{MR_2} - 2A}{\epsilon_{MR_2}} \quad .. \quad .. \quad .. \quad .. \quad (6)$$

Divide equation (4) by equation (6) and substitute for $[MR_2]/[HR]$ by introducing the reaction constant, so that

$${}^{*}K_{MR_2} = \frac{A}{C_R\epsilon_{MR_2} - 2A} \cdot \frac{[H]^2}{[HR]C_M}$$

or

$$C_R\epsilon_{MR_2} - 2A = \frac{A[H]^2}{{}^{*}K_{MR_2}C_M[HR]}$$

Multiply through by $1/A\epsilon_{MR_2}$ and re-arrange:

$$\frac{C_R}{A} = \frac{2}{\epsilon_{MR_2}} + \frac{1}{{}^{*}K_{MR_2}C_M\epsilon_{MR_2}} \cdot \frac{[H]^2}{[HR]} \quad .. \quad .. \quad .. \quad (III)$$

When the reagent makes a contribution to the absorbance, the expression for the total absorbance requires an additional term:

$$A = \epsilon_{MR_2}[MR_2] + \epsilon_{HR}[HR] \quad .. \quad .. \quad .. \quad .. \quad (4a)$$

The steps outlined above then give

$$\frac{C_R}{A} = \frac{2}{\epsilon_{MR_2}} + \frac{1}{{}^{*}K_{MR_2}C_M\epsilon_{MR_2}} \cdot \frac{(A - C_R\epsilon_{MR})}{A} \cdot \frac{[H]^2}{[HR]} \quad .. \quad .. \quad (IIIA)$$

In the presence of excess of reagent—Under these conditions, $[HR] = C_R$, the total reagent concentration, and if the reagent absorption is negligible, then

$$[MR_2] = \frac{A}{\epsilon_{MR_2}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

and if [MR] is negligible compared with [M] and $[MR_2]$, then

$$C_M = [M] + [MR_2] \quad .. \quad .. \quad .. \quad .. \quad (8)$$

so that

$$[M] = \frac{C_M\epsilon_{MR_2} - A}{\epsilon_{MR_2}} \quad .. \quad .. \quad .. \quad .. \quad (9)$$

Divide equation (7) by equation (9), substitute for $[MR_2]/[M]$ and re-arrange, to give

$$C_M\epsilon_{MR_2} - A = \frac{A[H]^2}{{}^{*}K_{MR_2}C_R^2}$$

Multiply through by $1/A\epsilon_{MR_2}$, and re-arrange, so that

$$\frac{C_M}{A} = \frac{1}{\epsilon_{MR_2}} + \frac{1}{{}^*K_{MR_2}C_R^2\epsilon_{MR_2}} \cdot [H]^2 \quad .. \quad .. \quad .. \quad .. \quad (IV)$$

When the reagent absorbance is not negligible, an extra term can be introduced. In practice, we found that either the reagent absorbance was negligible or it represented such a large contribution that internal compensations on the spectrophotometer had to be made.

Another important type of reaction is the hydrolysis reaction

$$MR_2 + OH^- \overset{K_{OH}}{\rightleftharpoons} MR_2OH^- \quad .. \quad .. \quad .. \quad .. \quad (10)$$

If it is assumed that the hydroxy-complex makes no contribution to the absorption, then in the presence of both excess of reagent and excess of metal ions the total absorbance, A, is given by

$$A = \epsilon_{MR_2}[MR_2]$$

For excess of metal ions, the total reagent concentration, C_R, is given by

$$C_R = 2[MR_2] + 2[MR_2OH]$$

For excess of reagent, the total metal-ion concentration, C_M, is given by

$$C_M = [M] + [MR_2] + [MR_2OH]$$

In the presence of excess of reagent:

$$K_{OH} = \frac{(C_M\epsilon_{MR_2} - A)}{A} \cdot \frac{1}{[OH]}$$

or

$$\log K_{OH} = \log\frac{(C_M\epsilon_{MR_2} - A)}{A} + pOH \quad .. \quad .. \quad .. \quad (V)$$

The derivation of equations in the presence of excess of metal ions is academic because, in most systems, the metal hydroxide would be formed preferentially and be precipitated.

The transformations for these and other systems are given in Table IV; some are in logarithmic form because this form is more convenient for use in calculations. All of the transformations can be expressed as a linear function, although some contain two variables, [H] and [HR], in one term. In these instances, as for example transformation (III), ϵ_{MR_2} was calculated from another transformation, (IV), or by simpler conventional means, and this was used to calculate [HR] by means of equation (6). The calculation procedure is very similar to that used for the acid-dissociation constants and the same checks were applied. However, even greater care is necessary because although a pH - absorbance curve reflects the course of several reactions, which allows these reactions to be detected and studied, it is easier to introduce "bad" points into the calculations. A further check was therefore always carried out. The values of the calculated constants were used to derive a pH - absorbance curve and this curve was then compared with the experimental curve.

Zinc(II) chelates of o-α-*PAN*, o-β-*PAN and* o-*PAP*—pH - absorbance curves obtained for the chelates of each reagent in the presence of excess of metal ions and of reagent are shown in Fig. 2. The absorption maxima of the zinc(II) chelate with *o*-α-PAN, *o*-β-PAN and *o*-PAP occurred at 548 and 590, 514 and 550, and 530 nm, respectively, the chelates of the naphthol derivatives each having two maxima, and the pH - absorbance curves were obtained at 590, 550 and 530 nm, respectively. These curves indicate that each chelate has a stoicheiometry of metal to ligand of 1:2. At the upper limits of pH, the absorbance values became inconsistent and no smooth curve could be drawn. Hence, over the pH range 6 to 8 in which the chelate is being formed, the basic reaction would appear to be

$$Zn + 2HR \rightleftharpoons ZnR_2 + 2H$$

Transformations (III) and (IV) were therefore used for the reactions with *o*-α-PAN and *o*-PAP and transformation (IIIA) was used for *o*-β-PAN, as the reagent contributed to the absorbance. The results are given in Table V, which shows that there is good agreement between the molar absorptivities and stability constants determined in the presence of both excess of reagent and excess of metal ions. The agreement between these values, together with the linearity of transformation (IIIA) and hence of transformation (VIA), confirm that the chelation reaction

TABLE IV

BASIC COMPLEX FORMATION REACTIONS AND LINEAR TRANSFORMATIONS

Principal reaction	Condition	Assumptions	Transformation	No.
$M + 2HR \rightleftharpoons MR_2 + 2H$	Excess of metal ions	[MR] and ϵ_{HR} negligible	$\frac{C_R}{A} = \frac{2}{\epsilon_{MR_2}} + \frac{[H]^2}{{}^*K_{MR_2} C_M \epsilon_{MR_2} [HR]}$	III
		[MR] negligible	$\frac{C_R}{A} = \frac{2}{\epsilon_{MR_2}} + \frac{[H]^2 (A - C_R \epsilon_{MR})}{{}^*K_{MR_2} C_M \epsilon_{MR_2} [HR] A}$	IIIA
	Excess of reagent	[MR] and ϵ_{HR} negligible	$\frac{C_M}{A} = \frac{1}{\epsilon_{MR_2}} + \frac{[H]^2}{{}^*K_{MR_2} C_R^2 \epsilon_{MR_2}}$	IV
$M + 2R \rightleftharpoons MR_2$	Excess of metal ions	[MR] and ϵ_{HR} negligible	$\log K_{MR_2} + 2pH = \log A / \{(C_R \epsilon_{MR_2} - 2A)[HR] K_{a_2}^2 C_M\}$	VI
		[MR] negligible	$\log K_{MR_2} + 2pH = \log (A - C_R \epsilon_{HR}) / \{(C_R \epsilon_{MR_2} - 2A)[HR] K_{a_2}^2 C_M\}$	VIA
	Excess of reagent	[MR] and ϵ_{HR} negligible [HR] not negligible	$\log K_{MR_2} + 2 \log a_1 = \log \frac{A}{(C_M \epsilon_{MR_2} - A) C_R^2}$	VII
$MR_2 + OH \rightleftharpoons MR_2OH$	Excess of reagent	[M], [MR], ϵ_{HR} and ϵ_{MR_2OH} negligible	$\log K_{OH} = \log (C_M \epsilon_{MR_2} - A)/A + pOH$	V
$M + HR \rightleftharpoons MR + H$	Excess of metal ions	[MR_2] and ϵ_{HR} negligible	$\frac{C_R}{A} = \frac{1}{\epsilon_{MR}} + \frac{[H]}{{}^*K_{MR} C_M \epsilon_{MR}}$	VIII
	Excess of reagent	[MR_2] and ϵ_{HR} negligible	$\frac{C_M}{A} = \frac{1}{\epsilon_{MR}} + \frac{[H]}{{}^*K_{MR} C_R \epsilon_{MR}}$	IX
$M + R \rightleftharpoons MR$	Excess of metal ions	[MR_2], ϵ_{HR} and ϵ_R negligible	$\log K_{MR} + pH = \log \frac{A}{(C_R \epsilon_{MR} - A) C_M K_{a_2}}$	X
	Excess of reagent	[MR_2], ϵ_{HR} and ϵ_R negligible [HR] not negligible	$\log K_{MR} + pH = \log \frac{A}{(C_M \epsilon_{MR} - A) C_R K_{a_2}}$	XI

suggested is correct and that the assumptions made in the derivation of the equations are valid. Each chelate investigated therefore has a stoicheiometry of metal to ligand of 1:2, and is involved in a chelation reaction of the type

$$M^{2+} + 2HR \rightleftharpoons MR_2 + 2H^+$$

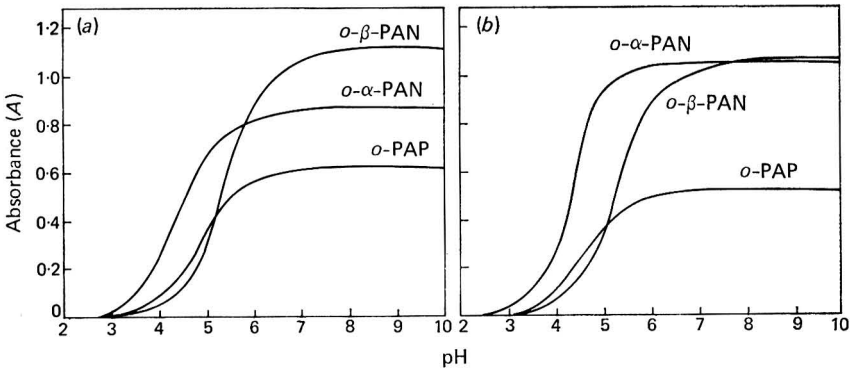

Fig. 2. Absorbance *versus* pH graphs for zinc(II) chelates:

(*a*) in the presence of excess of metal ions—

	C_M/M	C_R/M	λ/nm
o-α-PAN	$2{\cdot}0 \times 10^{-4}$	$4{\cdot}0 \times 10^{-5}$	590
o-β-PAN	$2{\cdot}0 \times 10^{-4}$	$5{\cdot}0 \times 10^{-5}$	550
o-PAP	$2{\cdot}0 \times 10^{-4}$	$5{\cdot}0 \times 10^{-5}$	530

(*b*) in the presence of excess of reagent—

	C_M/M	C_R/M	λ/nm
o-α-PAN	$2{\cdot}0 \times 10^{-5}$	$2{\cdot}0 \times 10^{-4}$	590
o-β-PAN	$2{\cdot}0 \times 10^{-5}$	$2{\cdot}0 \times 10^{-4}$	550
o-PAP	$2{\cdot}0 \times 10^{-5}$	$2{\cdot}0 \times 10^{-4}$	530

The values of the molar absorptivities and stability constants determined in this study were found to be consistent with the results of other workers.[14,18,20]

Manganese(II) chelates of o-α-*PAN,* o-β-*PAN and* o-*PAP*—The absorbance maxima of the manganese(II) chelates of *o*-α-PAN, *o*-β-PAN and *o*-PAP occurred at 546 and 586, 516

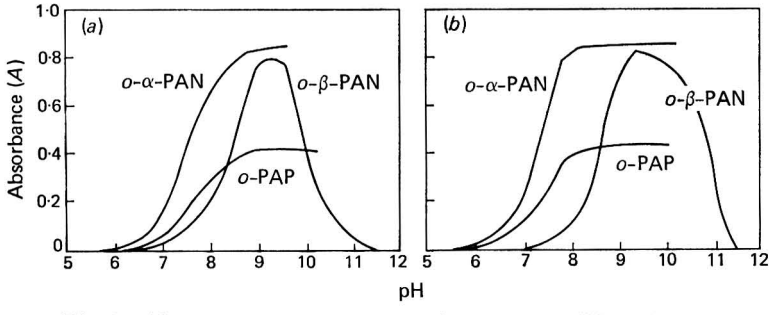

Fig. 3. Absorbance *versus* pH graphs for manganese(II) chelates:

(*a*) in the presence of excess of metal ions—

	C_M/M	C_R/M	λ/nm
o-α-PAN	$2{\cdot}0 \times 10^{-4}$	$4{\cdot}0 \times 10^{-5}$	586
o-β-PAN	$2{\cdot}0 \times 10^{-4}$	$4{\cdot}0 \times 10^{-5}$	546
o-PAP	$2{\cdot}0 \times 10^{-4}$	$4{\cdot}0 \times 10^{-5}$	530

(*b*) in the presence of excess of reagent—

	C_M/M	C_R/M	λ/nm
o-α-PAN	$2{\cdot}0 \times 10^{-5}$	$2{\cdot}0 \times 10^{-4}$	586
o-β-PAN	$2{\cdot}0 \times 10^{-5}$	$2{\cdot}0 \times 10^{-4}$	546
o-PAP	$2{\cdot}0 \times 10^{-5}$	$2{\cdot}0 \times 10^{-4}$	530

TABLE V

RESULTS FOR THE CHELATES OF ZINC(II)

Condition	Reagent	$y = mx + c$	Correlation coefficient	Standard error of slope, m	Standard error of estimate	$\epsilon_{MR_2} \times 10^{-4}$	log K_{MR_2}
Excess of metal ions	*o*-α-PAN	$y = 0{\cdot}087x + 4{\cdot}515$	1·000	0·0003	0·015	4·43	19·13 ± 0·07
	o-β-PAN	$y = 0{\cdot}453x + 4{\cdot}208$	0·999	0·0055	0·108	4·75	21·63 ± 0·08
	o-PAP	$y = 0{\cdot}804x + 8{\cdot}349$	1·000	0·0052	0·096	2·40	15·52 ± 0·09
Excess of reagent	*o*-α-PAN	$y = 0{\cdot}066x + 2{\cdot}212$	1·000	0·0002	0·016	4·52	19·12 ± 0·07
	o-β-PAN	$y = 0{\cdot}037x + 2{\cdot}222$	1·000	0·0002	0·015	4·50	21·45 ± 0·08
	o-PAP	$y = 0{\cdot}076x + 4{\cdot}165$	1·000	0·0003	0·025	2·40	15·48 ± 0·09

pK_{a_2} = 10·20 (*o*-α-PAN); 12·20 (*o*-β-PAN); 8·80 (*o*-PAP).

TABLE VI

RESULTS FOR CHELATES OF MANGANESE(II)

Condition	Reagent	$y = mx + c$	Correlation coefficient	Standard error of slope, m	Standard error of estimate	$\epsilon_{MR_2} \times 10^{-4}$	log K_{MR_2}
Excess of metal ions	*o*-α-PAN	$y = 0{\cdot}874x + 4{\cdot}823$	1·000	0·0006	0·029	4·15	13·54 ± 0·06
	o-β-PAN	$y = 0{\cdot}619x + 4{\cdot}945$	1·000	0·0006	0·011	4·04	15·77 ± 0·06
	o-PAP	$y = 0{\cdot}504x + 9{\cdot}201$	1·000	0·0012	0·059	2·17	10·52 ± 0·02
Excess of reagent	*o*-α-PAN	$y = 0{\cdot}086x + 2{\cdot}443$	1·000	0·0002	0·015	4·09	13·27 ± 0·05
	o-β-PAN	$y = 0{\cdot}045x + 2{\cdot}455$	1·000	0·0001	0·009	4·07	15·69 ± 0·08
	o-PAP	$y = 0{\cdot}265x + 4{\cdot}808$	0·999	0·0032	0·132	2·08	10·45 ± 0·05

pK_{a_2} = 10·20 (*o*-α-PAN); 12·20 (*o*-β-PAN); 8·80 (*o*-PAP).

and 546, and 530 nm, respectively, the chelates of the naphthol derivative each having two maxima, and the pH - absorbance curves (Fig. 3) were obtained at 586, 546 and 530 nm, respectively. Over the pH range 6 to 9 the curves are similar in appearance to those found for the zinc(II) chelates and the same analysis was applied. The results are shown in Table VI.

At higher pH values, the absorbance of the neutral chelate was found to decrease with increase in pH. The decreased absorbance was usually accompanied by the formation of a precipitate, which was presumed to be a hydroxy-form of the chelate. With *o*-α-PAN and *o*-PAP, it was not found possible to correlate absorbance with pH, and it was observed that the absorbance tended to zero on standing the solution. The manganese(II) chelate of *o*-β-PAN, however, gave reasonably smooth absorbance curves in the presence of both excess of reagent and excess of metal ions. The values tended to vary on standing the solution, but it proved possible to use them in transformation (V) (Fig. 4). From these values, $K_{MR_2(OH)}$ was found to be $10^{7\cdot57}$. The linearity suggests that the hydrolysis reaction that was proposed is reasonable, but because of the variation noted above, we have some reservations about these conclusions.

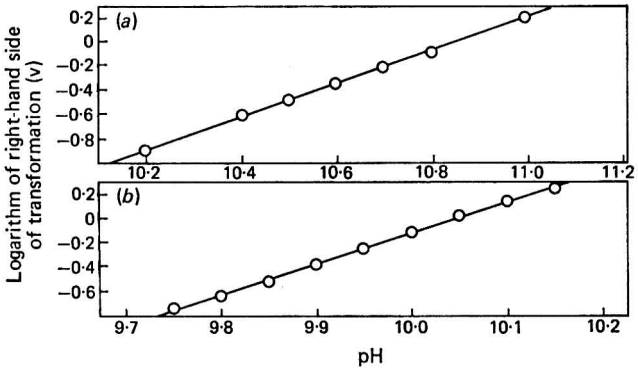

Fig. 4. Transformation (V) for the hydrolysis reaction of $Mn(o\text{-}\beta\text{-PAN})_2$: (*a*) excess of reagent; and (*b*) excess of metal. Conditions as in Fig. 3

Lanthanum(III) chelates of o-α-*PAN*, o-β-*PAN and* o-*PAP*—The chelation reactions of lanthanum(III) with *o*-α-PAN, *o*-β-PAN and *o*-PAP were investigated and absorbance curves in the presence of both excess of reagent and excess of metal ions were obtained.

Absorbance measurements were made at 550 and 514 nm, these wavelengths corresponding to the absorbance maxima of the *o*-α-PAN and *o*-PAP chelates, respectively. The absorbance curves are given in Fig. 5 and show that the extent of chelation is greatly affected by hydrolysis of the lanthanum species, particularly when the pH is above 7·5. The occurrence of a sharp hydrolysis effect above this pH may be expected because of the equilibrium position of lanthanum hydroxide, indicated by[21]

$$\text{Log}\,[La^{3+}] = 23{\cdot}02 - 3\text{pH}$$

When the reaction of *o*-β-PAN with lanthanum(III) was investigated, only a slight colour change occurred. As the formation of the *o*-β-PAN chelate may be expected to occur at lower acidities than those for the α-PAN chelate, this lack of reaction may be due to preferential hydrolysis of the lanthanum(III).

Unlike the absorbance curves for the manganese(II) and zinc(II) chelates, those shown in Fig. 5 give no direct indication of stoicheiometry. However, as the absorbance values in the presence of both excess of reagent and excess of metal ions are similar, the formation of 1:1 chelates can be anticipated. The neutral reagent species, HR, predominates over the pH range of chelation and so the suggested chelation reaction is

$$La^{3+} + HR \overset{K_{MR}}{\rightleftharpoons} LaR^{2+} + H^+$$

The validity of this postulate was tested by using transformation (IX) (Fig. 6).

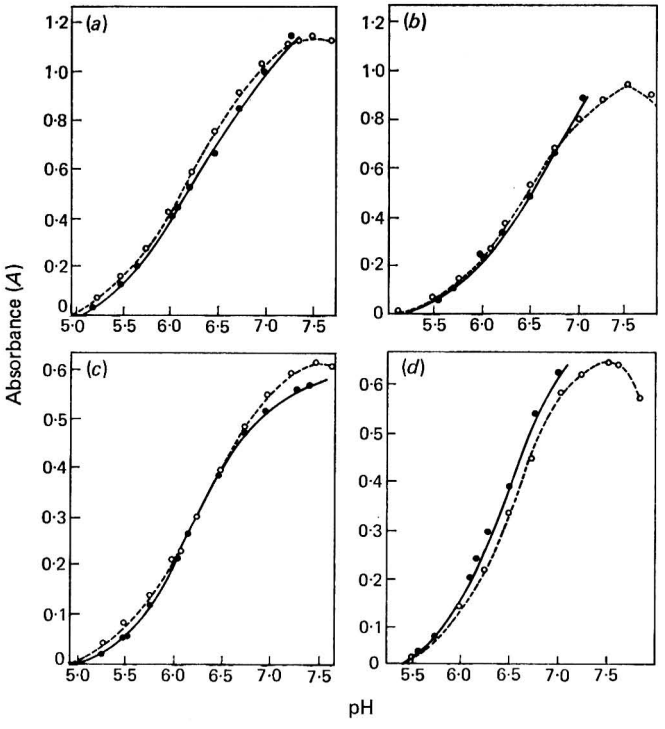

Fig. 5. Comparison of experimental and theoretical absorbance curves for La^{III}(*o*-α-PAN) [upper graphs: (*a*) excess of metal; and (*b*) excess of reagent] and La^{III}(*o*-PAP) [lower graphs: (*c*) excess of metal; and (*d*) excess of reagent]. Solid lines, experimental; and broken lines, theoretical. Concentrations: (*a*) C_R $5{\cdot}0 \times 10^{-5}$ M, C_M $5{\cdot}0 \times 10^{-4}$ M; (*b*) C_R $4{\cdot}0 \times 10^{-4}$ M, C_M $4{\cdot}0 \times 10^{-5}$ M; (*c*) C_R $5{\cdot}0 \times 10^{-5}$ M, C_M $5{\cdot}0 \times 10^{-4}$ M; (*d*) C_R $5{\cdot}0 \times 10^{-4}$ M, C_M $5{\cdot}0 \times 10^{-5}$ M

The formation of such an LaR^{2+} species is in agreement with the observation of Sommer and Novotna,[11] who have reported the reactions of lanthanum with PAR. These workers also found that a 1:1 chelate was formed and that severe hydrolysis interfered in the accurate determination of absorbances at higher pH.

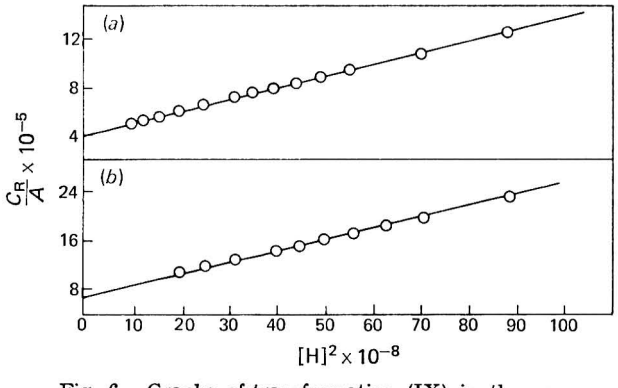

Fig. 6. Graphs of transformation (IX) in the presence of excess of lanthanum(III): (*a*) *o*-α-PAN; and (*b*) *o*-PAP. C_R $5{\cdot}0 \times 10^{-5}$ M and C_M $5{\cdot}0 \times 10^{-4}$ M

Agreement between the constants listed in Table VII is not quite as good as that observed for the manganese(II) and zinc(II) chelates, probably because of the ease of hydrolysis of lanthanum species. In order to determine precisely the hydrolysis effect, and to verify further the proposed chelation reactions, theoretical absorbance curves were determined by using the computed complex formation constants and known values for the hydrolysis of lanthanum(III).

TABLE VII

MOLAR ABSORPTIVITIES AND STABILITY CONSTANTS OF LANTHANUM(III) CHELATES

Reagent	Transformation	ϵ_{MR}	Transformation	log K_{MR}
o-α-PAN	IIIA	$2{\cdot}50 \times 10^4$	VIA	$7{\cdot}16 \pm 0{\cdot}02$
	IX	$2{\cdot}47 \times 10^4$	XI	$7{\cdot}08 \pm 0{\cdot}04$
o-PAP	IIIA	$1{\cdot}43 \times 10^4$	VIA	$5{\cdot}76 \pm 0{\cdot}04$
	IX	$1{\cdot}56 \times 10^4$	XI	$5{\cdot}58 \pm 0{\cdot}04$

pK_{a_3} = 8·80 (*o*-PAP); 10·20 (*o*-α-PAN).

(*i*) *In the presence of excess of lanthanum(III)*—In this instance, the absorbance is limited by the concentration of the reagent.

The absorbance, A, is given by

$$A = \epsilon_{MR} C_{HR_{Tot}} (1 - f) \quad .. \quad .. \quad .. \quad .. \quad (11)$$

where ϵ_{MR} = molar absorptivity of MR; $C_{HR_{Tot}}$ = total reagent concentration; and f = fraction of reaction completed.

$$f = \frac{C_R}{C_{HR_{Tot}}} = \frac{C_R}{C_R + C_{MR}}$$

$$= \frac{1}{1 + C_{MR}/C_R} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (12)$$

where C_R = unreacted reagent concentration.

The proposed chelation reaction is

$$M + HR \overset{{}^*K_{MR}}{\rightleftharpoons} MR + H^+ \quad .. \quad .. \quad .. \quad .. \quad (13)$$

The conditional reaction constant, ${}^*K'_{MR}$, is given by

$${}^*K'_{MR} = \frac{C_{MR}[H]}{C_M C_R} = \alpha_1 \beta {}^*K_{MR}$$

In the presence of excess of lanthanum(III), $C_M = C_{M_{Tot}}$, the total metal-ion concentration, and

$$C_R = \frac{C_{MR}[H]}{C_{M_{Tot}} {}^*K_{MR} \alpha_1 \beta} \quad .. \quad .. \quad .. \quad .. \quad (14)$$

where the side-reaction coefficients, α_1 and β, are $[HR]/C_R$ and $[M]/C_M$, respectively.

In the present study, $\alpha_1 = 1$ and β, if the major hydroxy-complex is $La(OH)_3$, is given by

$$\beta = \frac{[La^{3+}]}{C_{M_{Tot}}} \approx \frac{[La]}{[La] + [La(OH)_3]}$$

or

$$\beta = 1 + \frac{[La(OH)_3]}{[La^{3+}]} \quad .. \quad .. \quad .. \quad .. \quad (15)$$

The equilibrium constant involving hydrolysis of La^{3+} is given by[21]

$$La^{3+} + 3H_2O \rightleftharpoons La(OH)_3 + 3H^+$$

$$\text{Log } [La^{3+}] = 23{\cdot}02 - 3\text{pH}$$

Values of β obtained from equation (15) were used in equation (14) to calculate C_R values. Absorbances were then obtained by using equations (11) and (12).

(*ii*) *In the presence of excess of reagent*—Absorbance values are now limited by the metal-ion concentration and are given by

$$A = \epsilon_{MR} C_{M_{Tot}} (1 - f) \quad .. \quad .. \quad .. \quad .. \quad (16)$$

$$f = \frac{1}{1 + C_{MR}/C_M} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (17)$$

$$*K'_{MR} = \frac{C_{MR}[H]}{C_M C_R} = *K_{MR}\,\alpha_1\beta$$

In the presence of excess of reagent, $C_R = C_{HR_{Tot}}$, the total reagent concentration, and

$$C_M = \frac{C_{MR}\,[H]}{C_{HR_{Tot}} *K_{MR}\alpha_1\beta} \quad .. \quad .. \quad .. \quad .. \quad (18)$$

As before, $\alpha = 1$ and β is given by equation (15). Values of C_M obtained from equation (18) were then used to calculate absorbance from equations (17) and (16).

The molar absorptivity, reaction, stability and dissociation constants used for the above calculations are summarised in Table VII.

Theoretical absorbance curves were drawn and compared with the experimental curves (Fig. 5). Agreement between the theoretical and experimental curves is good, which confirms that the chelation reaction suggested is correct and that the decreased absorbance at high pH is due to hydrolysis of lanthanum species.

Reaction of 4-(2-pyridylazo)phenol with cobalt(II), nickel(II) and copper(II)—Spot tests show that *p*-PAP is selective in its reactions with metal ions, and will react principally with metals of Groups VIII and IB. Cobalt(II), copper(II) and nickel(II) react strongly, and the chelation reactions of these ions have been investigated.

Absorbance curves were obtained in the presence of both excess of reagent and excess of metal ions.

Absorbance measurements were made at 548, 520 and 517 nm, these wavelengths corresponding to the absorbance maxima of the copper, nickel and cobalt chelates, respectively. The absorbance curves are shown in Fig. 7. These curves indicate that maximum chelation occurs at a pH greater than the pK_{a_2} value of the reagent. Also, very little chelation occurs at pH values below the pK_{a_2} value, which suggests that the neutral form of the reagent has little tendency for chelation and that chelation occurs via the anionic form. This represents an unusual type of chelation because the protons that are lost do not originate in the chelating groups themselves.

Preliminary investigations of the nature of these chelates by continuous variation,[12] mole-ratio[13] and slope-ratio[22,23] methods showed that each chelate has a stoicheiometry of metal to ligand of 1:2. As the anionic form of the reagent is involved in chelation, then the suggested chelation reaction is

$$M + 2R^- \rightleftharpoons MR_2$$

Therefore, the application of transformations (VI) and (VII) was tried. The consistency of the calculated constants and linearity shown by the correlation coefficient in Table VIII indicated that this is the predominant reaction over the pH range 7 to 8.

The decrease in absorbance observed at higher pH indicates the formation of hydroxy-chelate species:

$$MR_2 + OH^- \overset{K_{OH}}{\rightleftharpoons} MR_2OH^-$$

This hydrolysis reaction is identical with that of the manganese(II) and zinc(II) chelates with *o*-β-PAN. The hydrolysis constant, $K_{MR(OH)}$, can therefore be calculated from identical transformations. The linearity of these transformations is shown in Fig. 8, and the hydrolysis constants were found to be $10^{4.58 \pm 0.02}$ and $10^{5.17 \pm 0.02}$ for the nickel(II) and cobalt(II) hydroxy-species, respectively.

SOLVENT-EXTRACTION STUDIES—

The theory of the solvent extraction of chelates is fairly well established.[24–27] If the distribution ratio, D, is defined as the concentration of the metal in the organic phase divided

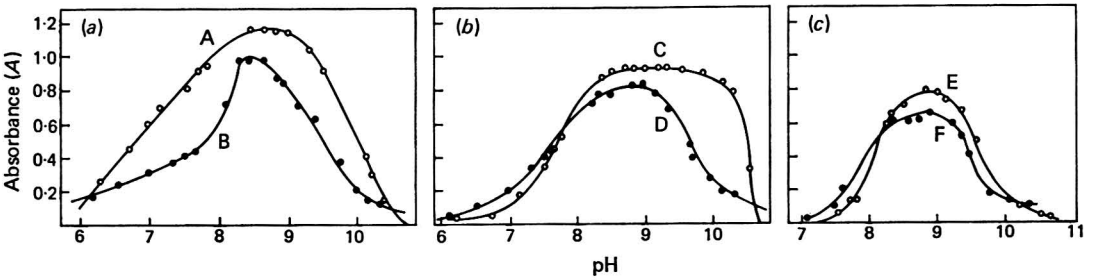

Fig. 7. Absorbance *versus* pH graphs for chelates of *p*-PAP in 5 per cent. aqueous methanol: (*a*) with copper(II); (*b*) with nickel(II); and (*c*) with cobalt(II). A, excess of reagent: C_M $2{\cdot}5 \times 10^{-5}$ M, C_R $1{\cdot}0 \times 10^{-4}$ M; B, excess of metal: C_M $1{\cdot}0 \times 10^{-4}$ M, C_R $2{\cdot}5 \times 10^{-5}$ M; C, excess of reagent: C_M $2{\cdot}5 \times 10^{-5}$ M, C_R $1{\cdot}0 \times 10^{-4}$ M; D, excess of metal: C_M $1{\cdot}0 \times 10^{-4}$ M, C_R $2{\cdot}5 \times 10^{-5}$ M; E, excess of reagent: C_M $5{\cdot}0 \times 10^{-5}$ M, C_R $1{\cdot}0 \times 10^{-4}$ M; F, excess of metal: C_M $1{\cdot}0 \times 10^{-4}$ M, C_R $5{\cdot}0 \times 10^{-5}$ M

Table VIII

Molar absorptivities and stability constants for cobalt(II) and nickel(II) chelates

Condition	Metal ion	$y = mx + c$	Correlation coefficient	Standard error of slope, m	Standard error of estimate	$\epsilon_{MR_2} \times 10^4$	log K_{MR_2}
Excess of metal ions	Ni(II)	$y = 0{\cdot}031x + 3{\cdot}820$	0·994	0·0011	0·088	5·23	$8{\cdot}95 \pm 0{\cdot}08$
	Co(II)	$y = 0{\cdot}198x + 6{\cdot}843$	0·998	0·0044	0·205	2·92	$7{\cdot}88 \pm 0{\cdot}07$
Excess of reagent	Ni(II)	$y = 0{\cdot}015x + 2{\cdot}031$	0·981	0·0009	0·146	4·92	$8{\cdot}69 \pm 0{\cdot}10$
	Co(II)	$y = 0{\cdot}208x + 3{\cdot}887$	0·999	0·0031	0·266	2·57	$7{\cdot}82 \pm 0{\cdot}06$

$pK_{a_2} = 7{\cdot}77$.

by the concentration of the metal in the aqueous phase, it follows, for the extraction reaction

$$M_w^{2+} + 2HR_o \rightleftharpoons MR_{2(o)} + 2H_w^+$$

that

$$\begin{aligned} D &= [MR_2]_o/([MR_2]_w + C_M) \\ &= K_{DX}/(1 + C_M/[MR_2]_w) \\ &= K_{DX}/(1 + [M]/\beta[MR_2]) \\ &= K_{DX}/\{1 + 1/(\beta K_{MR_2}\alpha_{2(D)}^2[HR]_o^2)\} \quad .. \quad .. \quad .. \quad (19) \end{aligned}$$

In equation (19) and subsequent equations K_{DX} and K_{DR} are the partition coefficients of the chelate and reagent, respectively.

$$\begin{aligned} \alpha_{2(D)} &= [R^-]/C_{HR} \\ &= K_{a_1}K_{a_2}/\{[H]^2 + K_{a_1}[H](1 + K_{DR}V_o/V_w) + K_{a_1}K_{a_2}\} \end{aligned}$$

where C_{HR} is the total concentration of reagent present initially in the organic phase of volume V_o and the other terms have been defined previously. It is assumed that the metal is present in the organic phase only as MR_2. In the absence of side-reactions that involve the metal ion ($\beta = 1$) and incomplete chelate formation ($D < K_{DX}$) and on the assumption that the reagent is present in the organic phase mainly as HR, this expression reduces to

$$D = K_{MR_2}K_{DX}K_{a_2}^2[HR]_o^2/K_{DR}^2[H]^2 \quad .. \quad .. \quad .. \quad (20)$$

For practical purposes, the percentage extracted, E, is often used, and is related to the distribution ratio by

$$E = \frac{D}{D + V_o/V_w} \cdot 100$$

The pH value at $E = 50$ per cent. is designated as $pH_{\frac{1}{2}}$, and the difference between the $pH_{\frac{1}{2}}$ values of two extractable chelates is a measure of their separability. If it is assumed that the partition coefficients for chelates of the same reagent are identical and there are no competing side-reactions, extraction curves (*E versus* pH) for the same reagent and a series of metal ions of the same charge will have identical shapes. The relative degree of extraction at a given pH will be governed by the relative values of the formation constant K_{MR_2}. Hence, if the values of the constants in equation (20) are known and a value of $[HR]_o$ is defined, curves of *E versus* pH can readily be calculated.

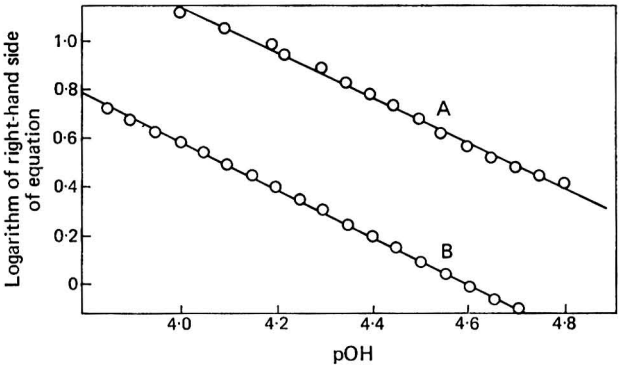

Fig. 8. Graphs of hydrolysis equations for cobalt(II) and nickel(II) chelates of *p*-PAP: A, cobalt(II); and B, nickel(II)

The values of all the terms in equation (20) except K_{DR} and K_{DX} can be determined by the spectrophotometric methods described above. K_{DR} must be determined independently. Therefore, in order to calculate the extraction curve, one must either assume a value of K_{DX} or determine it independently. Two approaches seem reasonable: (*i*) assume that $K_{DX} = K_{DR}$, which was applied to *o*-PAP systems; (*ii*) assume that K_{DX} is the same for similar systems, which was applied to *o*-α-PAN and to *o*-β-PAN systems, the value of 10^4 being taken from previous work.[14–18] The calculated curves were compared with those obtained

experimentally (Fig. 9). As would be expected from the above assumptions and the additional assumption that K_{MR_2} remains constant, not all of the experimental and theoretical curves coincide. Nevertheless, they are close enough for the analyst to use the method as a guide in the choice of his experimental conditions.

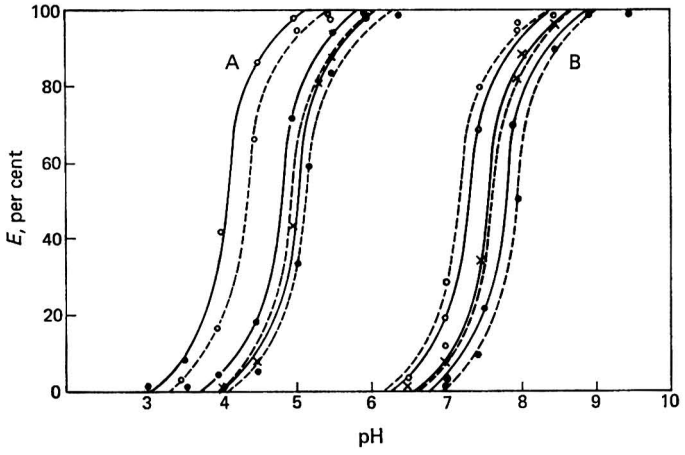

Fig. 9. Comparison of experimental and predicted extraction curves for the chelates of zinc and manganese: A, zinc; and B, manganese. Solid lines, experimental; and broken lines, calculated. Chelates: o, *o*-α-PAN; ●, *o*-β-PAN; and ×, *o*-PAP

A more valuable guide is provided when there are competing reactions, $\beta < 1$. The simplified equation (20) must be modified by including β in the numerator. The competing reaction might arise from the addition of a masking agent, L, which forms a series of complexes with the metal ion. If the formation constants are known, it is a straightforward matter to calculate $1/\beta$, which is given by $1 + \sum_0^n k_1 k_2 \ldots k_n[L]^n$. The spectrophotometric studies should reveal the presence of hydroxy-species, which can be taken into account in a similar way:

$$1/\beta = 1 + K_{MR_2(OH)}\,[OH] + K_{MR_2(OH)_2}\,[OH]^2$$

The extraction curve for the manganese(II) - *o*-β-PAN system, in which the presence of hydroxy-complexes had been established spectrophotometrically, was calculated with the aid of the formation constants determined spectrophotometrically. The curve is compared with the experimentally obtained curve in Fig. 10. The agreement is satisfactory and clearly

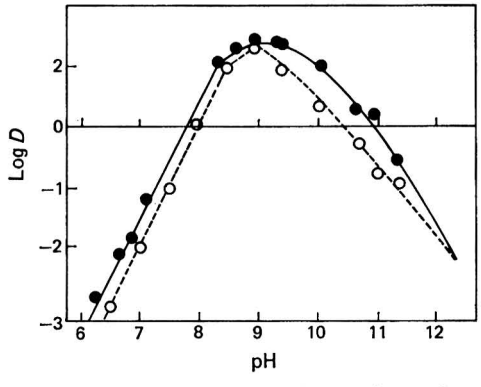

Fig. 10. Comparison of experimental and predicted extraction curves for $Mn(o\text{-}\beta\text{-PAN})_2$. Solid line, experimental; and broken line, predicted

demonstrates the need to select the extraction conditions with care. For more exact comparison, the calculated and experimental pH values are given in Table IX.

TABLE IX

COMPARISON OF EXPERIMENTAL SOLVENT-EXTRACTION CONSTANTS WITH CONSTANTS PREDICTED BY SPECTROPHOTOMETRY

		Experimental		Predicted	
Reagent	Metal ion	Log K_f	$pH_{1/2}$	Log K_f	$pH_{1/2}$
o-α-PAN	Mn(II)	13·30	7·30	13·40	7·22
	Zn(II)	19·60	4·10	19·13	4·35
o-β-PAN	Mn(II)	16·13	7·85	15·80	7·95
	Zn(II)	22·17	4·85	21·50	5·10
o-PAP	Mn(II)	10·42	7·60	10·50	7·55
	Zn(II)	15·58	5·00	15·50	5·07

pK_{a_2} = 9·63 (*o*-α-PAN); 11·62 (*o*-β-PAN); 8·68 (*o*-PAP).

K_{DX} = 10^4, assumed for each chelate.

It is more usual to deduce the values of the constants in equations (19) and (20) from the experimental curve, and this procedure was followed for the manganese(II) - *o*-β-PAN system so as to determine the values of $K_{MR_2(OH)}$ and $K_{MR_2(OH)_2}$. The value of $K_{DX}K_{MR_2}$ was calculated from the points on the rising part of the curve of log D *versus* pH and a value of β was calculated as a function of pH from equation (19) by using points from the descending part of the curve. β was then examined as a function of [OH] and it was deduced that $MnR_2(OH)_2^{2-}$ could not be detected, that $MnR_2(OH)$ was present and that log $K_{MnR_2(OH)}$ had a value of 7·64. The agreement between this value and that obtained spectrophotometrically is good, and is a little surprising because of the low number of acceptable experimental points in the solvent-extraction system.

CONCLUSIONS

The determination of reliable stability constants is a tiresome and time-consuming procedure, which can often produce results that are of limited applicability. The most accurate results are generally agreed to be those obtained by potentiometric titrations, and these results now have the advantage of the availability of well tested computer programs[28] that can be used in order to transmute the experimental points into results. However, inevitably, relatively large concentrations of reactants are used, which results in the use of non-aqueous solvents and the increased likelihood of the formation of polynuclear species. Methods based on solvent extraction and spectrophotometry have direct appeal to the analytical chemist as he may be able to set up his analytical method while measuring the stability constants. This is true of solvent extraction, although it may be difficult to obtain reliable constants without a great deal of experimentation and it is also true of the spectrophotometric method described above. The pH - absorbance curves upon which the method is based are essential in the development of the analytical procedure. These curves can also yield much information about the effect of varying the conditions, *e.g.*, reagent concentration, pH and masking agent. In this respect, as well as in terms of accuracy, the method involving these curves is far superior to Job's method and the related procedures that are commonly used. It has also been shown that the results can be used directly to predict solvent-extraction curves. The weakness of the method is that it depends upon extrapolation, and it requires careful experimental work and alteration of conditions so as to ensure that reliable results are obtained. We have concluded that it is just as time consuming as the other reliable methods, but we feel that because of the amount of information of direct analytical interest that is obtained, it is a very desirable method.

Of the four reagents studied, *o*-α-PAN is clearly the most suitable as it forms highly coloured stable complexes at lower pH values than *o*-β-PAN, *o*-PAP or *p*-PAP. *o*-β-PAN and *o*-PAP form complexes at about the same pH values but the molar absorptivities of PAN complexes are greater than those of PAP complexes.

Specific analytical applications will be described in subsequent papers.

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Determination of Chloride in Aqueous Soil Extracts and Water Samples by Means of a Chloride-selective Electrode

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The chloride contents of water samples and soil extracts have been determined with an Orion chloride-selective electrode. The chloride content, at levels up to 100 mg l^{-1}, is determined in a solution that is 0·5 M with respect to ammonium nitrate and 0·03 M with respect to nitric acid.

Comparison of this method with a colorimetric AutoAnalyzer method showed no significant difference between the results obtained, but for water samples low in chloride (less than 3 mg l^{-1}) the colorimetric method was more accurate.

CURRENTLY, the most widely used methods for the determination of chlorides are the gravimetric method (precipitation as silver chloride) and the argentimetric and mercurimetric methods (in which different types of coloured or potentiometric indicators are used).

Bremner[1] recommends the well known Mohr titrimetric method for the determination of chloride in aqueous soil extracts. This method, however, is not very sensitive, and is also subject to errors caused by adsorption effects and over-titration. Davey and Bembrick[2] used a silver - silver chloride electrode for the determination of chloride in aqueous extracts of soil. A potentiometric determination is much more sensitive than Mohr's method, and is therefore more suitable for determining small concentrations of chloride in soil extracts and water samples.

Technicon[3] recommend a colorimetric method based on the release of thiocyanate ion from mercury(II) thiocyanate by an equivalent amount of chloride. A red colour is formed by the reaction of thiocyanate with iron(III). This method is very sensitive and is well suited for large numbers of samples. Its use is becoming more widespread.

The Orion chloride-selective electrode appears to be convenient for the determination of chloride in soil extracts and water samples as it is more sensitive than Mohr's method and is portable, thus enabling measurements to be made in the field.

In this investigation, different types of soil and water samples have been analysed by this electrode method, and the results are compared with those obtained by the Technicon AutoAnalyzer method.

EXPERIMENTAL

APPARATUS—

An ion-specific meter, Orion Research, Model 401, with a chloride-selective electrode, Model 94–17, was used for the potentiometric determination of chloride in water and soil extracts. The measurements were made against the Orion double-junction reference electrode, Model 90–02.

A Technicon AutoAnalyzer, with a manifold system according to O'Brien,[4] was used for the colorimetric determination of chloride in water and soil extracts.

REAGENTS—

All reagents used were of analytical-reagent grade.

Standard solutions of chloride—A stock solution of chloride was prepared by dissolving 2·103 g of potassium chloride in water and diluting the solution to 1 litre so as to give a

concentration of 1 g l^{-1} of chloride. Standard solutions in the range 0 to 100 mg l^{-1} of chloride were made by diluting appropriate volumes of the stock solution with ammonium nitrate and nitric acid solutions. The final concentrations of ammonium nitrate and nitric acid were 0·5 and 0·03 M, respectively.

Ammonium nitrate solution, 0·5 M—Ammonium nitrate (40 g) was dissolved in distilled water and the solution was made up to 1 litre.

Nitric acid, 0·3 M—Concentrated nitric acid was diluted appropriately with distilled water.

Ammonium nitrate - nitric acid reagent—A solution was prepared that was 5 M in ammonium nitrate and 0·3 M in nitric acid.

PROCEDURE—

Soil samples—A 10-g amount of air-dried soil (dried at 30 °C and passed through a 2-mm sieve) was shaken for 15 minutes with 50 ml of 0·5 M ammonium nitrate solution. The extracts were either centrifuged, or filtered through Schleicher and Schüll No. 589 white ribbon filters; 2 ml of 0·3 M nitric acid were added to 20 ml of the extract before measurement with the electrode. The measured values were then compared with those given by the standard graph.

Water samples—Ammonium nitrate - nitric acid reagent (2 ml) was added to 20 ml of water and the chloride content was measured with the electrode.

RESULTS AND DISCUSSION

EXTRACTION TIME—

When four soils of various textures were shaken with water or 0·5 M ammonium nitrate solution for periods of 5, 30 and 60 minutes, the chloride values obtained after shaking the mixtures for 5 minutes were identical with those obtained after the longer periods of shaking. Results were the same with both extractants, provided that 2 ml of 0·3 M nitric acid per 20 ml of extract were added to the 0·5 M ammonium nitrate extracts and 2 ml of ammonium nitrate - nitric acid reagent to the aqueous extracts. These results seem reasonable as the chloride ions are only lightly bound to the negative soil particles.

EFFECT OF AMMONIUM NITRATE AND NITRIC ACID—

According to Orion[5] the presence of ammonia can cause some interference. To overcome this effect the soil was extracted with 0·5 M ammonium nitrate solution. At this high concentration of ammonium ions, the relatively small amounts of ammonia present in the soil will cause no significant errors. The ionic strength will also be nearly constant.

Hydroxyl ions may also interfere, and concentrations greater than eighty times the chloride concentration cause errors.[5] Varying the pH of the 0·5 M ammonium nitrate solution (containing 10 mg l^{-1} of chloride) by addition of nitric acid showed that the same results for chloride were obtained in solutions with pH values ranging from 1·6 to 5·0. The addition of 2 ml of 0·3 M nitric acid, which should allow for any carbonate extracted from calcareous soils, is advised. Davey and Bembrick[2] also found that a mixture of ammonium nitrate and nitric acid increased the accuracy of the method. We used a higher level of acidity, however.

RECOVERY TESTS—

The recovery of known amounts of chloride, added before extraction to four soils of various textures, ranged from 99·5 to 101 per cent. The chloride content found, expressed as milligrams of chloride per 100 g of soil, was constant, at least in the range 5 to 40 g of soil per 50 ml of extracting solution.

COMPARISON OF METHODS—

A series of soil extracts was prepared, and the chloride contents were determined by both the electrode and the colorimetric AutoAnalyzer methods. If the extracts were highly coloured, blank values were obtained by running the samples with water instead of mercury(II) thiocyanate reagent in the AutoAnalyzer method. Table I shows the results for thirteen soil samples treated as follows. A 10-g sample of air-dried soil was shaken with 50 ml of 0·5 M ammonium nitrate solution for 30 minutes and the mixture then centrifuged. The chloride content in the soil extract was determined by both the electrode and the AutoAnalyzer methods after nitric acid had been added to the extracts. A *t*-test gave no indication

TABLE I

DETERMINATION OF CHLORIDE IN SOIL EXTRACTS

Soil sample No.	Soil type	Loss on ignition, per cent.	pH_{H_2O}	Chloride content in soil extract/ mg l^{-1},* found by— electrode method	Chloride content in soil extract/ mg l^{-1},* found by— AutoAnalyzer method
1	Sandy peat soil	48·8	5·9	8·5	9·4
2	Sand	5·9	7·5	0·7	1·8
3	Sand	7·7	7·3	0·6	0·6
4	Sandy peat soil	75·3	4·6	11·0	13·0
5	Sand	5·7	5·5	1·9	0·6
6	Sand	5·9	7·5	1·4	1·2
7	Clayey sand	10·4	7·3	0·9	0·9
8	Sandy peat soil	38·0	4·6	10·0	9·4
9	Sandy peat soil	32·7	4·9	5·1	5·2
10	Sandy clay	7·7	6·0	1·4	1·0
11	Sandy clay	8·0	5·8	1·0	0·9
12	Sandy clay	7·8	5·9	1·6	1·4
13	Sandy peat soil	26·6	7·0	7·9	8·5

* The corresponding chloride contents in soil are five times greater and range from 3·0 to 65 p.p.m.

of difference ($P > 0·5$) between the results for the electrode and the colorimetric methods. Duplicate analyses of twenty-one water samples in the range 0·5 to 18·8 p.p.m., to 30 ml of each of which had been added 3 ml of a solution that was 5 M and 0·3 M with respect to ammonium nitrate and nitric acid, respectively, showed no indication of difference between the results for the two methods (Table II).

TABLE II

DETERMINATION OF CHLORIDE IN WATER SAMPLES

Sample No.	pH	Specific conductance/ μS cm^{-1}	Chloride content/mg l^{-1}, found by— electrode method Duplicate results	Chloride content/mg l^{-1}, found by— electrode method Mean	Chloride content/mg l^{-1}, found by— AutoAnalyzer method Duplicate results	Chloride content/mg l^{-1}, found by— AutoAnalyzer method Mean
1	6·0	40	1·9,3·0	2·5	2·4,2·3	2·4
2	6·3	42	1·2,2·6	1·9	1·8,1·9	1·9
3	6·5	83	8·1,8·5	8·3	7·6,7·6	7·6
4	6·4	95	10·3,10·3	10·3	9·6,9·5	9·6
5	6·2	75	8·5,8·9	8·7	6·9,6·9	6·9
6	5·9	63	5·4,5·4	5·4	5·9,5·8	5·9
7	6·2	191	17·0,18·8	17·9	16·8,16·8	16·8
8	6·4	130	11·1,12·0	11·6	10·7,10·7	10·7
9	6·3	35	2·6,2·3	2·5	1·9,1·8	1·9
10	6·0	30	0·5,1·9	1·2	1·6,1·5	1·6
11	5·3	84	0·7,1·7	1·2	1·3,1·3	1·3
12	4·0	87	16·0,16·2	16·1	17·5,17·5	17·5
13	6·2	39	1·2,2·7	2·0	2·3,2·3	2·3
14	6·5	28	2·4,2·4	2·4	2·4,2·4	2·4
15	6·0	30	2·8,2·8	2·8	2·5,2·5	2·5
16	5·5	19	2·0,1·7	1·9	1·4,1·4	1·4
17	7·0	25	2·6,2·2	2·4	1·9,2·0	2·0
18	5·1	23	1·4,1·1	1·3	1·6,1·6	1·6
19	7·0	23	1·2,1·9	1·6	1·6,1·9	1·8
20	4·6	30	1·6,2·2	1·9	2·7,2·8	2·8
21	5·8	54	4·8,4·9	4·9	4·7,4·7	4·7

SENSITIVITY AND PRECISION OF THE METHOD—

As the slope of the graph of millivolts *versus* concentration is not constant below a concentration of 10 p.p.m. (Fig. 1), the chloride content cannot be read directly from the meter. A calibration graph must therefore be drawn for the lower concentrations. The chloride concentration can then be measured down to 0·5 p.p.m. At this level, however, the reproducibility is poor. In duplicate analyses of thirteen soil extracts in the range

0·6 to 11 mg l^{-1} of chloride, the coefficient of variation was 4·5 per cent. For thirteen water samples with a relatively low content of chloride (0·5 to 3 mg l^{-1}), the coefficient of variation was as high as 31 per cent. For higher concentrations (4·8 to 18·8 mg l^{-1}) it was found to be about 5 per cent.

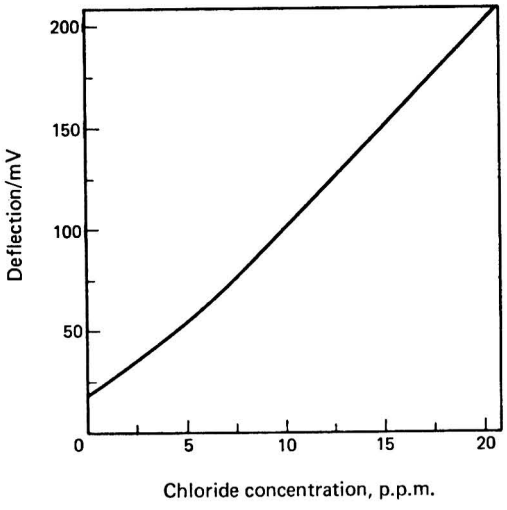

Fig. 1. Standard graph

The results indicate that for low chloride concentrations (below 3 mg l^{-1} of extract) it is better to use a colorimetric AutoAnalyzer method than the electrode method if accurate measurements are needed. Above this concentration, the chloride electrode seems to be satisfactory. The chloride content in the range 10 to 100 mg l^{-1} can be determined by direct read-out on the instrument.

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Precise Coulometric Determination of Acids in Cells Without Liquid Junction

Part III.* Determination of the Silver Error by Amperostatic Anodic Stripping†

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The plating and stripping of silver on platinum electrodes have been examined in the context of the determination of the silver error, which arises from the solubility of silver bromide when the deposition of bromide on a silver anode is used as the auxiliary reaction in the coulometric assay of acids. In order to calibrate the stripping method, it is necessary to plate known amounts of silver quantitatively on to platinum-gauze electrodes. Low recoveries are obtained when the platinum is not fully reduced. The oxidation and reduction of platinum electrode surfaces have been briefly examined, and it is demonstrated that oxide forms on an electrode when its potential is allowed to rise beyond 0·8 V, the termination potential in silver stripping. For calibration purposes, plating and stripping in a 0·1 M solution of silver nitrate in 0·1 M perchloric acid was first investigated. Amperostatic and potentiostatic reduction of the platinum electrode are shown to be ineffective, but chemical reduction leads to excellent plating and recoveries, provided great care is taken completely to remove all traces of reductant. Calibration being satisfactory, stripping in 0·1 M perchloric acid, as in an actual acidimetric assay, has been examined and shown to give excellent recoveries. The anodic stripping curves show an extended second wave, which is identified as arising from reduction of oxygen to hydrogen peroxide at the auxiliary stripping electrode, particularly when the latter becomes plated with silver. The hydrogen peroxide is oxidised at the stripping electrode, and the process is cyclic.

IN the coulometric determination of acids, the use of a silver auxiliary anode on which bromide is deposited has been canvassed.[1] The slight, but significant, solubility of silver bromide in the electrolyte gives rise to a "silver error" by deposition of silver on the working platinum cathode either by direct electro-reduction or by reduction of silver ion by hydrogen atoms in the compact layer (the combination of which, to give hydrogen molecules, is the rate-determining step of the main cathodic reaction). Additionally, any precipitate of silver bromide in the bulk of the solution is liable to be caught on the cathode and there reduced, although the experimental conditions are chosen so as to avoid the formation of such precipitates. The error incurred is about 1 to 2 C in a total of 5000 C, and a rapid and convenient method is needed for the determination of about 1 mg of silver deposited on a 125-cm^2 platinum-gauze electrode. If this amount can be determined with an accuracy of 1 per cent., it will then represent an over-all accuracy of about 2 to 4 p.p.m. in the determination of 0·05 mol of a monobasic acid. Amperostatic anodic stripping proved simple and rapid,[1] but is of unknown accuracy. In order to assess the accuracy a method must be discovered for quantitatively plating known amounts of silver on to platinum for calibration of the stripping process. Preliminary experiments showed that while the potential rise at completion of the stripping reaction was satisfactorily sharp, the accuracy was poor, recoveries of silver being only 70 per cent. This finding led to the investigation of plating of silver on to platinum, of oxidation of platinum surfaces, and therefore of the pre-conditioning of the platinum electrode. Mechanical stripping, *i.e.*, loss of some of the loose deposit, was suggested by Lord, O'Neill and Rogers[2] as the cause of low recoveries. Nisbet and Bard[3] obtained 100 per cent. recovery on a platinised platinum electrode, but low recoveries on an oxidised

* For particulars of Parts I and II of this series, see reference list, p. 425. For Part IV, see p. 426.

† Presented at the Second SAC Conference, Nottingham, 1968.

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electrode. A platinised surface was therefore prepared by a.c. electrolysis in 1 M perchloric acid, and the electrode was finally reduced almost until hydrogen was evolved. Silver was plated on to and then stripped from this electrode amperostatically, and the plating - stripping cycle was repeated several times with anodisation to +1·6 V each time; progressively shorter stripping times were found for the same plating time. Nisbet and Bard[3] reported similar results, which were claimed by them to show that some of the silver is retained on an oxidised platinum surface and can be removed only after reduction of the underlying oxide. Bixler and Bruckenstein[4] claimed 100 per cent. recovery when a reduced platinum electrode was used. They confirmed that repetition of the plating - stripping cycle with anodisation to +1·6 V gave short recovery times, but could find no evidence of retention of silver on the electrode. They suggested that the apparent loss of silver arose from partial reduction of the oxidised platinum surface during plating, together with mechanical loss.

Experimental

The apparatus and reagents used have been described previously.[5] The cell and circuit used in the present study are shown in Fig. 1. The milliammeter shown in series with the working electrodes was used to set the current to the nearest 10 μA, but in the later work was replaced with a 10-Ω standard four-terminal resistor and the current set to the nearest 1 μA by using the P3 potentiometer. Titanium(IV) sulphate was prepared by heating 10 g of titanium dioxide with 20 ml of concentrated sulphuric acid for 30 minutes, cooling, diluting the solution with 50 ml of cold water, allowing it to stand for several days and filtering it through a Whatman No. 42 filter-paper. All electrode potentials are given with reference to the standard hydrogen electrode (S.H.E.).

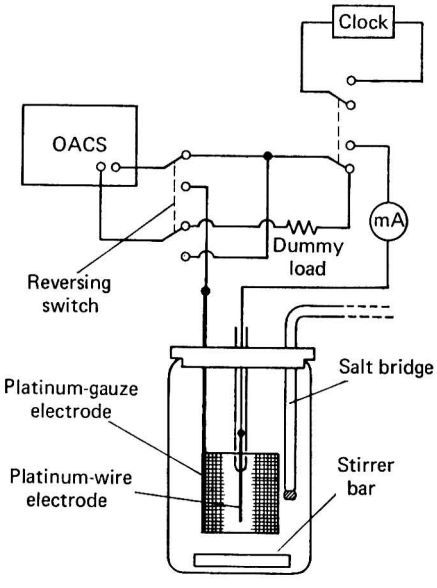

Fig. 1. Coulometric cell and circuit for the study of anodic stripping of silver from platinum gauze (OACS = operational amplifier constant-current source[5])

Results and comments

Preliminary plating experiments on untreated platinum-gauze electrodes gave well defined stripping waves, but recoveries were between 50 and 85 per cent. A second, poorly defined wave at +1·0 V is ascribed to oxidation of the platinum. The gauze electrode was reduced at 1 mA for 100 s in nitrogen-purged 0·1 M perchloric acid, and was allowed to stand in this solution for about 10 minutes until its potential became stabilised, before being

transferred to the plating - stripping medium consisting of a 0·1 M solution of silver nitrate in 0·1 M perchloric acid. Two cycles of plating and stripping are shown in Fig. 2. The amount of silver plated in each cycle was constant at 400 mC and the respective recoveries were 87 and 73 per cent. The beginning of the second stripping wave can be seen in each instance and, furthermore, in the second plating step the potential takes some time to reach the steady value indicative of silver deposition, which is taken to indicate at least partial reduction of the oxidised surface produced at the tail of the first stripping step. Decrease in stripping time on repetitive cycling has been observed before.[3,4] Clearly, oxide formation is involved and requires investigation.

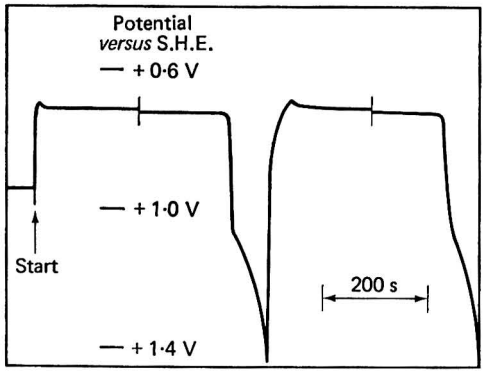

Fig. 2. Consecutive silver plating and stripping cycles in a 0·1 M solution of silver nitrate in 0·1 M perchloric acid. The short vertical lines indicate points where the current was switched on or off or reversed

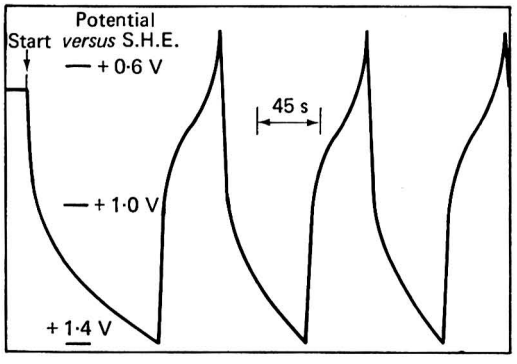

Fig. 3. Three cycles of oxidation and reduction of a 125-cm² platinum-gauze electrode at 2 mA in oxygen-free 0·1 M perchloric acid

Oxidation and reduction of platinum after the amperostatic cathodic pre-treatment was examined in nitrogen-purged 0·1 M perchloric acid at total currents of 0·5 to 2 mA. Fig. 3 shows the behaviour of an electrode, previously reduced at 2 mA for 200 s, during three cycles at 2 mA between 1·4 and 0·5 V. Electrode oxidation and reduction start at +1·0 and + 0·9 V, respectively, although the former is ill defined. The time taken for the potential to rise from 0·5 to 1·4 V decreases with continued cycling although the cathodic step remains essentially constant at 45 s. Similar behaviour was observed by Feldberg, Enke and Bricker,[6] who found that the ratio of anodisation to cathodisation times started at 2:1 and fell eventually to 1:1. In the present work, the initial ratio was about 2:1 but, after six or seven cycles, became constant at 1·2:1. Anodisation to potentials greater or less than 1·4 V produced longer or shorter cathodisation times, respectively, and the quantity of electricity required for cathodisation was virtually independent of the current; for example, halving the current produced an increase in cathodisation time by a factor of about 2·2. A mean value was found for the reduction over a variety of conditions of 0·74 mC cm^{-2}, assuming an electrode area of 125 cm². Kolthoff and Tanaka[7] reported a value of 0·92 mC cm^{-2} for anodic or chemical oxidation. Several chronopotentiometric determinations of oxide have been reported and are summarised in Table I.

TABLE I

CHRONOPOTENTIOMETRIC OXIDATION AND REDUCTION OF PLATINUM IN OXYGEN-FREE 1·0 M SULPHURIC ACID

Reference	Transition time measured	Electrode area/cm²	Current density/mA cm^{-2}	Quantity of electricity/mC cm^{-2}
8	Anodic	2	70–300	0·8
9	Cathodic	6	100	0·98
10	Anodic	0·25	60	0·94
11	Cathodic	0·33	180	0·6

The current densities were much higher than the 8 μA cm^{-2} used here, but the coverage values are all of similar magnitude. E. Bishop and B. Cooksey (unpublished work) have

shown that at potentials above 1·0 V the formation of molecular oxygen is in competition with oxide film formation, and attempted to develop growth laws. The oxidation and reduction of platinum are dealt with in detail elsewhere[12,13]; for the present purpose, it is clear that pre-conditioning of the electrode is necessary for quantitative plating of silver, and that oxidation of the electrode surface occurs when stripping is taken beyond 0·8 V.

PLATING AND STRIPPING OF SILVER IN SILVER NITRATE SOLUTIONS—

For the efficient quantitative plating of silver, a completely reduced platinum surface is clearly necessary. Three basic types of conditioning, amperostatic, potentiostatic and chemical, have been examined for this purpose. Plating and stripping were carried out in 0·1 M solutions of silver nitrate in 0·1 M perchloric acid. Between experiments, the platinum auxiliary electrode was always cleaned with 1 + 1 nitric acid so as to remove any silver deposited on it during the stripping step, which normally followed the plating step by reversal of the current.

Amperostatic cathodic reduction—The pre-treatment was performed in de-oxygenated 0·1 M perchloric acid at 2 to 500 mA. Before reduction, the platinum-gauze electrode was always in an oxidised condition that resulted from a previous anodic stripping run, from prior anodic oxidation to a potential higher than 1·4 V in de-oxygenated 0·1 M perchloric acid, or from immersion, together with the auxiliary electrode, in 1 + 1 nitric acid during the cleaning of the latter. The reduction was followed by treatment to remove any hydrogen remaining on the electrode surface. This treatment was carried out in the same solution and comprised either (*a*) allowing the electrode to stand for 2 to 20 minutes in the stirred pre-treatment solution, or (*b*) short-circuiting it to a S.C.E., connected via an intervening potassium sulphate salt bridge, for 5 to 50 minutes. The electrodes were then rapidly transferred to the silver solution.

When the cathodic pre-treatment was of short duration, so that the electrode potential did not become low enough for the evolution of hydrogen, the stripping curves were of the same shape as in Fig. 2, but the over-all recovery was only 85 per cent.

When the pre-treatment was more drastic and involved the evolution of hydrogen, and the electrodes were given treatment (*a*) above, then the stripping curves often showed an additional step just prior to the potential rise, which indicated completion of stripping. Measurement of the stripping time up to a potential of +0·8 V gave recoveries greater than 100 per cent. Fig. 4 shows two such curves at a stripping current of 2 mA for an electrode pre-treated by oxidation and reduction at 2 mA. Curve A was obtained with an electrode reduced to −0·048 V and allowed to stand for 3 minutes, and curve B with an electrode reduced to −0·072 V and allowed to stand for 2 minutes; the recoveries were 111 and 119 per cent., respectively. Compared with the normal stripping step as shown in Fig. 2, the distortion caused by oxidation of residual hydrogen is apparent, and the hydrogen is evidently underneath the silver plate. Reproducibility was poor, but, in general, the longer the time the electrode was left after pre-treatment the lower was the recovery of silver and the more

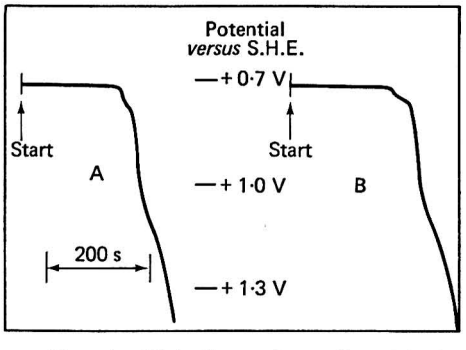

Fig. 4. Distortion of anodic stripping curves due to the presence of residual hydrogen on the electrode after cathodic pre-treatment and under the silver plate

closely the shape of the curve approached that in Fig. 2. Recoveries of 95 to 105 per cent. were obtained with electrodes left for 20 minutes and the stripping curve still showed a slower potential rise than was normal at the completion of stripping. Short-circuiting the electrode to the S.C.E. appeared effectively to remove the hydrogen and gave normal stripping curves, but the recovery averaged only 90 per cent. A similar recovery was obtained after using Bixler and Bruckenstein's method of pre-treatment A.[4] De-oxygenation of the solution for plating and stripping had no detectable influence on the shape of the plating curve or on the recovery of silver.

Potentiostatic cathodic reduction—Potentiostatic reductions were performed at command potentials of +0·6, +0·5 and +0·25 V in nitrogen-purged 0·1 M perchloric acid until the current became essentially constant. The platinum gauze was always in an oxidised form before treatment, as in the amperostatic method. The electrodes were then rapidly transferred into the silver nitrate solution. Currents in the reduction started at 1 to 4 mA and decreased rapidly, to one tenth of the initial value in 10 minutes, becoming constant at the two higher command potentials after 30 minutes and decreasing only slowly at +0·25 V; this condition produced the largest residual current, of the order of 0·1 mA. Reduction times from 35 minutes to 3 hours were used, but no significant decrease in current occurred after the first 60 minutes. Silver recoveries as high as 95 per cent. were attained, but the mean recovery in fourteen runs was only 90 per cent., and there was no appreciable difference between the effects of the three pre-treatment potentials on recoveries. De-oxygenation ofthe plating - stripping solution was without influence.

Chemical reduction—Reduction of oxidised platinum by immersing it in a solution of a reductant has been carried out several times. Kolthoff and Tanaka[7] used a 5-minute immersion in a 0·01 M solution of iron(II) sulphate in 0·05 M sulphuric acid, but found that a 0·01 M solution of arsenic(III) in 1 M hydrochloric acid had no effect in 60 minutes. Ross and Shain[14] used a 10-minute immersion in 0·1 M iron(II) perchlorate solution, Anson and Lingane[8] found an acidic iodide solution to be effective and Anson[15] used a 1-minute immersion in a 0·2 M solution of iron(II) sulphate in 1·0 M sulphuric acid. Trials with immersion of 2 to 10 minutes in 0·2 to 0·5 M solutions of iron(II) sulphate in 1·0 M sulphuric acid gave recoveries of silver between 90 and 99 per cent. Recoveries improved with increasing immersion times, and it became clear that a period of over 15 minutes was required for the platinum-gauze electrode to be reliably reduced after anodic oxidation or immersion in 1 + 1 nitric acid, and even longer times after cleaning in aqua regia. It also became clear that the potential displayed by the electrode when immersed in the plating solution gave a good indication of the efficiency of pre-treatments. A fully reduced electrode took up a potential of about 0·75 V, while incompletely reduced electrodes showed potentials between 0·85 and 0·9 V. This was confirmed by immersing two closely similar platinum-wire electrodes, one anodically oxidised and the other cathodically reduced, in the plating solutions. The potentials became stabilised at 0·90 V for the oxidised and 0·74 V for the reduced electrode, and when a clean silver-wire electrode and a platinum-wire electrode previously reduced for 30 minutes in the iron(II) solution were placed in the same plating solution, both immediately displayed the same stable potential of 0·72 V. This potential was also taken up by platinum-wire electrodes that had been treated with aqua regia, 1 + 1 nitric acid or chromic acid and by immersion, after washing, in the reduction solution for only 1 minute. The platinum-gauze electrode required prolonged immersion because the woven structure presented many hundreds of points of contact in the mesh, which created crevices that were relatively slowly accessible to the solution.

Contamination of the silver nitrate solution could arise if the gauze electrode was not completely washed before transfer from the reduction bath. This effect was examined first by adding 0·1 ml of reduction solution that had been diluted 1 + 9 with water to the plating solution just before starting a plating - stripping cycle. This treatment gave a recovery of about 115 per cent. and the stripping curve was much more rounded in the end-point region, while the time required for the potential to rise from +0·8 to +1·4 V was about 30 per cent. longer than usual. Secondly, a reduced electrode that had not been washed was plated at 2 mA for 100 s and immediately stripped at 2 mA. The initial stripping potential was 0·72 V and, after 1900 s, had decreased by only 5 mV. At this stage the current was increased to 5 mA, and after a further 180 s a fairly rapid rise in potential to 0·77 V occurred, followed by a gradual rise over 800 s to 0·8 V. When prolonged washing of the gauze electrode

was performed, by allowing it to stand, after initial thorough rinsing, in three successive batches of 200 ml of vigorously stirred water with thorough washing and draining between each washing, 100 per cent. recoveries of silver were obtained.

In addition to the initial potential of the electrode in the plating solution, the shape of the plating curve is also diagnostic of the extent of reduction of the electrodes. This is evident on comparison of Fig. 2, which shows incomplete reduction, with Fig. 5 (curve A), which shows a complete plating - stripping cycle at 2 mA in a 0·1 M solution of silver nitrate in 0·1 M perchloric acid with a chemically reduced electrode. The short vertical lines in all of the chronopotentiograms indicate points at which the current was switched on or off. The plating curve in Fig. 5 (curve A) is smooth, while those in Fig. 2 show small negative-going peaks at the beginning of plating. Nisbet and Bard[3] observed a similar phenomenon during plating on to incompletely reduced electrodes. Once again de-oxygenation of the plating solution had no influence on recoveries of silver.

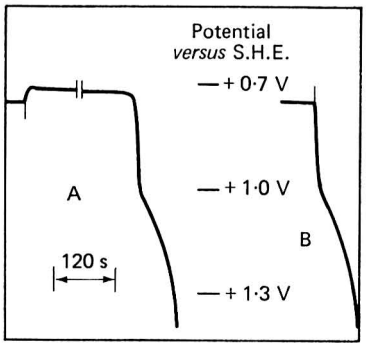

Fig. 5. Plating and stripping of silver (curve A) and stripping of a silver-free electrode (curve B) by using fully reduced platinum-gauze electrodes

PLATING - STRIPPING EFFICIENCIES IN A 0·1 M SOLUTION OF SILVER NITRATE IN 0·1 M PERCHLORIC ACID—

As a result of the foregoing investigations, a standard pre-treatment procedure for the gauze electrodes was adopted. A minimum immersion time of 20 minutes for oxidised electrodes, or 3 hours, but preferably overnight, for electrodes treated with aqua regia, was used in a stirred 0·2 M solution of iron(II) sulphate in 1·0 M sulphuric acid. After being thoroughly washed, the electrodes were immersed in clean water for at least 5 minutes.

Pre-treated platinum gauze was dried in warm air, weighed, re-treated and plated with about 3 mg of silver. After thoroughly washing it, the electrode was again dried in warm air and re-weighed. The increase in mass was well within 1 per cent. of that calculated from the quantity of electricity passed, thus confirming the quantitativeness of the plating process. Plating and stripping were performed at currents of 2 or 5 mA, the crystal clock was automatically triggered on starting and stopping the plating and on starting the stripping, and was switched off manually when the stripping potential reached 0·8 V. Stripping was started 15 to 30 s after plating so that accurate times could be noted. A series of twenty-two cycles gave the results shown in Table II. The precision improves as the amount of silver increases. The 95 per cent. confidence limits are $\pm 1{\cdot}6$ per cent. for 0·2 mg of silver and $\pm 1{\cdot}0$ per cent. for larger amounts. The uncorrected recoveries calculated from the stripping time to 0·8 V exceed 100 per cent. for amounts of 0·4 mg of silver or less, and increase as the amount of silver and the stripping current decrease. The stripping time for a clean, unplated electrode (curve B, Fig. 5) was $3{\cdot}5 \pm 0{\cdot}5$ s at 2 mA. If the recoveries are corrected for this effect, they become 99·4 per cent. for 0·2 mg of silver and 99·5 per cent. for 0·4 mg of silver. This "blank" stripping time could be due to a small amount of oxidation of the electrode at 0·75 to 0·8 V, or to the chemical deposition of a partial monolayer of silver on the electrode. Even assuming the extreme value of 100 μF cm^{-2} for the double-layer capacitance,

only 0·3 s at 2 mA would be required for charging over the potential range involved. Allen and Hickling[16] claimed that platinum was coated with silver on immersing it in 1 M silver nitrate solutions after cathodic reduction. They detected silver colorimetrically after dissolution from a 100-cm² platinum foil, and also observed a step in the stripping curve of a pre-reduced 1-cm² platinum electrode between 0·7 and 0·8 V, corresponding to about 3·5 mC of electricity. On the assumption of a roughness factor of 2, they calculated that a layer of silver seven atoms thick was formed on immersion of platinum in silver nitrate solution, which in the present instance would represent about 0·4 mg of silver, whereas the "blank" stripping time corresponds to 7 μg of silver. It is likely that the deposit, and the stripping step observed by Allen and Hickling, arose from residual hydrogen from the cathodic reduction; no steps taken to remove this deposit were described.

TABLE II

AMPEROSTATIC ANODIC STRIPPING OF SILVER IN A 0·1 M SOLUTION OF SILVER NITRATE IN 0·1 M PERCHLORIC ACID

Stripping current/mA	Approximate mass of silver plated/mg	Number of tests	Mean recovery, per cent.	Relative standard deviation, per cent.
2	0·2	10	102·9	0·7
2	0·4	6	101·2	0·4
5	0·5 to 1·1	6	100·1	0·4

ANODIC STRIPPING OF SILVER IN PERCHLORIC ACID SOLUTION—

Having obtained a satisfactory recovery in silver nitrate solutions, it was then necessary to check the recoveries under the conditions appertaining to "silver error" determinations at the end of an acid assay. After plating in the silver nitrate - perchloric acid solution, the platinum-gauze electrode was removed from the plating solution, drained, carefully and thoroughly washed with water, and allowed to stand in about 100 ml of water for several minutes before being transferred to a second coulometric cell, as in Fig. 1, containing 0·1 M perchloric acid. It was then stripped at 2 or 5 mA, the clock being automatically started and manually stopped at a stripping potential of 0·8 V. The elapsed time between completion of plating and starting of stripping was usually about 10 minutes. Craig, Law and Hamer[17] have demonstrated that the rate of dissolution of finely divided silver in perchloric acid solutions is so slow that it can be neglected with confidence. The results of thirteen experiments involving 0·2 to 1·2 mg of silver are summarised in Table III, and again show an improvement in precision as the amount of silver and the stripping current increase.

TABLE III

AMPEROSTATIC STRIPPING OF SILVER INTO 0·1 M PERCHLORIC ACID

Stripping current/mA	Approximate mass of silver plated/mg	Number of tests	Mean recovery, per cent.	Relative standard deviation, per cent.
2	0·2 to 1·2	9	100·9	1·0
5	0·8 to 1·1	4	100·3	0·7

The 95 per cent. confidence limits were $\pm$2·3 per cent. at 2 mA and $\pm$2·2 per cent. at 5 mA. Recoveries are again slightly high, but the bias decreases as the amount of silver increases, and is insignificant for amounts in the region of 1 mg. When silver-free, reduced electrodes were stripped, it was found that their initial potential in 0·1 M perchloric acid was about +0·9 V, and so there is no blank stripping time under these conditions. Typical stripping curves for about 0·4 mg of silver and for a reduced electrode at 2 mA are shown in Fig. 6. The potentials displayed by a clean silver-wire electrode and a reduced platinum-wire electrode in 0·1 M perchloric acid were approximately 0·43 and 0·98 V, respectively.

THE SECOND ANODIC WAVE—

It was observed during silver error determinations[1] that the second wave in the stripping curve associated with oxidation of platinum was abnormally long. Fig. 7 shows a typical curve for a silver error determination at 2 mA; the rise time from 0·8 to 1·4 V corresponds to about 500 mC in this instance, and values ranging from 200 to 700 mC are commonly obtained. The silver deposit in these experiments was produced under different conditions and in a different medium from the calibration plating described above. Values of about

110 mC were found in the preliminary work described in this paper, but pertained to partly reduced electrodes; values for the second wave on stripping in silver nitrate solutions at 2mA were 165 to 170 mC for both silver-plated and silver-free electrodes. For stripping into perchloric acid, as described in the preceding section, similar extended second waves appeared. Although variable, the results for the corresponding quantities of electricity were 180 to 380 mC, and longer stripping times were associated with longer second waves.

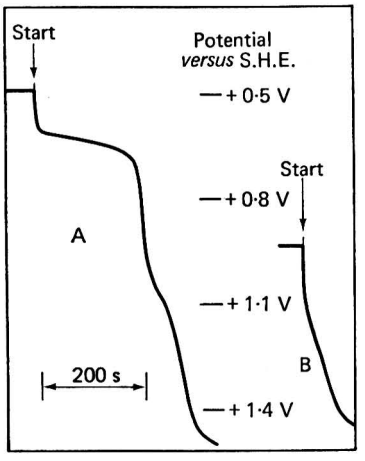

Fig. 6. Anodic stripping at 2 mA in 0·1 M perchloric acid of A, silver-plated platinum; and B, silver-free platinum

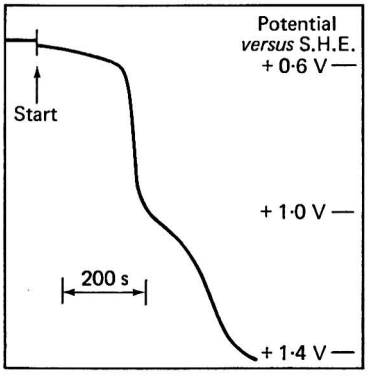

Fig. 7. Extended second wave obtained during a "silver error" determination at 2 mA

These second waves are pertinent to the ensuing pre-treatment of electrodes, and they warranted exploration. It is postulated that they are due to the anodic oxidation of hydrogen peroxide introduced into the solution by the reduction of dissolved oxygen at the auxiliary electrode during the stripping process. Laitinen and Kolthoff[18] claimed that hydrogen peroxide was a product of reduction of dissolved oxygen at a platinum electrode,

$$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2$$

but later studies[19–21] have shown that this is so only under certain conditions of the state of the electrode surface. Peters and Mitchell[21] demonstrated spectrophotometrically that significant amounts of hydrogen peroxide appeared in the bulk of the electrolyte when reduction was performed at an "aged" electrode, which was produced by allowing a freshly reduced electrode to stand in oxygen-saturated electrolyte for over 24 hours, but could detect no hydrogen peroxide when the reduction was performed with freshly reduced or pre-oxidised electrodes. They supposed that hydrogen peroxide was also produced at a freshly reduced electrode, but immediately disproportionated to water and oxygen at the "active" platinum surface, and that as the electrode "aged" it lost the ability to catalyse the disproportionation. In the present instance, the pre-reduced auxiliary electrode will be oxidised during plating then at least partially reduced during the first part of the stripping step, and then, concurrently with the reduction of dissolved oxygen, some of the silver stripped from the anode will be deposited on it in increasing amount as the stripping time increases. Kolthoff and Laitinen[22] found that dissolved oxygen was reduced at silver at more positive potentials (less charge-transfer overpotential) than at platinum.

It did not seem that the condition of the auxiliary electrode was suitable for hydrogen peroxide formation in the present work, and so reduction of dissolved oxygen at silver electrodes was investigated. Deliberate addition of trace amounts of hydrogen peroxide, either during the stripping of silver in 0·1 M perchloric acid, or just prior to stripping a silver-free reduced electrode, produced extended second waves. This observation agrees with reports[23–26] that hydrogen peroxide is oxidised at an unoxidised platinum electrode, but

only qualitative correlation could be made between the amount of hydrogen peroxide added and the increase in duration of the second wave. When oxygen-free 0·1 M perchloric acid was used for silver stripping no extension of the second wave occurred, even with long stripping times, and the recovery of silver was unchanged. When the auxiliary electrode was pre-plated with silver and the solution contained oxygen, significantly extended second waves appeared, even with short stripping times, and hydrogen peroxide was detected spectrophotometrically in the cell electrolyte. In two examples with silver stripping times of 120 and 500 s, the second waves were equivalent to 340 and 550 mC, respectively.

The peroxodisulphatotitanic(IV) acid method was used to determine hydrogen peroxide. The absorption spectrum of the complex showed a broad peak with $\lambda_{max.} = 410$ nm. A linear Beer's law graph was used as a calibration graph; the molar absorptivity of the complex at 410 nm was 40 l mol^{-1} mm^{-1}. Blanks of freshly prepared 0·1 M perchloric acid electrolyte were used. A 10-ml sample of the cell electrolyte, after about 80 per cent. of the silver had been stripped, was treated with 2 ml of the titanium(IV) reagent and the absorbance at 410 nm was measured. The amount of hydrogen peroxide found in the electrolyte was of the order of 10^{-5} mol l^{-1}, but could be only qualitatively correlated with the extension of the second wave. The reaction is probably cyclic.

Discussion

Clearly, the efficiency of plating silver on incompletely reduced platinum electrodes is significantly below 100 per cent., and the loss is due to the concurrent reduction of remanent oxide. The oxidation and reduction of platinum show behaviour in accord with other work, but the interpretation is still contentious and is dealt with elsewhere. Insufficient attention seems to have been paid to the competitive formation of molecular oxygen in the oxidation half-cycle. Failure of the electro-reduction methods to give fully reduced active electrodes for plating is puzzling, but is tentatively ascribed to electro-sorption of impurities of which minute traces exist in sulphuric acid[12] or insufficient prior oxidation, or both. Later work suggests that repeated anodic - cathodic cycling is necessary in preparing a fully active electrode. The iron(II) reduction method, when correctly applied, gives electrodes at which good plating efficiency is attained, but very thorough washing of the electrode is essential, otherwise cyclic oxidation and reduction of iron(II) and iron(III) at the two electrodes occurs and no silver is plated on the electrode.

On the basis of plating calibrations involving the use of electrodes pre-conditioned by chemical reduction with iron(II), silver stripping recoveries both in silver nitrate solutions and in pure perchloric acid solutions are excellent for 0·2 to 1·2 mg of silver and are of a precision entirely adequate for the determination of silver errors. The blank found in silver nitrate solutions but absent in perchloric acid shows that about one tenth of a monolayer of silver is deposited chemically on platinum immersed in a silver solution, and this finding is supported by the potentials of silver and platinum electrodes in these media. Hydrogen peroxide is produced at the auxiliary electrode by reduction of dissolved oxygen during the stripping of silver into perchloric acid, and gives rise to an extended second wave in the stripping chronopotentiogram. The deposition of stripped silver on the auxiliary electrode favours this process because of the lower charge-transfer overpotential of reduction of oxygen on this metal. The phenomenon is absent in de-oxygenated media, and in any event does not affect the recovery of silver; it does, however, add emphasis to the importance of adequate pre-treatment of platinum electrodes on to which silver is to be plated.

Conclusions

The present study has shown that silver present on a platinum-gauze electrode can be determined by amperostatic anodic stripping with an accuracy and precision that are adequate for the required "silver error" determination, and that such an electrode can be washed and transferred into the stripping solution without significant loss of silver. The amount of silver present on the working electrode at the end of an acid assay that involves the passage of 5000 C can be determined simply and rapidly by this method. Extended second waves (which do not affect the silver determination) on the stripping curves arise from the oxidation of hydrogen peroxide produced at the auxiliary electrode or oxidation of residual hydrogen on the electrode surface following the acid determination, or both.

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NOTE—References 1 and 5 are to Parts II and I, respectively, of this series.

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Precise Coulometric Determination of Acids in Cells Without Liquid Junction

Part IV.* The Assay of Primary Standard Sulphamic Acid†

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The precise (1 to 2 p.p.m.) location of the end-point in the pre-titration of the supporting electrolyte and in the titration of sulphamic acid has been examined, and d.c. differential electrolytic potentiometry gives excellent results. The methods and simple apparatus previously described in Parts I, II and III are applied to the assay of primary standard sulphamic acid previously collaboratively assayed by mass titrimetry, and give results with an accuracy and precision of 100 p.p.m., and a 95 per cent. confidence level of 0·02 per cent., but with a positive bias of 0·014 per cent., the reasons for which are canvassed. The method is of high merit; it is simple, fast and direct, and is capable of further refinement.

EARLIER work has established that current sources of adequate stability and a timing device of adequate accuracy are available for high-precision amperostatic acidimetry[1]; that suitable conditions can be chosen that permit the use of a level of deposition of more than 5000 C of bromide on a silver anode as the auxiliary reaction in the same compartment in which the cathodic determination of the acid is conducted[2]; and that the error arising from the solubility of silver bromide in the cell electrolyte and consequent deposition of silver on the working cathode can be evaluated with adequate accuracy and precision.[3] There remained for investigation first, a means of locating the end-point of the reaction with adequate accuracy and precision, and secondly, the testing of the whole method by the assay of an independently standardised primary standard acid. For the latter, sulphamic acid, which was collaboratively assayed by the Analytical Standards Sub-Committee of the Analytical Methods Committee of the Society for Analytical Chemistry and recommended and accepted as an international primary standard,[4,5] was selected. For end-point location, d.c. differential electrolytic potentiometry has an adequate reserve of sensitivity.[6]

EXPERIMENTAL

The equipment used has been described previously.[1] The cell used in the final determinations is shown in Fig. 1. The platinum-gauze cathode was the larger Model 72020. The silver anode comprised two electrodes, one each of sizes A and B, of total area 275 to 315 cm^2. The twin antimony differential electrolytic potentiometric electrodes were mounted centrally so as to be out of the generating current field, and were held in a rubber bung, which was replaced with a plain bung when the indicating electrodes were removed from the cell. Pure oxygen, humidified by passage through a water bubbler, was passed over the surface of the solution, and served to exclude carbon dioxide and to oxygenate the solution for the benefit of the antimony electrodes.[7] Excess of oxygen escaped through an exit tube that was provided with a spray trap. The platinum-gauze electrode was initially cleaned by immersion for 1 to 2 minutes in freshly prepared aqua regia, followed by very thorough washing with and storage in water. Subsequently, after "silver error" determinations, it was immersed in a 0·2 M solution of iron(II) sulphate in 1·0 M sulphuric acid for at least 30 minutes before further use.[3] Other electrodes were treated as described previously.[1] The circuit, in which the cell is indicated in plan view, is shown in Fig. 2. The constant-current sources were run continuously, being switched to dummy loads when not in use. The selector switch on the P3 potentiometer was used to select the standard resistor that was required when power supplies were exchanged. Switching in power supplies to the cell automatically triggered the clock, and switching over to the dummy load stopped the clock.

* For particulars of Parts I, II and III of this series, see reference list, p. 431.

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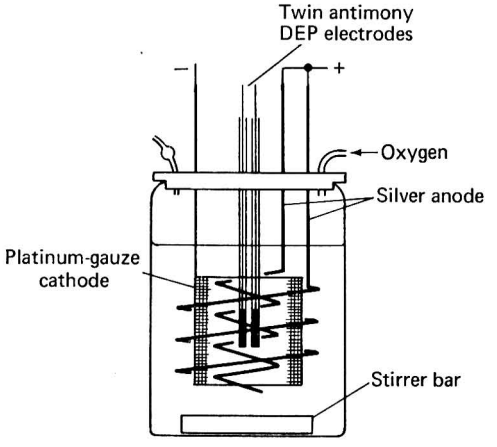

Fig. 1. Coulometric cell for acid determination (DEP denotes differential electrolytic potentiometric)

SULPHAMIC ACID—

Samples were taken from a 100-g batch of sulphamic acid provided in a sealed container by the Analytical Standards Sub-Committee. The sample had been collaboratively assayed with reference to atomic-mass grade silver at 100·001 per cent. purity. The samples were dried under vacuum over fresh magnesium perchlorate for at least 24 hours before use.

WEIGHING AND TRANSFER OF SAMPLES—

Catch-weights of 4 to 5 g of dry sulphamic acid were weighed in small glass weighing bottles that had outside-fitting lids, with a hole drilled in each ground face so that pressure could be equalised by turning the lid to register the holes. Preliminary rough weighings to the nearest 1 mg were made on a CL3 balance, and the accurate weighings made on the

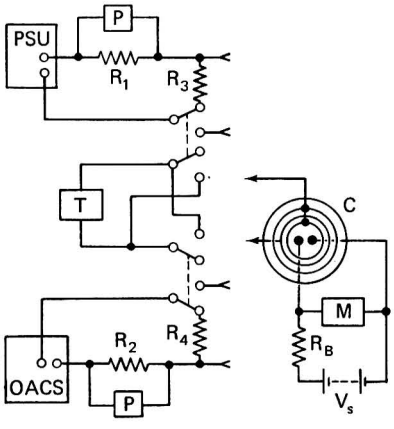

Fig. 2. Circuit for coulometric acidimetry: C, plan view of coulometric cell; PSU (power supply unit), 2-A source AS 1411; OACS, operational amplifier constant-current source; P, P3 potentiometer; T, crystal clock; M, 39A pH meter; V_s, DEP voltage source; R_1, 0·5-Ω standard resistor (two 1-Ω standards in parallel); R_2, 10-Ω standard resistor; R_3, dummy load resistor, about 0·6 Ω; R_4, 10-Ω dummy load resistor; and R_B, DEP ballast resistor

special atomic-mass balance that had a standard deviation of 1·3 μg on 100 g and was provided with both 5 and 0·5-mg riders. Once the riders had been located in the correct notch, the balance was left for 30 minutes, then released and the swings were observed by telescope from a distance of 20 feet. The sequence of measurements were zero, weighing bottle *plus* sample, sensitivity, zero, empty weighing bottle, sensitivity, zero. Buoyancy corrections were made by using 8·0 g cm^{-3} for the density of the weights and 2·126 g cm^{-3} for the density of sulphamic acid. The sample was transferred into the cell, which had already been filled with pre-titrated electrolyte, with oxygen passing through it, via a small glass funnel inserted in the lid. Most of the crystals passed straight through into the cell. The lid of the weighing bottle was replaced and the bottle re-weighed. Before adding the sample to the cell, 20 ml of the neutral electrolyte were withdrawn into a hypodermic syringe, and this solution was used to wash the funnel thoroughly, which was then removed and the hole closed with a bung.

END-POINT LOCATION—

A conventional differential electrolytic potentiometric circuit[8] was used as indicated in Fig. 2. The source voltage was 240 V and the ballast resistance was 960 MΩ, giving a differentiating current density of about 4 μA cm^{-2}. Differential potentials were measured on the 39A pH meter and recorded on a 10-mV recorder. The electrodes were inserted for pre-titration, then removed and replaced within 1 C of the end-point.

Preliminary appraisal of the response was made by titrating 7 to 10 mg of sulphamic acid at concentrations of 2·5 to 3·5 × 10^{-4} M at currents of 10 mA in 0·03 M potassium bromide solution. Satisfactory differential peaks, 50 to 80 mV in amplitude, were obtained at differentiating current densities of 2·2 to 6·6 μA cm^{-2} and ballast loads of 3·6 × 10^{10} to 1·1 × 10^{11} VΩ, but with continuous generation the results showed a positive bias of 1 to 2 per cent. Bishop and Short[6] determined similar amounts of perchloric acid by continuous generation at 2 to 10 mA but found a bias that was not greater than 0·2 per cent. The cause of the bias (electrolyte retention in the meshes of the electrode) was not immediately apparent, but it was concluded that incremental generation, with automatic time integration with the crystal clock, would be more apposite in high-precision work. With incremental generation, relatively long times were required for the differential potential to become stabilised near the end-point. Times of 4 to 5 minutes were usual in pre-titration (see below) and 6 to 10 minutes during the final end-point determination. The positive-going drifts were not caused by the electrodes, because glass indicator electrodes referenced to a saturated mercury(I) sulphate electrode showed similar drifts to higher pH values. The drift is due to slow diffusion of hydroxyl ions from the interstices of the gauze electrode into the bulk of the solution. Eckfeldt and Shaffer[9] observed similar drifts in unbuffered solutions when using an electrode constructed in the form of a mesh of platinum strips, and found that the drift was eliminated when smooth platinum wire was used.

Satisfactory end-points were achieved in sulphamic acid determinations by using incremental generation in the vicinity of the end-point, although the long equilibration times between increments made the procedure rather tedious. Differential potentials were considered to be stable when a drift of less than 0·2 mV min^{-1} was recorded. A typical end-point determination is shown in Fig. 3 for incremental generation at 10 mA. Exact end-points could be extracted from such curves geometrically,[6] but could usually be estimated visually with sufficient accuracy; an error of 1 s in the end-point location corresponded to an over-all error of 2 p.p.m. in the determination. Curves for the pre-titration were identical, although peak heights were greater by about 10 mV.

Pre-titration of the cell electrolyte, before addition of the sample, was carried out at a current of 5 mA so as to correct for any residual carbon dioxide in the water or acidic impurities in the potassium bromide. This pre-titration required about 0·05 C, corresponding to a residual carbon dioxide concentration of 1·7 × 10^{-6} M, assuming this to be the only impurity present, and is in good agreement with the earlier value[6] of 1·6 × 10^{-6} M.

PROCEDURE FOR SULPHAMIC ACID ASSAY—

From the approximate mass of the sample, the theoretical amount of potassium bromide was calculated, and this amount *plus* an excess of 1·0 to 1·1 g was weighed. The power supply to the crystal clock was switched on at this stage: as the circuit is entirely of the low-power solid-state type, the clock reaches thermal equilibrium quickly and does not need

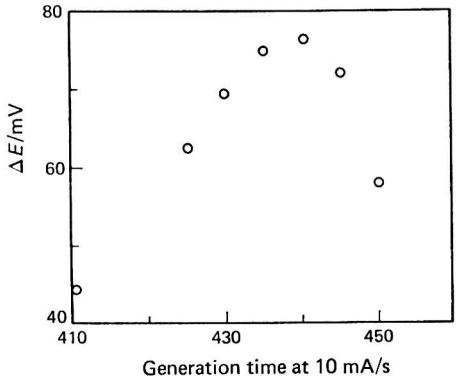

Fig. 3. Typical end-point location graph

to be run continuously. The pre-conditioned cell was rinsed with carbon dioxide free water, the potassium bromide and magnetic follower were placed in it, the lid and electrode assembly fitted and the flow of oxygen was started. About 300 ml of carbon dioxide free water were dispensed from the reservoir into the cell through a spare hole in the lid, which was then closed with a bung and the stirrer switched on. The operational amplifier constant-current source was set to give an output of 5 mA, and the potential drop across the standard resistor and the temperature of the latter were noted. Pre-titration was performed by generation in increments of 2 to 4 s, allowing the differential potential to become stabilised between increments. The values of the cumulative generation time and the differential potential were noted after each increment, and generation was continued until the differential potential showed a marked fall. The quantity of electricity passed after the differential electrolytic potentiometric peak was calculated. The antimony indicator electrodes were removed and washed with and stored in water, the hole in the lid being then closed with a bung.

The 2-A current source with output settings of 2·0 A and 39·9 V (the maximum setting) was monitored, and the sulphamic acid sample was transferred into the cell. The crystal clock was re-set to zero. The potential drop across the standard resistors and their temperatures were noted and generation at 2 A was started. The theoretical quantity of electricity, Q_T, required for neutralisation was calculated, and generation at 2 A was continued to within 50 C of Q_T. The lid and walls of the cell, the electrode stems and the spray trap were carefully washed down, which was effected by fitting a 20-ml hypodermic syringe with a suitably bent needle, opening the spare hole in the lid, withdrawing 10 to 15 ml of cell electrolyte into the syringe and using this solution for the washing down, further portions of electrolyte being withdrawn if necessary. Use of the bent needle enabled all of the washings to be carried out without removing the lid. Generation at 2 A was continued to within 5 C of Q_T, when the 2-A current source was disconnected, the generation time at 2 A was noted and the washing operations were repeated. Measurements of the current flowing were made at 2-minute intervals during electrolysis at 2 A.

The operational amplifier source, set to 10-mA output, was then monitored, the crystal clock re-set to zero and generation continued to within 1 C of Q_T. After a further washing operation, the antimony indicator electrodes were rinsed with carbon dioxide free water, inserted in the cell and the differential electrolytic potentiometric circuit activated. Generation at 10 mA was continued in 10 to 20-s increments until the differential potential showed a significant increase, when a final washing down was performed. The final part of the generation was conducted in 4 to 5-s increments, noting the time and stabilised differential potentials after each increment, and was continued until four or five points after the end-point had been passed.

The platinum-gauze electrode was then carefully removed from the cell, gently washed with water and drained several times, and immersed in water for 5 to 10 minutes. It was then mounted in a stripping cell (Fig. 1 in Part III[3]) containing 0·1 M perchloric acid electrolyte, and the 39A pH meter was connected between the gauze electrode and the saturated mercury(I) sulphate electrode. The operational amplifier source was set to 5 mA, the crystal

clock re-set and the silver stripped from the gauze electrode as previously described,[3] the time taken to reach a potential of +0·8 V being measured by stopping the clock manually at this stage.

Calculation of results—

The end-point was located graphically as in Fig. 3, for generation time at 10 mA, and the total number of coulombs used in the acid determination, Q_F, was calculated as follows—

$$Q_F = Q_D + Q_E - Q_S$$

where Q_D is the number of coulombs passed at 2 A, calculated from the mean of the measured values of the current, Q_E is the number of coulombs passed at 10 mA in reaching the end-point *plus* any excess of generation at 5 mA in the pre-titration, and Q_S is the number of coulombs required for the anodic stripping of silver. The result of the coulometric assay was therefore the ratio of Q_F to Q_T, expressed as a percentage.

Results and discussion

The results obtained on one batch of sulphamic acid, comprising eight assays of 4 to 5-g portions, are shown in Table I and are typical. The values of Q_T were calulated, to the nearest 0·01 C, by using the recommended value of the Faraday constant[10] of 96 486·70 ± 0·5 A s mol^{-1} and a relative molecular mass of 97·093 for sulphamic acid. Evidently, the method is capable of high precision: the 95 per cent. confidence limits are ±0·02 per cent. The two results, 99·999 and 100·028, attenuate the precision rather severely, but cannot be excluded because they are, although only just, statistically significant.

Table I

Coulometric assay of Batch 3 sulphamic acid

Sample mass/g	Quantity of electricity Q_D/C	Q_E/C	Q_S/C	Assay, per cent.
4·850 03	4815·25	7·422	2·543	100·008
4·496 97	4468·38	4·645	2·194	99·999
4·702 20	4672·73	3·131	2·246	100·016
5·138 46	5104·42	5·675	2·637	100·021
4·325 46	4297·32	4·432	2·101	100·028
4·320 23	4289·51	6·316	2·173	100·009
4·683 28	4654·33	2·968	2·400	100·018
4·895 63	4864·78	3·863	2·506	100·022
		Mean		100·015
		Relative standard deviation ..		0·009 per cent.

It is clear that the results show a positive bias, being 0·014 per cent. higher than in the mass titrimetric assay, which in one respect is fortunate in that it shows that cancellation of errors had not occurred: it is probable that several factors contribute to the bias. A bias in the measurement of the 2 A current was adumbrated earlier,[1] and it is possible that the uncertainty of ±50 p.p.m. in the values of the two 1-Ω standard resistors used for measurement of high currents could account for one third of the bias. The possibility that the measured silver errors, whose constancy reflects the fact that the total times occupied by the acid determinations were similar in all instances, were low because of some mechanical loss of silver from the gauze electrode cannot be entirely discounted, although such a loss might be expected to show larger variations in the value of Q_S. It is not improbable that anodic reactions other than halide deposition could occur, which could be significant particularly towards the end of the determination when the pH is rising rapidly. These reactions might include the anodic directions of

$$AgOH + e \underset{i_a}{\overset{i_c}{\rightleftharpoons}} Ag + OH^-$$

$$O_2 + 4H_3O^+ + 4e \underset{i_a}{\overset{i_c}{\rightleftharpoons}} 6H_2O$$

$$O_2 + 2H_2O + 4e \underset{i_a}{\overset{i_c}{\rightleftharpoons}} 4OH^-$$

and, although the solution is oxygenated it is not purged, so that some molecular hydrogen in solution may give a small anodic current due to its re-oxidation—

$$2H_3O^+ + 2e \underset{i_a}{\overset{i_c}{\rightleftharpoons}} H_2 + 2H_2O$$

It is also possible that 1 or 2 p.p.m. of the anodic current produces bromine from the bromide, and the bromine would hydrolyse at pH above 5, thus producing hydrogen ions.

The drifting differential potentials near the end-point made the finish of the determinations rather tedious, so that a complete determination required about 5 hours, although this is much quicker than the titrimetric assay, which takes 3 to 5 days. That the drifting is caused by diffusion of hydroxyl ions from the interstices of the platinum gauze is in agreement with previous findings.[3] It also explains the difference in equilibration times between pre-titration and final end-point location, because the concentration of residual hydroxyl ions on the electrode would be expected to be much larger near the end of the reaction. A coiled platinum rod or perforated heavy gauge sheet would be better than gauze, and could reduce the experimental time by 90 minutes.

The measured values of the large current were found to change only very slowly over the 35 to 40 minutes of generation, and the maximum deviation was only 20 p.p.m. The cell resistance was less than 0·5 Ω initially and rose to 2 Ω at the end of the high-current generation period: the temperature of the cell electrolyte rose by 5 to 6 °C from the initial 20 °C.

Conclusions

Results obtained in the assay of primary standard sulphamic acid show that a precision and accuracy in the region of 100 p.p.m. can be achieved with the simple cell and equipment described. Refinement of the method, by using better current measuring equipment, smooth platinum instead of gauze and purging of the electrolyte with 1 + 5 oxygen - nitrogen or oxygen - argon mixture, could enhance the precision and reduce the time required.

Operation in the differential mode, with two cells in series, for the intercomparison of chemical standards would certainly yield improved precision, and would give the method even more marked advantages over the conventional methods with multicompartment cells.

One of us (M.R.) is deeply indebted to the Charitable and Educational Trust of the Worshipful Company of Scientific Instrument Makers for financial support in the form of a Research Studentship.

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Note—References 1, 2 and 3 are to Parts I, II and III, respectively, of this series.

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A Quantitative Tunable Element-selective Detector for Gas Chromatography

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A detector based on the atomic-emission spectra that result when organic compounds are decomposed in a low-pressure, microwave-sustained helium plasma is described. All of the non-metallic elements normally found in organic compounds can be sensitively and selectively detected in a linearly proportional and quantitative manner by means of conventional diffraction grating spectrometer equipment. A controlled amount of a scavenger gas is used to prevent carbon deposition inside the plasma tube. The chromatographic column outflow is split between the element-selective detector and a non-selective flame-ionisation detector. The latter acts as a reference for interpreting element-selective detector results and assists with the determination of atomic ratios and the empirical formulae of organic compounds.

The gas-chromatographic detection of organic compounds by emission spectroscopy with a microwave-powered plasma was first reported by McCormack, Tong and Cooke[1] and subsequently developed by Bache and Lisk[2,3] and others.[4,5] The organic compounds emanating from the gas chromatograph are fragmented in the high-energy plasma to produce emission spectra, which are then monitored with a suitable spectrophotometric detection system. In principle, the technique is applicable to a very wide range of elements, but most work to date has centred around the elements of interest in pesticide analysis, for example, sulphur, phosphorus and chlorine. Our objectives were to extend this range and to improve the quantitative characteristics of the system, and because of the latter objective we preferred to use a low-pressure helium plasma to produce the atomic-emission lines. The lower energy of an argon plasma is insufficient to prevent the association of atoms into pairs and this leads to the production of complex band-emission spectra, which reduces the spectral selectivity on atomic lines. The association of atoms into pairs also reduces the population of free atoms, and for quantitative work this effect adds a complicating mass-action influence to atomic emission and gives compound-specific effects. The higher energy of the helium plasma greatly inhibits formation of atom pairs, to the obvious benefit of the atomic-emission characteristics.

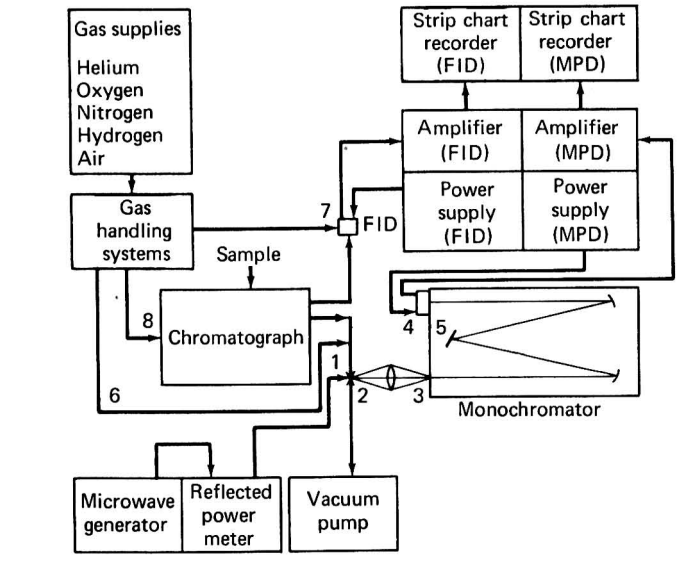
In our early work, both the qualitative and the quantitative performance were hampered by persistent deposition of carbon on the inner walls of the plasma tube, but a dramatic improvement resulted when a small amount of air was continuously bled in. Subsequently, it was found that either oxygen or nitrogen would act as a carbon scavenger, and this discovery enabled either element to be included in the range of the technique by using the other as scavenger.[6]

Apparatus—

The apparatus is shown diagrammatically in Fig. 1.

Gas chromatograph—We normally used a Pye 104 gas chromatograph but other makes have been used with equal success. Any column with low bleed characteristics can be used; the conditions for the chromatograms shown in this paper were—

Column	3 m × 2·5 mm, packed with 10 per cent. Apiezon L on 60 to 80-mesh DCMS-treated Chromosorb W
Temperature	112 °C (pre-heater 200 °C)
Pressures	Head of column, 170 kN m^{-2}; tail of column, 35 kN m^{-2}
Detector splitting ratio ..	1:1
Scavenger gas	Oxygen (or nitrogen): 0·1 to 1 per cent. of total plasma gas according to demand



1. Microwave cavity
2. Plasma discharge
3. Monochromator entrance slit
4. Exit slit and photomultiplier
5. Diffraction grating
6. Scavenger gas supply
7. Air - hydrogen supply
8. Helium supply to chromatograph

Fig. 1. Block diagram of the apparatus

Microwave plasma detector (MPD)—The plasma emission is contained in a thick-walled quartz capillary tube of 10 mm o.d. and 1 mm i.d., with an over-all length of 15 cm. This tube is mounted vertically in an assembly that also holds the microwave cavity in position. The pressure within the plasma is adjustable from an arbitrary 0·25 torr to higher pressures by means of a vacuum pressure regulator in the line connecting the plasma to the vacuum pump (Fig. 2). Microwave power, generated by a 0 to 200-W generator (Electro-Medical Supplies Limited, London) at 2·45 GHz from 100 to 200 W, is supplied to the tuned 214L cavity via a reflected power meter and flexible wave guide. The tuning stubs on the cavity are adjusted until the reflected power is the minimum attainable. With this type of cavity, the power reflected can be made as low as 1 per cent.

The plasma is initiated by means of a Tesla coil and gives an intense plasma discharge about 10 cm long.

Gas supplies—High-pressure sources of the following gases were used—

Helium	Grade A	Carrier gas
Oxygen	Electrolytic grade	Scavenger gases
Nitrogen	White spot grade	
Air	Laboratory supply	Flame-ionisation detector support gases
Hydrogen	Electrolytic grade	

Grade A helium was purified by passing it through a B.O.C. helium purifier, in which oxygen and nitrogen were removed by the hot titanium sponge and hydrocarbons were oxidised to carbon dioxide and water by hot copper(II) oxide; these products were then removed in a modified 5A molecular sieve unit placed externally to the purifier and maintained at −80 °C. The scavenger gases were dried by passing them through a cold trap at −80 °C. Because of the relative amounts of each gas used, the purity of helium is approximately one hundred times more critical than that of the scavenger gases, so for the more common elements carbon, nitrogen, hydrogen and oxygen, the greater the spectral purity of the helium, the higher is the sensitivity.

It was realised at an early stage that the value of element-selective results was much enhanced by the simultaneous recording of non-selective results, *e.g.*, those from a flame-ionisation detector. This realisation led us to develop an interface system that enabled a

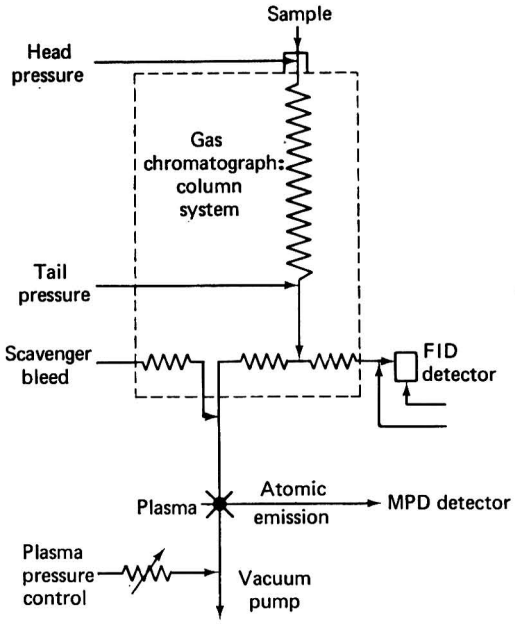


Fig. 2. The chromatograph and the interfacing system to two detectors

gas-chromatographic system to be coupled with two or more detectors that were operated at atmospheric or lower pressures. The principle is illustrated in Fig. 2. The exit of the column system is maintained at a pressure in excess of that of the atmosphere by a separate supply of carrier gas; the extra supply then merges with the column exit flow and splits into equal parts across specially designed flow restrictors to the detectors. By allowing the total flow-rate to the detectors to be more than the optimum flow-rate through the gas-chromatographic column, no additional constraints are imposed upon the chromatography.

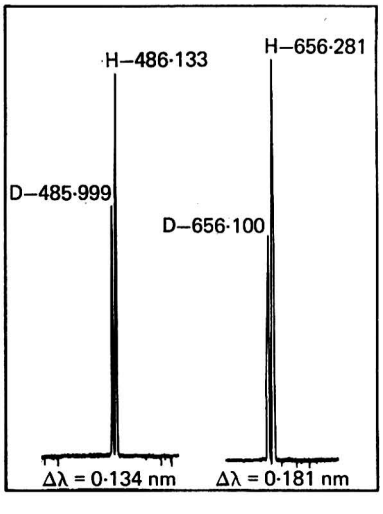


Fig. 3. Resolution of the hydrogen - deuterium atomic-emission lines (wavelengths in nanometres)

Spectrophotometer—The monochromator used was a Hilger and Watts Monospek 1000 with a 102 × 102-mm diffraction grating of 1200 lines mm^{-1} (blazed at 300·0 nm) to give a dispersion of 0·88 nm mm^{-1}. The original IP28 side-window photomultiplier was replaced with a similarly designed Hamamatsu R446 photomultiplier, which extended the optical range available from 190·0 nm to greater than 900·0 nm with an excellent degree of sensitivity.

SPECTRAL CHARACTERISTICS—

The spectroscopic system gave good line spectra for all of the elements examined with very little evidence of molecular band emission. As examples, Fig. 3 shows the resolution of the hydrogen and deuterium lines and Fig. 4 the resolution of the triplets of oxygen and nitrogen. The preferred wavelengths for the elements examined are shown in Table I. The technique should be equally applicable to boron and mercury[7] or, indeed, any element that can be introduced into the plasma. Energy levels involved in the emission of atomic spectra from non-metals are included in Table I and are illustrative of the high energy of the helium plasma.

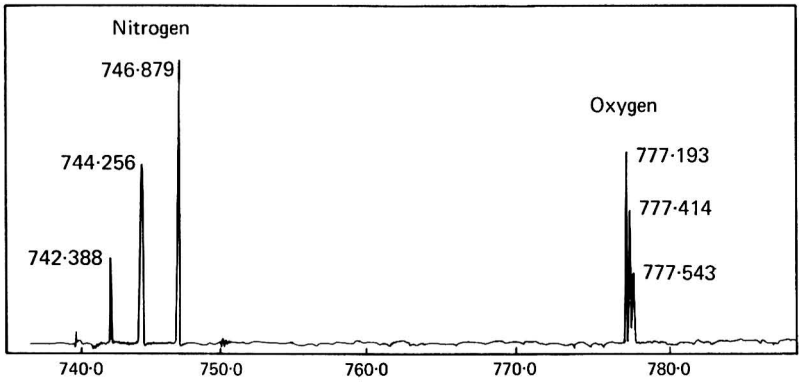


Fig. 4. Atomic-emission spectra for nitrogen and oxygen (wavelengths in nanometres)

QUALITATIVE ELEMENT-SELECTIVE DETECTION—

An artificial mixture containing most elements of interest was made up and run through the system to illustrate the element selectivity (Fig. 5). To compare the selectivity for the various elements, n-heptane was used as a standard carbon and hydrogen containing compound, and in Table II the selectivity factor given is the ratio of the mass flow-rate of heptane to the mass flow-rate of the element required to give equal signals at the element-selective emission wavelengths. Inter-element effects are dealt with later.

TABLE I

ELEMENT-SELECTIVE EMISSION WAVELENGTHS AND EXCITATION ENERGIES

Element	Emission wavelength/nm	Ionisation state	Energy levels/eV E_2 → E_1
C	247·857	1	12·69 → 7·69
H	486·133	0	15·29 → 12·74
D	656·100	0	13·98 → 12·09
F	685·602	1	16·31 → 14·50
Cl	479·454	2	18·54 → 15·95
Br	470·486	2	17·03 → 14·4
I	516·119	2	13·51 → 12·11
S	545·388	2	18·21 → 15·94
P	253·565	1	12·08 → 7·2
N	746·879	1	— → —
O	777·193	1	12·34 → 10·73
He	587·562	1	25·17 → 23·06

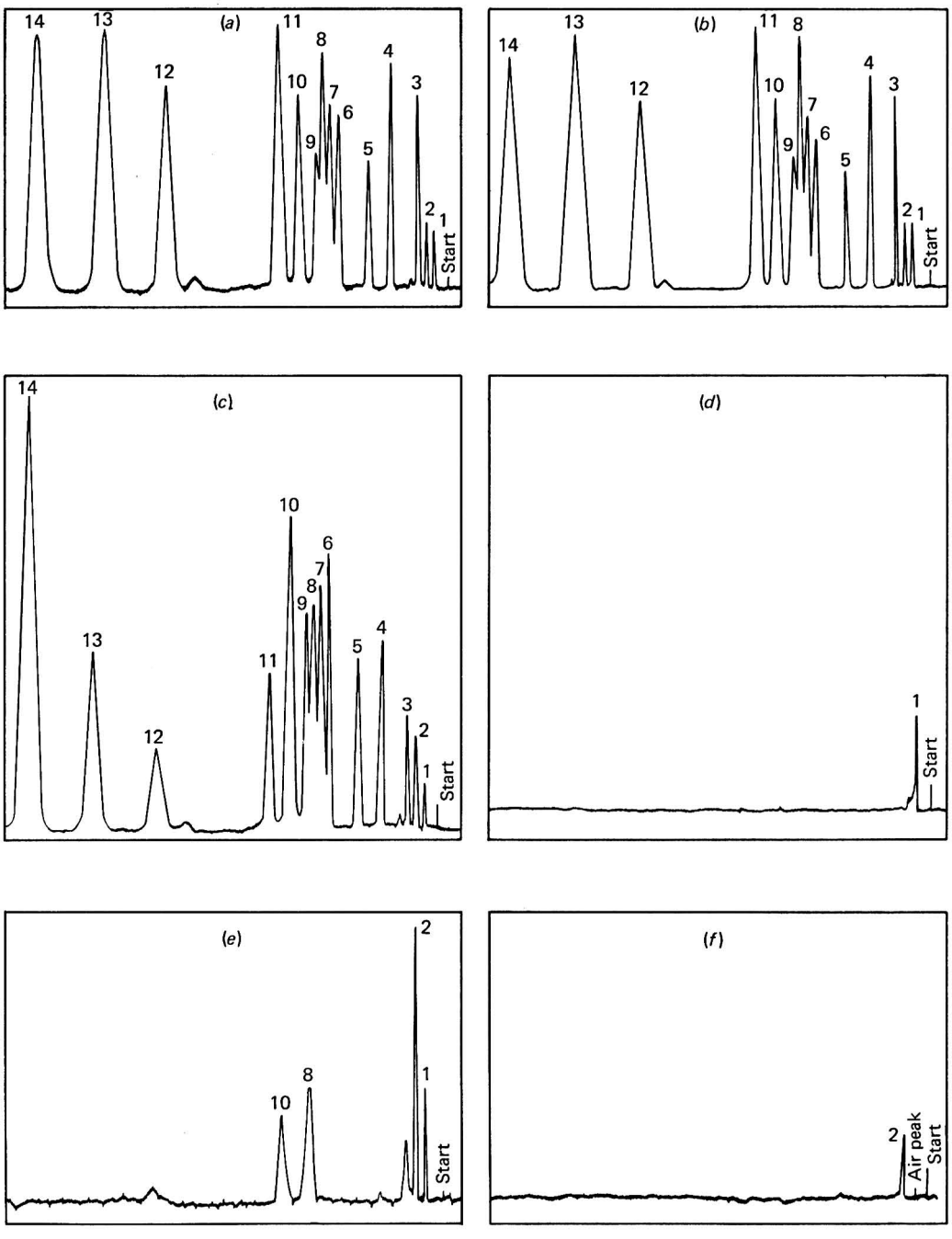


Fig. 5. Element-selective traces on a test sample for C(*b*), H(*c*), D(*d*), O(*e*), N(*f*), F(*g*), Cl(*h*), Br(*j*), I(*k*) and S(*l*) *versus* a flame-ionisation detector reference (*a*). Emission wavelengths are: C, 247·857 nm; H, 656·281 nm; D, 656·100 nm; O, 777·193 nm; N, 746·879 nm; F, 685·602 nm; Cl, 479·454 nm; Br, 470·486 nm;

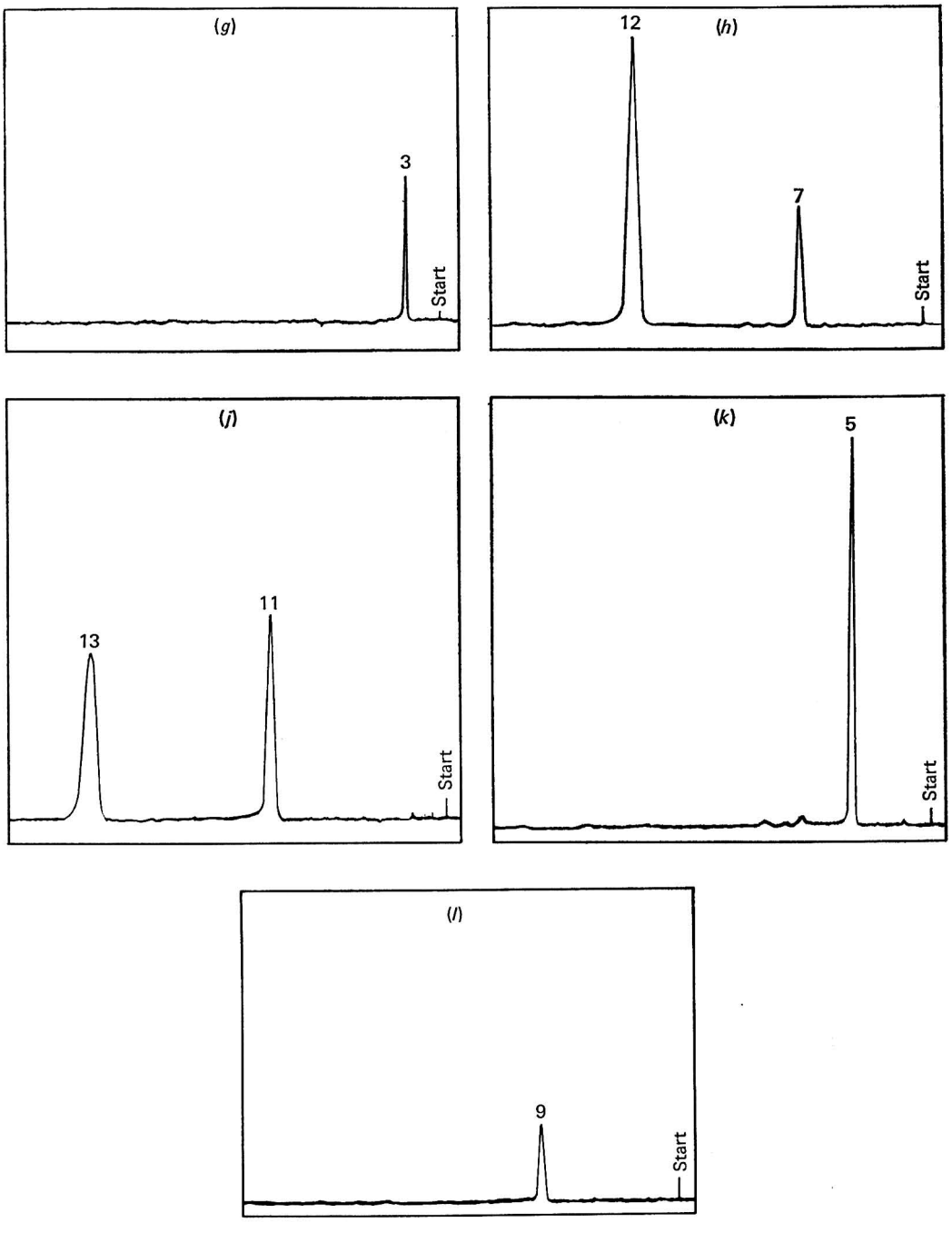


Fig. 5, continued

I, 516·119 nm; and S, 545·388 nm. Throughout, peaks are: 1, deuteroacetone; 2, nitroethane; 3, fluorobenzene; 4, toluene; 5, n-butyl iodide; 6, n-nonane; 7, chlorocyclohexane; 8, anisole; 9, diethyl disulphide; 10, octan-2-one; 11, bromobenzene; 12, *o*-dichlorobenzene; 13, *o*-bromotoluene; 14, n-undecane

TABLE II

DETECTION LIMITS, SPECTRAL BACKGROUND LEVELS AND SELECTIVITY IN DETECTION

Element	Detection limit*/ng s^{-1}	Total background as element/ng s^{-1}	Selectivity ratio *versus* n-heptane*
C	0·08	0·81	—
H	0·03	0·22	—
D	0·09	0·17	880
F	0·06	0·091	2300
Cl	0·06 (0·06)	0·46	510 (44)
Br	0·091 (0·02)	0·72	1300 (38)
I	0·05 (0·05)	0·56	400 (38)
S	0·09 (0·05)	1·1	390 (22)
P	— (0·009)	—	— (1000)
N	2·9	113·0	—
O	3·0	98·0	—

* Figures in parentheses are values obtained by Bache and Lisk[2] for detection limits and selectivity ratio *versus* phenanthrene.

QUANTITATIVE ELEMENT-SELECTIVE DETECTION—

Linearity of dual detection system—The flow to the two detectors maintained a constant splitting ratio irrespective of sample size. This property is illustrated in Fig. 6 and demonstrates the linear emission characteristics of the element detector relative to the flame-ionisation detector.

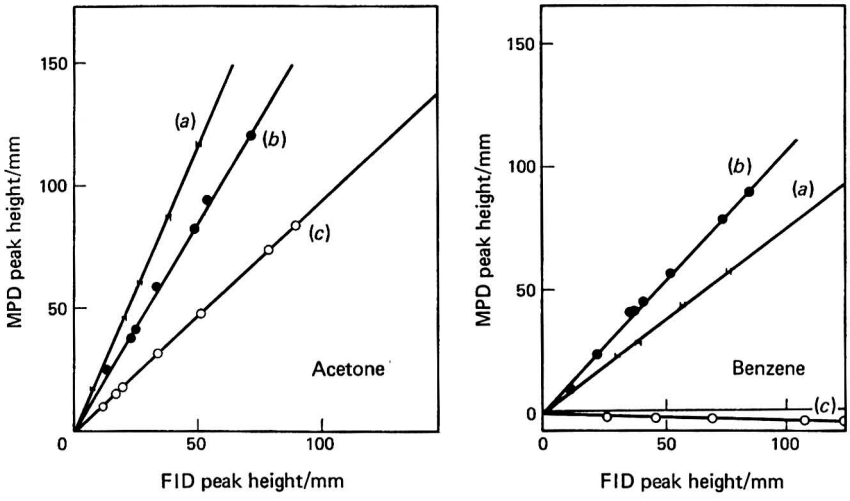


Fig. 6. Linear response of the dual detection system on H(*a*), C(*b*) and O(*c*) *versus* a flame-ionisation detector reference for acetone and benzene. Emission wavelengths are: C, 247·8 nm; H, 486·1 nm; and O, 771·1 nm

Sensitivity and dynamic range—The linear dynamic range is subject to an upper limit, which occurs when the concentration of a component is too large and either the scavenger is insufficient to prevent deposition of carbon or a quenching effect occurs, which perturbs the linear emission characteristics. At the lower end of the range, the limits of detection are subject to the values of the background signal levels at the element-selective wavelengths. Within these limits, the linear dynamic range for fluorine, for example, covers four decades. The best detectable limits and background levels so far obtained are shown in Table II. The detectable limits given are twice the noise level observed on the background. The background is composed of photo-tube dark current, stray light and spectral contamination due to impurities, and the levels stated are calculated in terms of mass flow-rate for purposes of comparison.

Determination of atomic ratio and empirical formulae—With a manually tuned, single-channel spectrometer it is convenient to use the element-selective emission as a peak height ratio with the flame-ionisation detector signal. Effectively, this ratio is equivalent to the slopes of the graphs shown in Fig. 6. Let actual slopes be defined as—

$$\frac{\partial C}{\partial FID}, \quad \frac{\partial H}{\partial FID}, \quad \frac{\partial O}{\partial FID}, \quad \ldots, \text{etc.}$$

For compound X,

$$\left(\frac{\partial C}{\partial FID}\right)_X = \frac{F_{MPD} \times R_C \times n_C n_m}{F_{FID} \times (R_F)_X \times n_m} = \frac{K_C}{(R_F)_X} \times n_C$$

where $\frac{F_{MPD}}{F_{FID}}$ is the flow-rate (splitting) ratio to the two detectors, R_C is the microwave plasma detector response per gram-atom of carbon, n_C is the number of carbon atoms per molecule, n_m is the number of gram-moles of compound X and $(R_F)_X$ is the response factor per gram-mole of compound X on the flame-ionisation detector.

Similarly,

$$\left(\frac{\partial O}{\partial FID}\right)_X = \frac{K_O}{(R_F)_X} \times n_O$$

and, on division—

$$\left(\frac{\partial O}{\partial C}\right)_X = \frac{K_O}{K_C} \times \frac{n_O}{n_C} = \text{constant} \times \text{oxygen to carbon atomic ratio.}$$

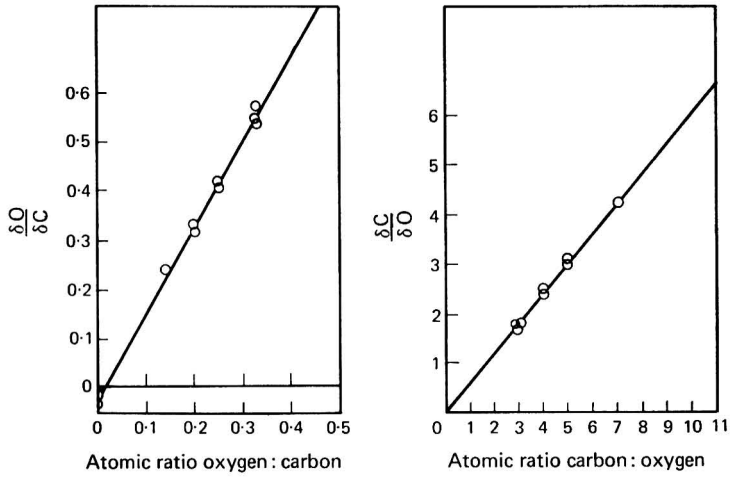


Fig. 7. Calibration graphs for oxygen to carbon and carbon to oxygen ratios

The constant K_O/K_C is independent of the compound-specific response factor of the flame-ionisation detector and can be evaluated by reference to any known oxygen-containing compound. The independence of the emission signal from molecular properties is illustrated in Fig. 7, where the signal ratio $\frac{\partial O}{\partial C}$ is a linear function of the known oxygen to carbon ratios in a variety of compounds. The inverse ratio, $\frac{\partial C}{\partial O}$, also expresses the carbon number if there is only one oxygen atom per molecule. Further results for hydrogen to carbon ratios, obtained by using ethylbenzene as a single reference standard, are shown in Table III. Similar behaviour has been noted for the other elements detected selectively by this technique.

Discussion

The highly selective detection of the elements carbon, hydrogen, deuterium, oxygen, nitrogen, fluorine, chlorine, bromine, iodine, sulphur and phosphorus in a linearly proportional and quantitative manner with good sensitivity has been a continuing feature of this work, and it is now possible to use the technique in order to obtain the empirical formulae of organic compounds separated by gas chromatography as a step towards the identification of compounds. Undoubtedly, the major factor leading to quantitative element-selective detection has been the use of a scavenger gas. As carbon is not appreciably volatile below 3500 °C (boiling-point 4200 °C) and silica melts at 1700 °C (boiling-point 2200 °C), it is to be expected that elemental carbon will plate out on the relatively cold walls. When organic compounds are pyrolysed in the plasma, the action of the scavenger is to hold the carbon in its volatile elemental state—

$$(i)\quad \underset{\text{solid, } ex \text{ pyrolysis}}{\text{C}} + \text{O} \longrightarrow \underset{\text{gas}}{\text{CO}} \qquad (1)$$

$$(ii)\quad \underset{\text{gas}}{\text{CO}} \xrightarrow[\text{energy}]{\text{plasma}} \underset{\text{free atom}}{\text{C}} + \text{O} \qquad (2)$$

when the necessary oxygen (or nitrogen) scavenging atoms are produced as a result of the plasma discharge. The bond strength of C–O (256·7 kcal mol^{-1}) is equivalent to 11·1 eV (C–N is equivalent to 7·8 eV) and virtually complete dissociation into separate atoms, as in equation (2), is readily achieved by the plasma energy available. An indication of the energy of the plasma is given in Table I, where energies of 12 to 19 eV are required in order to produce atomic emission from the non-metallic elements.

In this work, oxygen (and nitrogen) scavenger gas levels in the plasma gas were kept in the 0·1 to 1·0 per cent. *V*/*V* range. Below 0·1 per cent., deposition of carbon was a problem. Above 1·0 per cent., deposition of carbon was not a problem, but the amount of carbonaceous material that could be tolerated could exceed that required to overload the linear atomic-emission characteristics of the plasma. This effect marks the upper limit of the dynamic range of the technique.

Table III

Hydrogen to carbon atomic ratios found in hydrocarbons

	H to C ratio found	Theoretical H to C ratio
Cyclopentane	1·990	2·000
Cyclohexane	2·020	2·000
Cyclooctane	2·023	2·000
Methylcyclohexane	2·015	2·000
Dimethylcyclohexane	2·012	2·000
Trimethylcyclohexane	2·019	2·000
Isopropylcyclohexane	2·008	2·000
Cyclohexene	1·652	1·667
Pent-1-ene	1·997	2·000
Hex-1-ene	2·052	2·000
Hept-3-ene	2·047	2·000
Oct-1-ene	2·027	2·000
Dec-1-ene	2·041	2·000
n-Hexane	2·347	2·333
n-Heptane	2·335	2·286
n-Octane	2·300	2·250
n-Nonane	2·266	2·222
n-Decane	2·249	2·200
n-Undecane	2·251	2·182
Benzene	0·982	1·000
Toluene	1·142	1·143
Ethylbenzene (reference standard)	5/4	5/4
o-Xylene	1·253	1·250

The lower end of the dynamic range is set by the noise level of the background signal at the various element-selective wavelengths. While some elements are detected more sensitively than others, in all instances the level of the background signal has a major effect

on the sensitivity. This effect is illustrated by the data shown in Fig. 8 and shows good correlation between detection limits and background. It is significant that the least sensitive elements are oxygen and nitrogen, followed by hydrogen and carbon; attention to the following details can noticeably improve performance. The vacuum lines and joints should be tested very carefully for leaks, the gas-chromatographic columns should be pre-conditioned *in situ*, and the helium gas supply should be dried once more between the pressure regulators and the gas chromatograph by means of tubes containing phosphorus pentoxide.

Also of great importance is the provision of very smooth and stable power supplies to the microwave generator and phototube. While the detection limits for some elements can be limited by contamination levels in the plasma, the background limitations on the less common elements are due to continuous radiation (plasma emission and stray light) phototube properties, *e.g.*, dark current, spectral range and sensitivity, monochromator resolution and the optics of the light collection and filtration system. The shape of the emission source is optimised in the form of a cheaply replaceable, 1-mm bore, thick walled, clear silica tube.

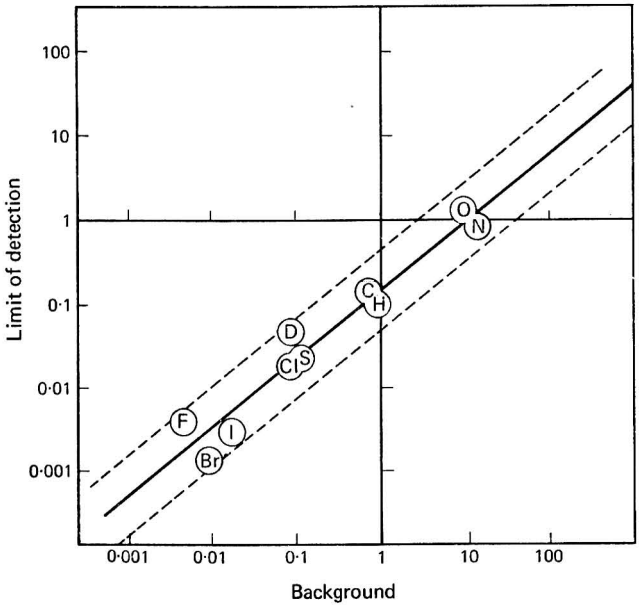


Fig. 8. Effect of background signals on the limit of detection. (These data show that the limit of detection is more a function of spectral background than element identity.) Basic units are gram-atoms $\times 10^{-9}$ per second

Interference effects are restricted to spurious spectral band emission when the plasma is overloaded but this is instantly recognisable from the magnitude of the flame-ionisation detector response. A chemical effect peculiar to fluorine and chlorine gives rise to phantom oxygen emission through the possible reaction scheme—

$$\underset{\text{wall}}{SiO_2} + F \xrightarrow[\text{energy}]{\text{plasma}} \underset{\text{gas}}{SiF} + 2O \longrightarrow \text{oxygen emission}$$

$$\underset{\text{gas}}{SiF} \xrightarrow{\text{plasma}} \underset{\text{atomic}}{S} + F \longrightarrow \text{silica emission}$$

This effect makes the detection of oxygen in polyfluoro and polychloro compounds very difficult by this technique. Equally, it inhibits the selective detection of silicon. An alternative plasma tube material to silica would be useful in solving this particular problem.

The original idea of adding a second, non-selective, detector to act as a reference for comparing the element-selective data has been extended to assist in the quantitative interpretation of the data into atomic ratios. Determination of the necessary atomic ratios for an evaluation of empirical formulae can be seen to be a very laborious process if the single-channel form of this technique described here is used. It is very much more efficient to use a multi-channel spectrometer with simultaneous detection of many elements and work is proceeding on the construction of an instrument of this type. Modern techniques of data handling could lend themselves to an automatic print-out of the empirical formulae of organic compounds eluted from a gas chromatograph. Because the amount of a compound is the sum of its atomic parts, a means of quantitative analysis is made available which is not compound-specific in its response and which does not require to be calibrated by use of the compounds being analysed.

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The Determination of Tin and Antimony in Lead Alloy for Cable Sheathing by Atomic-absorption Spectroscopy

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A method has been evolved for the rapid determination of tin and antimony at levels of about 0·4 and about 0·2 per cent., respectively, in lead alloy used for sheathing electric cables.

The sample is dissolved in a mixture of fluoroboric acid and hydrogen peroxide and the determination is completed by atomic-absorption spectroscopy with the use of an air - acetylene flame for antimony and a nitrous oxide - acetylene flame for tin. The method of dissolving the sample avoids the precipitation reactions that are likely to arise from lead, antimony or tin if conventional acid dissolution processes are used and hence permits a direct and rapid analysis by the atomic-absorption technique.

Calibration for antimony must be effected with a solution containing the dissolution mixture and, in calibration for tin, lead must additionally be present.

THREE alloys of lead, in addition to unalloyed lead, are commonly used as sheathing materials for electric cables. One such alloy, which was the subject of this investigation, is alloy E, in which the alloying elements are tin and antimony at the levels of 0·4 and 0·2 per cent., respectively. Table I gives the composition specified for alloy E.[1]

TABLE I

COMPOSITION OF ALLOY E AS SPECIFIED IN B.S. 801:1953

Element	Content, per cent. Minimum	Maximum
Antimony	0·15	0·25
Tin	0·35	0·45
Tellurium	—	0·005
Silver	—	0·005
Copper	—	0·06
Bismuth	—	0·05
Zinc	—	0·002
Other elements (total)	—	0·01
Lead	Remainder	Remainder

For controlling the composition of alloy E, the determination of the alloying elements tin and antimony is of particular concern. Published methods for these determinations[2,3] are commonly based on titrimetric methods, with the use of iodine and bromate as the titrants for tin and antimony, respectively. However, the determination of these elements by atomic-absorption spectroscopy appeared to offer a more convenient and rapid means of controlling the composition of the alloy, and the evolution of such a procedure is described in this paper.

EXPERIMENTAL

The steps involved in developing the proposed method were as follows: choice of flames; dissolution of samples; and study of interferences.

Of particular importance in the choice of flames was the necessity to ensure that adequate sensitivity could be achieved for the determination of tin; antimony, which can be measured with higher sensitivity than tin by flame-absorption methods, was not expected to cause difficulties. The choice of a dissolution procedure for lead-alloy samples was also of importance,

as lead, tin and antimony tend to give rise to precipitation reactions in the presence of the acids that are commonly used for the dissolution of these metals. Clearly, the ideal dissolution procedure should be capable of dissolving and retaining in solution all the constituents of the alloy. The investigation of these aspects of the proposed method and of possible interferences is described in the following sections.

CHOICE OF FLAMES—

The flame generally used for the determination of antimony is the air - acetylene flame,[4,5] which gives adequate sensitivity for antimony but poor sensitivity for tin. The use of both air - hydrogen[6] and nitrous oxide - acetylene[7] flames for determining tin has been reported.

The optimum conditions were established for each flame and the signal to noise ratio on a standard solution containing 40 μg ml^{-1} of tin was measured in each instance. (This concentration of tin corresponds to 1 g of lead alloy containing 0·4 per cent. of tin in 100 ml of solution.) The results are given in Table II.

TABLE II

EFFECT OF TYPE OF FLAME ON THE SIGNAL TO NOISE RATIO FOR TIN

Flame	Oxidant flow-rate/l min^{-1}	Fuel flow-rate/l min^{-1}	Signal to noise ratio	Comments
Air - hydrogen	5·0	7·0	11·3	—
Air - acetylene	5·0	2·1	4·6	—
Nitrous oxide - acetylene ..	5·0	4·8	10	Smoky flame
Nitrous oxide - acetylene ..	5·0	4·2	9·2	Satisfactory flame

The hydrogen flow-rate of 7·0 l min^{-1} was of necessity measured with a flow meter of higher capacity than that fitted on the instrument. A conversion factor relating the two flow meters was obtained, and when applied it gave the figure of 7·0 l min^{-1} quoted in Table II.

The nitrous oxide - acetylene flame conditions that gave the maximum sensitivity resulted in a very sooty flame, which tended to cause blocking of the burner. The signal to noise ratio for a non-luminous nitrous oxide - acetylene flame, with which it is far easier to work, was also measured and is included in Table II.

The loss in sensitivity incurred by using the less luminous flame was not great, so these conditions were used when working with the nitrous oxide - acetylene flame. During the development of the method, a modified design of the burner head, with grooves parallel to the slot, was obtained. This burner head reduced still further the frequency with which the burner had to be cleaned of soot, but did not enable the acetylene flow-rate, and hence the sensitivity, to be increased without the incidence of serious sooting.

As the best signal to noise ratio was obtained with an air - hydrogen flame, a study of the interferences that occurred with this flame was undertaken. A serious decrease in the instrumental response was observed when the flame was used in the determination of tin in a solution containing hydrochloric and nitric acids (see the following section). Different solutions of alloys prepared by using these acids were examined with the use of both an air - hydrogen and a nitrous oxide - acetylene flame. The results obtained are given in Table III.

TABLE III

DETERMINATION OF TIN IN ALLOY SOLUTIONS WITH THE USE OF DIFFERENT FLAMES

Solution number	Nominal tin* content/μg ml^{-1}	Tin found/μg ml^{-1}	
		Air - hydrogen flame	Nitrous oxide - acetylene flame
1	41	38·5	39
2	40	35	37·5
3	51	50	51·5
4	41	28·5	41·5
5	41	29·5	43·0
6	40	27·5	37·5
7	40	31·5	39

* Concentrations in solutions calculated from the stated composition of the lead-alloy samples used in their preparation.

It can be seen that the results obtained with the air- hydrogen flame were always lower than those obtained with the nitrous oxide - acetylene flame, in some instances seriously so. The use of the air - hydrogen flame was therefore discontinued and all further investigations on the determination of tin were carried out with the nitrous oxide - acetylene flame.

The effect of using an aperture in order to select radiation passing through the core of the flame was also examined. A rectangular aperture, 5 × 3 mm, was inserted in the attenuator carriage of the instrument, *i.e.*, about 90 mm from the centre of the burner on the monochromator side.

It was found that the use of this aperture combined with a wider slit improved the signal to noise ratio by a factor of two when measured on a standard solution containing 40 μg ml^{-1} of tin and 1 per cent. m/V of lead.

DISSOLUTION OF SAMPLES—

The first method examined for dissolving the sample was based on the first step of the British Standard procedure.[2] Samples of alloy E were treated with a mixture of hydrogen peroxide and glacial acetic acid, which dissolved the lead and left a residue that contained mainly tin and antimony. This residue was removed by filtration, dissolved in 1 + 1 nitric acid - hydrochloric acid and the solution obtained was used for the determination of tin and antimony. Two samples of alloy E, and also a mixture of lead, tin and antimony metals, were examined by this method and the results are given in Table IV. As the results for the alloys were low, the tin and antimony contents of the filtrates were also determined and the results are also given in Table IV.

TABLE IV

EXAMINATION AFTER TREATMENT OF ALLOY E WITH ACETIC ACID - HYDROGEN PEROXIDE

	Nominal content		Found in residue		Found in filtrate		Total	
Sample	Tin, per cent.	Antimony, per cent.	Tin, per cent.	Antimony, per cent.	Tin, per cent.	Antimony, per cent.	Tin, per cent.	Antimony, per cent.
A	0·41	0·21	0·325	0·175	0·073	0·023	0·398	0·198
B	0·40	0·20	0·345	0·185	0·060	0·010	0·405	0·195
Mixture of lead, tin and antimony metals	0·40	0·23	0·395	0·215	0·005	0·003	0·400	0·218

The method proved to be unsatisfactory, for the following reasons. (*a*) The residue that remains after treating the alloy with the cold acetic acid - hydrogen peroxide mixture is difficult to filter; the residue could be coagulated by boiling, but this treatment caused some dissolution of the tin and antimony (see Table IV). (*b*) An X-ray diffraction examination of the residue given by alloy E after treatment with the acetic acid - hydrogen peroxide mixture showed that it consisted of an antimony - tin intermetallic compound, which indicates that the insolubility of tin and antimony in a mixture of acetic acid and hydrogen peroxide is likely to depend on the relative amounts of the two elements present. Evidence of such an effect was provided by examining an alloy that contained tin and cadmium but no antimony; this alloy was found to dissolve completely in the acetic acid - hydrogen peroxide mixture.

Overall, the evidence obtained showed that no reliance could be placed on all of the tin and antimony being present in the insoluble fraction after the dissolution with acetic acid - hydrogen peroxide. The consequent necessity for separate determinations of the two elements in the soluble and insoluble fractions to be made led to the abandonment of this approach.

A further attempt was then made to adapt the dissolution step of the British Standard method[2] so as to permit the use of atomic-absorption spectroscopy. The British Standard methods for determining tin and antimony both start with the treatment of the sample with an acetic acid - hydrogen peroxide mixture; hydrochloric acid is then added in order to dissolve the tin and antimony, the resultant precipitate of lead chloride is filtered off

and the tin and antimony are determined on the filtrate. The amounts of reagents used in this British Standard method give a solution that is too dilute for the determination of tin by atomic-absorption spectroscopy. A series of experiments was therefore carried out in order to assess the effect of using a smaller final volume. The results obtained from these experiments (Table V) indicate a loss of tin, which is probably caused by the retention of tin by the lead chloride precipitate.

TABLE V

RESULTS OBTAINED WITH THE MODIFIED BRITISH STANDARD METHOD OF DISSOLUTION

	Nominal content		Found in solution	
Sample	Tin, per cent.	Antimony, per cent.	Tin, per cent.	Antimony, per cent.
A	0·41	0·21	0·400, 0·378	0·205
B	0·40	0·20	0·358, 0·348	0·192

In view of the difficulties experienced with the selective dissolution procedure discussed above, a search was made for a single-stage procedure that is capable of dissolving and retaining in solution all of the constituents of the lead alloy. As the fluoroborates of tin and lead were known to be soluble, *e.g.*, from their use in plating solutions, the use of fluoroboric acid appeared to be worthy of a trial.

It was found that 1-g amounts of alloy E could readily be dissolved with 5 ml of 42 per cent. *m/m* fluoroboric acid provided that 4 ml of 100-volume hydrogen peroxide were also added as oxidising agent. This treatment completely dissolved the alloy in a few minutes and the solution obtained could be diluted with water to 100 ml without the formation of a precipitate. The same procedure was adopted later for dissolving pure lead to give a lead solution for addition to calibration standards in order to simulate alloy sample solutions.

STUDY OF INTERFERENCES—

Following the evolution of the method of dissolution with fluoroboric acid - hydrogen peroxide, it was necessary to establish whether the presence of the dissolution mixture and also of lead had any effect on the determination of tin and antimony by the flame-absorption technique. In the experiments that were carried out in order to investigate such effects, the flame systems used were those previously chosen, *viz.*, air - acetylene for antimony and nitrous oxide - acetylene for tin.

It was found that additions of hydrogen peroxide or fluoroboric acid to solutions that contain tin enhance the instrumental response to this element, although the effect of both additives together is similar to that of either additive alone; the additional presence of lead causes a further enhancement. The results of these experiments are given in Table VI.

TABLE VI

EFFECT OF MATRIX AND SOLVENT ON THE RESPONSE OF THE INSTRUMENT TO TIN

Sample	Instrument reading
40 p.p.m. of tin as fluoroborate in water	30
40 p.p.m. of tin + 5 per cent. of HBF_4	39
40 p.p.m. of tin + 4 per cent. of H_2O_2	40
40 p.p.m. of tin + 5 per cent. of HBF_4 + 4 per cent. of H_2O_2	38
40 p.p.m. of tin + 5 per cent. of HBF_4 + 4 per cent. of H_2O_2 + 1 per cent. of Pb	43

Additions of antimony at a level equivalent to 0·2 per cent. in lead alloy to a solution containing all the other constituents did not further affect the response of the instrument to tin. A corresponding set of experiments was carried out on a solution of antimony, and in this instance additions of hydrogen peroxide and fluoroboric acid increased the instrumental response by about 8 per cent. Additions of lead and tin to solutions containing fluoroboric acid and hydrogen peroxide did not further affect the instrumental response to antimony.

These results showed that for the determination of antimony, the calibration solutions should contain fluoroboric acid and hydrogen peroxide, while for determination of tin, the calibration solutions should contain lead in addition to the mixture used for dissolution.

METHOD

APPARATUS—

A Pye-Unicam SP90 atomic-absorption spectrophotometer was used with an SP94 nitrous oxide attachment and an SP93 air compressor. The experimental conditions used when determining individual elements are given in Table VII.

TABLE VII

INSTRUMENTAL CONDITIONS

Parameter	Antimony	Tin
Wavelength	**217·6 nm**	**286·3 nm**
Slit width	0·1 mm	0·4 mm
Burner	Air - acetylene, 10-cm slot	Nitrous oxide - acetylene, 5-cm slot
Observation height	1·4 cm	1·0 cm
Oxidant	Air	Nitrous oxide
Oxidant flow-rate	5 l min^{-1} (36 p.s.i.)	5 l min^{-1} (36 p.s.i.)
Fuel	Acetylene	Acetylene
Fuel flow-rate	1·6 l min^{-1} (10 p.s.i.)	4·2 l min^{-1} (10 p.s.i.)
Coarse gain	7	4
Damping	2 or 3*	2 or 3*
Lamp current	15 mA	8 mA
Aperture	Not used	Used

* Position 2 gives a meter reading; position 3 gives a recorder reading.

REAGENTS—

Hydrogen peroxide, 100 volume—AnalaR grade.

Fluoroboric acid, 42 per cent. m/m HBF_4—Laboratory-reagent grade.

Standard antimony solution—Dissolve 274 mg of AnalaR grade antimony potassium tartrate in water and dilute to 100 ml.

1 ml of solution ≡ 100 μg of antimony.

Standard tin solution—To 50 mg of AnalaR grade metallic tin in a platinum vessel add 2 ml of 40 per cent. *m/m* analytical-reagent grade hydrofluoric acid. Add 100-volume hydrogen peroxide dropwise until the tin has dissolved; care must be taken at this stage because if the peroxide is added too fast a precipitate of tin oxide is formed. When all of the tin has dissolved, add 2 g of AnalaR grade boric acid and 20 ml of water and heat the mixture gently until a clear solution is obtained. Transfer the solution into a 500-ml calibrated flask (glass is satisfactory for the short period of contact involved), make up to the mark with water, mix and transfer it into a clean plastic bottle.

1 ml of solution ≡ 100 μg of tin.

Standard lead solution—Mix 65 ml of fluoroboric acid and 50 ml of 100-volume hydrogen peroxide in a plastic beaker. Add 12·5 g of pure AnalaR grade lead, piece by piece, and when all of the lead has dissolved transfer the solution into a 250-ml calibrated flask. Make up to the mark with water, mix and transfer the solution into a plastic bottle.

1 ml of solution ≡ 50 mg of lead.

CALIBRATION—

Transfer 0, 2·5, 5·0 and 7·5-ml volumes of standard antimony solution into four separate 25-ml calibrated flasks. To each flask add 1·25 ml of fluoroboric acid and 1 ml of 100-volume hydrogen peroxide, make up to the mark with water, mix and transfer the solution into a plastic bottle.

Transfer 0, 7·5, 1·0 and 12·5-ml volumes of standard tin solution into four separate 25-ml calibrated flasks. To each flask add 5 ml of standard lead solution, make up to the mark with water, mix and transfer the solution into a plastic bottle.

With the instrument conditions as given in Table VII, aspirate each of the appropriate solutions into the flame and measure the absorption. Prepare calibration graphs of absorption against the amount of antimony or tin.

ANALYSIS OF SAMPLES—

If necessary, cut the sample into small pieces. Weigh 1·00 g of sample into a clean plastic beaker, add 5 ml of fluoroboric acid and then add 4 ml of 100-volume hydrogen

peroxide very slowly. When dissolution is complete, transfer the solution into a 100-ml calibrated flask, dilute to the mark with water, mix and transfer the solution into a clean plastic bottle. With the instrumental conditions as given in Table VII, measure the absorption that can be attributed to tin and antimony and by use of the calibration graphs deduce the tin and antimony contents of the sample.

Results

Three experiments were carried out in order to check the validity of the method.

The precision of measurement was examined by taking ten replicate readings from a single solution that contained tin and antimony at levels equivalent to 0·2 per cent. of antimony and 0·4 per cent. of tin in lead alloy. The results are given in Table VIII.

Table VIII

Standard deviations for replicate measurements on one solution

Element	Standard deviation, per cent. (10 determinations)
Tin (0·4 per cent.)	0·018
Antimony (0·2 per cent.) ..	0·022

The over-all reproducibility was checked by applying the method to pairs of samples taken from adjacent regions on each of two lengths of cable sheath. The results obtained are given in Table IX.

Table IX

Determination of tin and antimony in adjacent samples of cable sheath

Sample	Sample portion	Antimony, per cent.	Tin, per cent.
Sheath A	1	0·21	0·38
	2	0·21	0·39
Sheath B	1	0·22	0·40
	2	0·21	0·41

The method was checked for bias by taking the mass of independently analysed white metal (B.C.S. 177/1) that is required to give amounts of antimony and tin similar to those in alloy E, and adding sufficient pure lead to give a total mass of 1 g. The mixture was then treated as a sample. The results are given in Table X.

Table X

Determination of antimony and tin in B.C.S. 177/1 diluted with lead metal

Element	Calculated content, per cent.	Amount found, per cent.
Antimony	0·24	0·23
Tin	0·46	0·45

Conclusion

The method evolved is simple and direct and hence is appropriate for use in the control of alloy composition. A particular advantage of the method is that complete dissolution of the sample is effected in a single step. The chemical properties of lead, tin and antimony are such that one or another of them will give rise to precipitation reactions in the presence of any of the acids that are commonly used for dissolution of these metals. The use of the fluoroboric acid - hydrogen peroxide mixture for dissolution overcomes this problem and permits full advantage to be taken of the virtue of many flame methods, that is, the ability to effect determinations directly on a sample solution without the need for chemical separations to be carried out.

The method has been shown to give an accuracy and precision that are acceptable for the routine determination of alloy composition.

It should be noted that the use of a dissolution mixture containing fluoroboric acid for the analysis of a lead-base alloy by atomic-absorption spectroscopy has also found favour elsewhere: after the work described in this paper had been completed, a method was described by Gouin, Holt and Miller[8] for the determination of tin and antimony in type metal by atomic-absorption spectroscopy. These authors used a mixture of fluoroboric and nitric

acids for dissolution of the sample, with subsequent addition of tartaric acid to ensure the retention of antimony in solution. The amounts of antimony (3 to 17 per cent.) and tin (3 to 7 per cent.) that were determined by these authors were much greater than those of concern to us in alloy E.

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Replacement of Platinum Vessels with a Pressure Device for Acid Dissolution in the Rapid Analysis of Glass by Atomic-absorption Spectroscopy

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The rapid analysis of glass is made possible by replacing the crucibles in which time-consuming fusion is carried out by a device for quantitative acid dissolution under pressure and subsequent atomic-absorption spectroscopic determinations of the elements.

The sample is decomposed by hydrofluoric acid at 105 °C in a decomposition vessel consisting of a crucible-shaped stainless-steel container fitted with a removable PTFE crucible and a stainless-steel screw-cap with a PTFE disc inserted in the metal body. Subsequent addition of boric acid forms the analysis matrix of fluoroboric acid - boric acid for the atomic-absorption determinations of silica, alumina, iron, titanium, magnesium, calcium, sodium and potassium.

This procedure obviates the use of platinum vessels, prevents losses of constituents due to alloying, reduction and volatilisation, does not introduce extraneous cations, and is reliable, simple and rapid to perform.

THE conventionally used chemical methods for the determination of major and minor constituents of glass are based on its fusion with suitable fluxes in platinum crucibles. Appropriate mixtures of acids (hydrofluoric acid *plus* sulphuric or perchloric acid) are also used for constituents other than silica. The subsequent determinations are carried out by gravimetry, spectrophotometry or atomic-absorption spectroscopy.

Platinum crucibles conventionally used to date in the step involving decomposition of glass by fusion may present serious analytical as well as financial disadvantages. The initial investment involved in the acquisition of platinum ware, especially if the latter is needed for simultaneous batch work on many series, may be prohibitive. In addition, the use of platinum ware may account for sample contamination and cause losses of some of the constituents by reduction and formation of alloys or by volatilisation.

All fusion techniques require lengthy manipulations and the introduction of excessive amounts of alkalis over the mass of sample taken, frequently to avoid difficulties that occur during the decomposition stage. Thus, besides precluding the direct determination of the alkali metals present in the sample from a single decomposition, excessive amounts of extraneous cations derived from the fusion mixtures may cause subsequent chemical interferences and undesirable instrumental or spectral effects, or both, especially when atomic-absorption spectrophotometry is used in the determination of the individual elements.

The common practice of effecting decomposition by using mixtures of acids suffers from two major disadvantages. One is that the time-consuming removal of hydrofluoric acid by evaporation is required in conventional acid-decomposition procedures. The second major disadvantage is that under these conditions silica cannot be determined.

For an over-all simplification of the procedure for glass analysis, a modified method has been successfully applied. This method was earlier reported by Bernas[1] for the acid decomposition under pressure and comprehensive analysis of silicates. A subsequent paper[2] describes the chemical analysis of Apollo 14 lunar samples by the same method[1] with confirmatory conclusions concerning the satisfactory precision and accuracy of the results obtained.

The modified method for the analysis of glass obviates the use of platinum vessels, prevents losses of constituents, in particular losses caused by volatilisation, does not introduce extraneous cations and is simple to perform. The procedure consists in the acid decomposition

under pressure, in a specially designed decomposition vessel,* of a 100 to 150-mg sample ground to 100 mesh. This vessel consists of a crucible-shaped stainless-steel container fitted with a removable PTFE crucible, which is closed by hand-tightening a stainless-steel screw cap with an inserted PTFE disc on to the metal body. A PTFE pouring spout, which facilitates the quantitative transfer of the solution of the decomposed sample, is snapped on to the periphery of the rim of the crucible. Decomposition is effected with 4 ml of 48 per cent. hydrofluoric acid in the presence of about 0·3 ml of aqua regia and by placing the vessel into a drying oven at 105 °C for 30 minutes. On cooling the vessel to ambient temperature, 3·0 g of boric acid that had been previously dissolved in hot water are added to the sample solution, thus forming the fluoroboric acid - boric acid matrix. The solution is then transferred into a 100-ml calibrated flask for accurate volume adjustment. The contents should then be transferred within 2 hours into a plastic storage bottle. Appropriate dilutions are made whenever necessary.

For the determination of each element, identical concentrations of fluoroboric acid - boric acid matrix are used in the sample and standards. The determinations are then carried out by atomic-absorption measurements with air - acetylene and nitrous oxide - acetylene flames. The determinations of silicon, iron and titanium are carried out by direct comparison with single-component standards in the matrix. To take account of any possible inter-element effects in the determinations of aluminium, magnesium, calcium, sodium and potassium, the sample and standard solutions contain, in addition to the matrix, high concentrations of either sodium or potassium ions.

It was earlier established that during the residence time of the sample solution in the calibrated glass flask, no analytically significant contamination occurred.[1] Furthermore, the fluoroboric acid - boric acid matrix is known to ensure the stability in solution of both samples and standards for at least several weeks.

Results for the determination of eight constituents in a single sample can be reported within 5 to 7 hours, depending on the type of instrument used, while the actual operation time needed is 4 hours, as compared with about 15 hours required by the conventional methods used to date.

A comparison of the results for standard sample No. 93 [borosilicate glass, National Bureau of Standards (N.B.S.)] and standard glass No. 1 (standard soda - lime - magnesia - silica glass, Department of Glass Technology, University of Sheffield) by the rapid method of acid decomposition under pressure with their respective certified values is shown in Table I.

TABLE I

COMPARISON OF RESULTS FOR STANDARD SAMPLES BY THE RAPID METHOD OF ACID DECOMPOSITION UNDER PRESSURE WITH CERTIFIED VALUES

	N.B.S. standard sample No. 93		Standard glass No. 1	
Constituent	Certified values	Rapid method of acid decomposition under pressure	Certified values	Rapid method of acid decomposition under pressure
SiO_2	80·6	80·1	71·74	72·8
Al_2O_3	1·94	1·89	1·55	1·34
Fe_2O_3	0·076	0·078	0·15	0·16
TiO_2	0·027	0·029	0·05	0·05
MgO	0·026	0·023	3·56	3·3
CaO	Not detected	Not determined	8·49	8·3
Na_2O	4·16	4·22	13·25	13·1
K_2O	0·16	0·14	0·80	0·7

The permission of the management of IMI Institute for Research and Development, Haifa, to publish this paper is gratefully acknowledged.

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Thermometric Assay of Some Sulphonamides of Pharmaceutical Importance

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The thermometric determination of several sulphonamides used in pharmaceutical preparations is described. The sulphonamide is dissolved in the minimum amount of dilute sodium hydroxide solution and the pH adjusted to 8·9 with thymolphthalein as indicator. The solution is then made up to 10 cm³ with an appropriate buffer solution (pH 8·0 or 9·18). In these controlled alkaline conditions, the sulphonamide is titrated directly with silver nitrate solution, the equivalence point being determined thermometrically. The effects of several matrix ingredients in common use in pharmaceutical preparations have been determined. The time of the titration is approximately 1 minute and the accuracy is within ±2 per cent.

The proven bactericidal properties of compounds containing the sulphonamido group have ensured the continued, widespread use of sulphonamides as medicaments. These compounds are used either singly or in combinations with related sulphonamides. The methods of the British Pharmacopoeia[1] for determining sulphonamides involve either a potentiometric titration with sodium nitrite solution or, for some selected sulphonamides, a non-aqueous (dimethylformamide) acid - base titration with a solution of lithium methoxide in toluene - methanol.

Several workers have suggested the use of silver nitrate for the gravimetric[2,3] or titrimetric[4–9] determination of various sulphonamides.

Only two thermometric methods have been proposed: the heat of neutralisation of some of these bases with sulphuric acid has been used for their determination,[10] while Schäfer and Wilde[11] made use of the heat of oxidation of some sulphonamides with sodium hypochlorite. In some dosage forms, the sulphonamides may be mixed with magnesium stearate, lactose and starch; hence thermometric titrimetry with a strong acid or a strong oxidising agent has obvious limitations in such instances.

The titration of these sulphonamides with silver ions in controlled alkaline conditions obviates these difficulties[6] and thus affords the opportunity for a rapid thermometric method involving the dosage forms to be used.

Experimental

Apparatus—

Details of the apparatus have been previously described.[12,13] The titrant was delivered to the sample by a constant-speed peristaltic pump. The reaction vessel was thermally insulated in a suitable manner and the temperature changes were recorded as the imbalance voltage from a Wheatstone bridge containing a 10 000-Ω thermistor as one of its arms. The thermistor acted as the temperature sensor. The titrant and the sample were both initially at room temperature.

Reagents—

Sulphonamides—Samples of the following sulphonamides were used as supplied by the drug manufacturers—

Sulphathiazole [2-(4-aminobenzenesulphonamido)thiazole].
Sulphadiazine [2-(4-aminobenzenesulphonamido)pyrimidine].
Sulphamerazine [2-(4-aminobenzenesulphonamido)-4-methylpyrimidine].
Sulphadimidine [2-(4-aminobenzenesulphonamido)-4,6-dimethylpyrimidine].
Sulphafurazole [5-(4-aminobenzenesulphonamido)-3,4-dimethylisoxazole].
Sulphamethizole [2-(4-aminobenzenesulphonamido)-5-methyl-1,3,4-thiadiazole].

Succinylsulphathiazole {2-[4-(3-carboxypropionamido)benzenesulphonamido]thiazole monohydrate}.

Sulphapyridine [2-(4-aminobenzenesulphonamido)pyridine].

Buffer solution 1—This solution, at pH 9·18, was a 0·1 M aqueous solution of sodium tetraborate (borax).

Buffer solution 2—This solution, at pH 8·0, was a 0·1 M solution of boric acid, adjusted to pH 8·0 with 0·1 M sodium hydroxide solution.

Silver nitrate solution—A 0·30 M aqueous solution of silver nitrate was made up and standardised against sodium chloride solution by Mohr's method.

METHOD—

Dissolve a known amount of the sulphonamide (between 10 and 70 mg) in the polythene vessel[12] in the minimum volume of 0·1 M aqueous sodium hydroxide solution (2 to 5 cm^3). Adjust the pH to 8·9 (with thymolphthalein as indicator) by dropwise addition of 0·1 M nitric acid. Adjust the volume to 10 cm^3 with the appropriate buffer solution. Place the titration vessel in the block of insulation[12] and allow the mixture to stand at room temperature for 3 to 5 minutes so as to allow thermal equilibrium to be attained.

Titrate the sulphonamides against the standardised silver nitrate solution. The amount of sulphonamide present can then be calculated from the enthalpogram.

DISCUSSION

Although the sulphonamides are soluble in either dilute mineral acids or dilute alkali solutions, the silver salts are precipitated only in neutral or slightly alkaline conditions. The reaction must therefore be carried out in the latter conditions. The alkalinity must,

TABLE I

SOME TYPICAL RESULTS ON PURE SULPHONAMIDES

Results are for (*a*) the minimum, and (*b*) the maximum amount of sulphonamide taken

Compound	pH	Amount taken/mg	Amount found/mg
Sulphathiazole	8·0	(*a*) 24·4	24·5
		(*b*) 58·4	55·3
	9·18	(*a*) 22·4	22·2
		(*b*) 63·4	63·0
Sulphafurazole	8·0	(*a*) 34·9	33·9
		(*b*) 54·1	54·2
	9·18	(*a*) 30·8	30·5
		(*b*) 83·9	84·0
Sulphadiazine	8·0	(*a*) 21·7	21·3
		(*b*) 45·7	45·6
	9·18	(*a*) 16·6	16·8
		(*b*) 56·1	56·5
Sulphamethizole	8·0	(*a*) 29·2	29·2
		(*b*) 61·6	62·0
	9·18	(*a*) 27·0	30·7
		(*b*) 52·8	56·0
Sulphadimidine	8·0	(*a*) 21·2	20·8
		(*b*) 57·1	57·2
	9·18	(*a*) 25·5	25·6
		(*b*) 51·7	52·0
Sulphamerazine	8·0	(*a*) 26·3	26·7
		(*b*) 42·5	42·6
	9·18	(*a*) 7·9	7·9
		(*b*) 70·3	70·0
Succinylsulphathiazole	8·0	(*a*) 28·6	29·6
		(*b*) 31·1	30·9
	9·18	(*a*) 30·0	29·6
		(*b*) 52·6	52·5
Sulphapyridine	8·0	Compound insoluble	
	9·18	(*a*) 39·0	40·8
		(*b*) 38·1	40·0

however, be controlled so that the formation and precipitation of hydroxy compounds of silver are avoided. If any titrant is consumed by such processes, erroneous results are obtained.

From the results given in Table I it can be seen that of the two buffers used, that at pH 9·18 gave the optimum results over a larger range of amounts of compounds and is thus recommended for all compounds except sulphamethizole.

The consistently high results obtained with sulphapyridine are probably caused by the formation of the silver salt of the amido group and also some silver - pyridine complex.

The upper limit for the amount of the various compounds taken is a direct result of the geometry of the apparatus. Above this limit, the bulk of the precipitate causes poor heat transfer throughout the reaction mixture. The resultant curvature of the enthalpogram at the end-point makes extrapolation necessary, with a concomitant loss in accuracy. Thus the optimum range recommended is between $2{\cdot}5 \times 10^{-5}$ and $2{\cdot}5 \times 10^{-4}$ mol of sulphonamide in the 10 cm³ of solution, *i.e.*, a $2{\cdot}5 \times 10^{-3}$ to $2{\cdot}5 \times 10^{-2}$ M solution.

Detailed results for the determination of sulphathiazole are given in Table II.

TABLE II

DETAILED RESULTS FOR THE DETERMINATION OF SULPHATHIAZOLE

Amount taken/mg	Amount found/mg	Error, per cent.
22·4	22·2	−0·90
29·8	30·3	+1·6
30·6	31·0	+1·3
38·4	38·6	+0·5
38·5	38·2	−0·8
40·1	39·8	−0·75
50·4	50·4	0·00
55·3	55·0	−0·54
61·2	61·5	+0·49
63·4	63·0	−0·64

pH of all solutions = 9·18.

The results obtained for the sulphonamides in admixture with some of the usual excipients, *viz.*, lactose, magnesium stearate and starch, indicate that the method has potential use for the determination of single sulphonamides in the dosage forms (Table III). As the dosage form is usually a tablet containing about 500 mg of sulphonamide and 100 mg of excipient, it is necessary to crush the tablet and to use a nominal 50-mg sample. The finely powdered sample is stirred with the sodium hydroxide solution for approximately 3 to 5 minutes in the reaction cell, during which time the sulphonamide dissolves. The pH of the solution is adjusted as previously described. When thermal equilibrium has been achieved, the solution is titrated.

TABLE III

EFFECT OF EXCIPIENTS

Compound	Excipient	Amount taken/mg	Amount found/mg
Sulphadimidine	Lactose (30 mg)	30·5	30·7
	Lactose (60 mg)	30·8	31·0
	Starch (30 mg)	35·1	35·3
	Starch (60 mg)	32·9	33·5
	Magnesium stearate (30 mg)	31·2	31·0
	Magnesium stearate (60 mg)	25·0	25·3

pH of all solutions = 9·18.

The over-all time taken for the determination of duplicates from one tablet is approximately 10 minutes, excluding crushing and weighing. The actual time taken for each titration is approximately 1 minute.

In practice, we have found this method to have several advantages over those given in the British Pharmacopoeia, which recommends dead-stop titrations with sodium nitrite solution for all the sulphonamides listed here, except for sulphafurazole, which is titrated with lithium methoxide solution. The lithium methoxide method requires that the titrant

be protected against carbon dioxide contamination, and it is always necessary to titrate a blank sample.

The use of sodium nitrite necessitates frequent re-standardisation with sulphanilic acid. While it is necessary to re-standardise the silver nitrate solution used in the method described here, the frequency of re-standardisation is low.

The electrodes used in the dead-stop titration need to be cleaned frequently, and in practice we have found that the platinum coils require more prolonged washing between titrations so as to ensure cleanliness than does the thermistor used in the proposed method.

We thank Boots Pure Drug Co., Ciba-Geigy Ltd. and May and Baker Ltd. for the gifts of the sulphonamides used in this work.

One of us (J.K.G.) thanks the Science Research Council for the award of a Studentship.

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Analytical Methods Committee

REPORT PREPARED BY THE FISH PRODUCTS SUB-COMMITTEE

Nitrogen Contents of Raw Fish

THE Analytical Methods Committee has received the following Report from its Fish Products Sub-Committee. The Report has been approved by the Analytical Methods Committee and its publication has been authorised by the Council.

REPORT

The Fish Products Sub-Committee has recommended nitrogen factors for use in the analysis of food products containing cod[1] and coal fish (saithe).[2] Both recommendations were based on the results of determinations of the nitrogen contents of the whole fish. These

TABLE I

NITROGEN CONTENTS OF RAW FISH SPECIES

Common name	Systematic name[3]	Range of nitrogen contents,* per cent.
Anchovy	*Engraulis encrasicholus*	2·45
Brill	*Scophthalmus rhombus*	3·17
Catfish (rockfish)	*Anarhichas* sp.	2·58 to 3·14
Cod	*Gadus morhua*	2·21 to 3·20
Crab	*Cancer pagurus*	2·4
King	—	1·10 to 2·36
Norwegian	—	2·14 to 3·43
Crayfish	*Astacus fluviatilis*	3·86
Dab	*Limanda limanda*	2·05 to 3·04
Dogfish	*Squalus acanthias*	2·02 to 3·24
Eel	*Anguilla* sp.	1·86 to 3·41
Flounder (fluke)	*Platichthys flesus*	2·69 to 2·77
Haddock	*Melanogrammus aeglefinus*	2·33 to 3·25
Hake	*Merluccius* sp.	2·64 to 2·98
Halibut	*Hippoglossus hippoglossus*	2·78 to 3·27
(Greenland, black, mock)	*Reinhardtius hippoglossoides*	1·98
Herring	*Clupea harengus*	2·56 to 3·41
Lemon sole	*Microstomus kitt*	2·63 to 2·94
Ling	*Molva molva*	2·63 to 3·56
Lobster	*Homarus* sp.	2·70
Mackerel	*Scomber scombrus*	2·57 to 3·66
Pilchard	*Sardina pilchardus*	2·45 to 3·20
Plaice	*Pleuronectes platessa*	2·51 to 3·02
Pollack (lythe)	*Pollachius pollachius*	3·06 to 3·46
Porbeagle	*Lamna nasus*	3·68 to 4·32
Prawn (deep water)	*Crangon* sp., *Pandalus* sp.	2·38 to 2·86
Redfish	*Sebastes* sp.	2·69 to 3·17
Saithe (coal fish, coley)	*Pollachius virens*	2·51 to 3·46
Salmon		
Atlantic	*Salmo salar*	3·60
Sockeye	*Oncorhynchus nerka*	2·83 to 3·50
Chinook	*Oncorhynchus tschawytscha*	3·06
Pink	*Oncorhynchus gorbuscha*	3·20
Sardine	small *Sardina pilchardus*	3·07
Shark (basking)	*Salache Maxima*	2·43
Skate (ray, roker)	*Raja* sp.	2·92 to 3·87
Shrimp	*Crangon* sp., *Pandalus* sp.	1·68 to 3·78
Trout	*Salmo trutta*	2·80 to 3·67
Tuna	*Thunnus* sp., *Neothunnus* sp., *Euthynnus* sp.	3·84
Whiting	*Merlangius merlangus*	3·04 to 3·18
Whiting (blue)	*Micromesistius poutassou*	2·22 to 2·55
Witch	*Glyptocephalus cynoglossus*	2·33 to 2·52
Wrasse	*Labrus* sp.	3·08 to 3·15

* Where a range is not given the figure is the average result of a number of determinations.

determinations were carried out for the Sub-Committee on fish that had been landed over a period of at least 1 year. It had originally been the intention to carry out similar investigations on all the more important fish species that are used for manufacturing purposes, but, during the work on coal fish, considerable difficulty was experienced in obtaining sufficient fish on which to base a recommendation. The Sub-Committee was of the opinion that this difficulty would increase for the less frequently used species and would thereby make the collection of sufficient information an extremely long process. In consequence, it was decided not to proceed with this aspect of the work.

It is realised, however, that some analysts still require, from time to time, information on fish species other than those already dealt with by the Sub-Committee. Some information on the nitrogen contents of raw fish species was known to be contained in the literature and some members of the Sub-Committee had access to other, unpublished, information. In the belief that it will be of value to analysts who are required to examine fish products, this information has been collected and is contained in Table I. The Sub-Committee has not, however, attempted to draw any conclusions from these figures, nor does it make any specific recommendations. It is emphasised that the figures are not the results of analyses carried out at the request of the Sub-Committee and, for the most part, the absolute reliability of the information cannot be attested. For this reason, no attempt has been made to give mean values for the different species or to derive an average factor for all fish or groups of similar fish.

The Sub-Committee thanks, for their help and communications, The Ministry of Agriculture, Fisheries and Food, Torry Research Station and The Official Norwegian Quality Control Institute for Canned Fish Products, Stavanger.

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Analyst, June, 1973, Vol. 98, *pp.* 458–460

Analytical Methods Committee

REPORT PREPARED BY THE METALLIC IMPURITIES IN ORGANIC MATTER SUB-COMMITTEE

The Determination of Small Amounts of Zinc in Organic Matter by Atomic-absorption Spectroscopy

THE Analytical Methods Committee has received the following Report from its Metallic Impurities in Organic Matter Sub-Committee. The Report has been approved by the Analytical Methods Committee and its publication has been authorised by the Council.

REPORT

The constitution of the Metallic Impurities in Organic Matter Sub-Committee responsible for the preparation of this Report was: Dr. L. E. Coles (Chairman), Mr. W. Cassidy, Dr. J. C. Gage, Dr. R. A. Hoodless, Miss E. M. Johnson, Mr. D. A. Lambie, Dr. H. Liebmann, Dr. R. F. Milton, Mr. W. L. Sheppard, Mr. G. B. Thackray and Mr. C. A. Watson, with Mr. P. W. Shallis as Secretary.

In 1967, the Sub-Committee recommended a procedure involving the use of dithizone for the determination of small amounts of zinc in organic matter.[1] This method is still considered to be satisfactory, but advances in instrumentation and technique have, in the opinion of members of the Sub-Committee, made atomic-absorption spectroscopy equally satisfactory for the determination of zinc and, in general, it is more convenient and rapid in application. This Report gives details of conditions that have been found to be satisfactory and the Sub-Committee recommends that either the dithizone procedure[1] or atomic-absorption spectroscopy should be used for the determination of zinc in organic matter; the method selected will depend on the material to be analysed.

GENERAL CONSIDERATIONS—

Atomic-absorption measurements of zinc solutions are normally carried out at 213·8 nm. In this region of the electromagnetic spectrum, energy is maintained by using wider slits and a higher voltage compensates for reduced photomultiplier sensitivity. The products of incomplete combustion also absorb light to a greater extent in this region than at longer wavelengths.

Copper has absorbance lines in the vicinity of 213·8 nm. Monochromators of good resolving power are therefore necessary so as to ensure minimum interference when zinc is to be determined in solutions containing more than an equal amount of copper.

Compounds that yield elemental sulphur on burning also interfere at this wavelength and due care should be taken when separations with ammonium pyrrolidine dithiocarbamate (APDC) are effected.

SAMPLE PREPARATION—

The determination of zinc in organic materials by atomic-absorption spectroscopy is not materially affected by the use of different acids. It is, however, advisable to use the same acid composition and concentration for standards and blanks as are used for the samples. In general, the acid concentration should not exceed about 2 N in the aspirated solution, although with "high solids" burners the use of considerably higher acid concentrations may be satisfactory.

Dry or wet ashing is suitable for the destruction of organic matter before the determination of zinc. For certain types of liquid samples, *e.g.*, ready-to-drink beverages, and for semi-solid foodstuffs, alternative satisfactory procedures are described.

DRY ASHING—

If the organic matter can be readily dry ashed below 500 °C it is still necessary to check the recovery of zinc, which may not be complete.[2] Porcelain crucibles should not be used, as zinc can be extracted from the glaze.[3] It is sometimes advantageous to mix approximately 0·2 g of calcium carbonate with the sample before ashing. This mixing results in an aerated mass that does not fuse into the material of the container and dissolution in acids is facilitated. The residue from a dry-ashing procedure is best dissolved in a mixture of hydrochloric acid and water (1 + 1 *V*/*V*). If the zinc in the sample is not completely dissolved in this mixture, a 2 + 1 + 3 *V*/*V* mixture of hydrochloric acid, nitric acid and water can be used.

WET ASHING—

Any of the usual techniques[4] can be used, but the easiest method of digesting many organic materials is with sulphuric acid and dropwise addition of 50 per cent. hydrogen peroxide.[5] The use of glassware that has been etched with boiling solutions of strong alkalis should be avoided, as zinc can be leached from the glass during the oxidation process.

For both wet and dry ashing, sample masses and final volumes can be chosen so as to give the optimum sensitivity required.

READY-TO-DRINK BEVERAGES—

These beverages can be aspirated without prior destruction of the organic matter. A suitable dilution with water should be prepared so as to minimise the effect of the presence of soluble solids in the drink. Soluble solids are troublesome in the aspirated sample only at concentrations above about 3 per cent.

SEMI-SOLID FOODSTUFFS—

A rapid method for foodstuffs is based on that described by Simpson and Blay.[6] To 10 g of the homogenised sample are added 40 ml of water and 10 ml of concentrated hydrochloric acid. The mixture is heated to boiling and then simmered gently for not more than 5 minutes. The solution is then cooled, transferred to a 100-ml calibrated flask, diluted to volume and mixed. Sufficient solution (normally 10 to 20 ml) for the analysis is removed and filtered.

It is essential not to prolong the boiling, as charring might occur that could hold back trace amounts of the metal at the filtration stage. Similarly, a higher acid concentration can also increase charring and for this reason the mixture recommended here is less concentrated than that used by Simpson and Blay.[6]

OILS, FATS AND FATTY FOODS—

These materials may be difficult and sometimes impossible to wet oxidise to give an aqueous solution. At zinc contents below 0·1 p.p.m., contamination from reagents and vessels used to prepare aqueous solutions can be greater than the actual zinc contents. It is then simpler to aspirate solutions of the fatty matter in an organic solvent directly into the flame.

When this direct aspiration is used, care must be taken that the spraying characteristics of the reference sample are identical with those of the unknown. Oils and fats from different sources having different physical properties (*e.g.*, density and viscosity) will give different background responses and also modify the atom-producing capacity of the flame. It is, therefore, preferable to use the maximum possible dilution of the fatty matter in an appropriate solvent. When dilution causes too great a loss in sensitivity it is possible to aspirate a 50 per cent. *m*/*m* solution of fatty matter in the solvent, but the aspirating air must be preheated and solutions should be incubated to the same temperature (30 to 40 °C). Fats can then be aspirated without precipitation in the nebuliser and all oils will tend towards common spraying characteristics at the higher temperature. A calibration graph is prepared by supplementing a similar metal-free oil with an organozinc compound, such as zinc oleate or naphthenate.

Pentyl acetate (metal free) is a good general solvent for this type of work.

Suitable adjustments to the fuel flow will be necessary to compensate for the burning capacity of the fat and solvent. It may be necessary to separate fatty matter from formulations, *e.g.*, from carbohydrates by solvent extraction, and from the aqueous phase by stirring at 80 °C for fat - water emulsions such as margarines.

THE USE OF AMMONIUM PYRROLIDINE DITHIOCARBAMATE—

This reagent, which was introduced by Malissa and Schoffmann,[7] can be used for the extraction of zinc from a wide range of aqueous solutions into an organic solvent suitable for direct atomic-absorption spectrophotometry.[8] Extraction of the zinc into an organic phase for atomic-absorption spectrophotometry offers several advantages: the concentration of the metal in the organic phase can be 100 times that in the aqueous phase, enabling smaller amounts to be determined; the atomic-absorption signal for zinc in an organic solvent is considerably enhanced in comparison with that obtained from a similar concentration in aqueous solution; and the zinc is separated from the high concentration of salts, which inevitably arises when certain organic materials are wet digested, ashed or diluted.

The sensitivity of zinc determination by atomic absorption varies with the equipment being used, but in organic solvents such as 4-methylpentan-2-one it is usually between 0·01 and 0·1 p.p.m., and a linear calibration graph is normally obtained up to at least 10 p.p.m., so that if the zinc is extracted into 10 ml of solvent the method can be used for amounts of zinc from between 0·1 and 1 μg to between 10 and 100 μg, according to the equipment available.

The zinc - APDC complex can readily be extracted from aqueous solution within the range from strongly acidic (5 N) to a pH of 10 into polar organic solvents such as chloroform, 4-methylpentan-2-one and heptan-2-one. Chloroform is useful if very high concentration factors are required, but leads to flame instability and attack on the nebuliser with some equipment when sprayed directly. For most purposes 4-methylpentan-2-one or heptan-2-one is more satisfactory, the latter having a lower solubility in acidic aqueous solution.

Owing to the solubility of the solvents in acidic aqueous solutions, the solutions should be saturated with the solvent before extraction of the zinc - APDC complex, which is formed immediately on addition of the APDC. For amounts of zinc below 100 μg two extractions with 4 ml of solvent, each after the addition of 1 ml of 1 per cent. aqueous APDC, will remove all the detectable zinc from 100 ml of solution; the two extracts are then combined, diluted to 10 ml in a calibrated flask and sprayed into the atomic-absorption spectrophotometer. The calibration graph must be prepared by extraction of standard amounts of zinc under conditions similar to those used for the samples, as the sensitivity may vary according to the solvent composition.

Extraction of zinc with APDC can be applied directly to the aqueous solutions obtained from the above general methods of sample preparation provided that they are diluted, when necessary, so that the acidity is not greater than 5 N.

OPERATING CONDITIONS—

The optimum operating conditions recommended by the instrument manufacturer should be used. The zero should be set by using an appropriate blank, and standard solutions for the calibration should be prepared so as to have the same degree of acidity as the samples.

The instrument should be set up with a zinc hollow-cathode lamp operated at the recommended current, the monochromator at 213·8 nm and with the slit width adjusted to give an acceptable signal to noise ratio. Neon-filled zinc cathode lamps should be used; the use of brass cathode lamps or argon-filled lamps should be avoided.

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Book Reviews

NEUERE METHODEN ZUR ANALYSE VON TENSIDEN. By H. KÖNIG. Pp. viii + 239. Berlin, Heidelberg and New York: Springer-Verlag. 1971. Price DM58; $17.70 (approx.).

The book consists essentially of two chapters, one on methods for the separation and identification of surfactants (177 pages) and the other on methods for their quantitative determination (49 pages). There is a list of contents but no index.

After an introduction, the first chapter comprises a section on the separation of types of surfactant (by ion exchange) followed by four sections on the separation and four on the identification of anionics, amphoterics, non-ionics and cationics. One third of each section, on average, is a literature survey covering both old and new methods, while half comprises infrared and nuclear magnetic resonance spectra and thin-layer chromatography diagrams for numerous commercial products.

The chapter on quantitative analysis is a combination of a literature survey, which refers indiscriminately to both good and bad analytical methods, and brief accounts of the author's own experiments, which, so far as I have studied them, fall largely into the latter category. Widely discrepant results by different methods are quoted without any suggestion as to the correct figures or the reasons for error, and serve only to warn the reader not to follow the author's unenlightened approach to his subject. The section on phosphate esters (3½ pages) displays such unfamiliarity with ion-exchange procedures as applied to surfactants as to cast serious doubts on the usefulness of the review of the technique in the previous sections.

On reviewing the heterogeneous mixture, I find it difficult to imagine who will benefit from the book. The literature surveys are not very extensive (total references, 180); the infrared spectra are on a small scale, each 103 × 35 mm, and better treatments of the subject are available elsewhere, and the thin-layer chromatograms of single commercial substances do not appear to be of great practical use. This leaves the nuclear magnetic resonance spectra (fifty-six in number, each 126 × 60 mm) and a few lists of commercial products and their R_F values in thin-layer chromatography as the principal parts of any potential value.

König's book may be of use to someone who desires a compact collection of infrared spectra, or a glimpse at the possibilities of nuclear magnetic resonance spectroscopy for analysing surfactants. It may also be appreciated by an analyst who is new to the subject and who desires a review of the types of product that are commercially available. To other potential readers, the work has little to offer.

W. B. SMITH

ÉTUDE ANALYTIQUE DE DÉRIVÉS FLUORES: APPLICATIONS À L'ANALYSE PHARMACEUTIQUE. By M. HANOCQ. Pp. 241. Brussels: Editions Arscia S.A.; Paris: Librairie Maloine S.A. 1972. Price Belg.F490.

The applicability of several standard methods of isolation and determination of fluorine to the analysis of organofluorine compounds, certain pharmaceutical products and blood and urine is described, in French, in this volume. After a brief general introduction on the significance of fluorine in therapeutics, dentistry and toxicology, there follow two chapters on the determination of fluoride by the alizarin fluorine blue method and by the fluoride-selective electrode and one on the separation of fluorine by microdiffusion. Each chapter is a self-contained technical report comprising an introduction, a detailed experimental section and conclusions. They are supported by a comprehensive bibliography, which covers the published literature up to 1969. The experimental section mostly confirms earlier studies by other authors; the amount of new information is limited and concerns mainly the use of dimethyl sulphoxide to enhance the sensitivity of the alizarin fluorine blue method and the use of the fluoride-selective electrode in mixed aqueous - organic solvents. A short chapter is devoted to the analysis of a range of organofluorine compounds of medical interest and the final chapter gives details of methods for the determination of fluorine in samples of pharmaceutical significance. The book concludes with two summaries, one in French and the other in English; the translation into English would scarcely do justice to a good O-level student and the reviewer found the French easier to follow.

Although bound in soft covers, the book is excellently produced on good quality paper, but its content is such that it is difficult to judge for whom it is intended; research workers will find the bibliography useful and the book may be of limited use as a laboratory manual.

J. K. FOREMAN

AUSGEWÄHLTE METHODEN DER WASSERUNTERSUCHUNG. Band 1. CHEMISCHE, PHYSIKALISCH-CHEMISCHE, PHYSIKALISCHE UND ELEKTROCHEMISCHE METHODEN. Edited by the INSTITUT FÜR WASSERWIRTSCHAFT, Berlin, with assistance from the FORSCHUNGSINSTITUTES FÜR MIKROBIOLOGIE UND HYGIENE, Bad Elster. Loose-leaf. Pp. xvi + 250. Jena: VEB Gustav Fischer Verlag. 1971. Price DM35.50.

This book, prepared by an East German team, covers the chemical and physical analysis of natural fresh waters and waste waters, and is a worthy addition to the growing collection of books on the subject. The "Elektrochemische" in the title presumably refers to methods, such as conductivity, which are not yet available, otherwise its inclusion seems pointless. The methods recommended are all of the so-called "traditional" type, usually requiring a titrimetric or colorimetric finish. Atomic-absorption and gas-chromatographic methods are not included, neither is the electrode method for dissolved oxygen. The organic section covers only phenols and anionic surfactants.

Within the above limitations, this seems to be a sound and well prepared book, especially as the methods were subjected to collaborative testing and modified when necessary. An examination of selected parts of the book yielded no surprises; the salicylic acid method for nitrate and the boiling permanganate method for low C.O.D. values deserve attention in this country. The B.O.D. test is defined unequivocally as a test for organic matter, and nitrification is regarded as an interference. In the section on the C.O.D. test, chloride interference is said to occur by oxidation to chlorine, which can be corrected for; this is surely wrong when samples contain ammonia, as they usually do. The use of mercury(II) sulphate for eliminating chloride interference is mentioned, however. There is a particularly good introduction to the section on cyanide.

The book is well produced in loose-leaf form with a ring binder. The style is concise, lucid and explicit, with very few long sentences, and should pose few problems even to those who, like this reviewer, have only a modest knowledge of German. H. A. C. MONTGOMERY

LITHIUM-DRIFTED GERMANIUM DETECTORS, THEIR FABRICATION AND USE. AN ANNOTATED BIBLIOGRAPHY. Compiled by INA CALLOWAY BROWNRIDGE. Pp. xiv + 210. New York, Washington and London: IFI/Plenum. 1972. Price $23.

Lithium-drifted germanium detectors are used increasingly for gamma-ray spectrometry. They operate by using an electric field to sweep out charge carriers produced by the interaction of gamma-rays with the detector; the total amount of charge collected is proportional to the energy dissipated in the intrinsic region. They provide very high resolution by comparison with sodium iodide - scintillator detection systems, and are now used extensively for activation analysis.

This bibliography lists 790 entries from the international literature, covering articles published up to May, 1971. Many of the references refer to the fabrication of detectors and the associated electronics covering items such as material selection, encapsulation, mounting, charge collection, efficiency measurements, cryostat design and the design or optimisation of various types of spectrometer. The references to applications appear to be less extensive, but the subject index lists activation analysis (26 entries), biological applications (9), criminology (1), fall-out (3), fission-product analysis (10), fuel elements (8) and space applications (7).

Overall, a very useful combination of references is provided, particularly for those involved in detector fabrication (74) and system design. For those interested in using germanium detectors for analytical work, the subject index is a little disappointing and requires close examination to locate references of interest—for example, the entry "computer analysis" refers to only three papers on computer methods for analysing spectra, but many more can be found via "peak fitting" or "spectrum analysis." R. K. WEBSTER

INTRODUCTION TO MOLECULAR PHOTOCHEMISTRY. By C. H. J. WELLS. Pp. xii + 146. London: Chapman and Hall. 1972. Price £1·70.

This book is intended to provide undergraduates with an introduction to photochemistry. It is written clearly and has an abundance of well drawn figures that complement the text. Great emphasis is placed on the definition and explanation of the basic terms used by photochemists. Some of the principles of electronic spectroscopy are also described.

In addition, there is a chapter on the kinetics of photochemical processes and two chapters, comprising nearly one third of the book, on photochemical reactions. Inevitably, many interesting fields are excluded by the terms of reference, but students faced with a new course on photochemistry will find this book very useful. D. BETTERIDGE

QUANTITATIVE MEASUREMENTS AND CHEMICAL EQUILIBRIA. By ERNEST H. SWIFT and ELIOT A. BUTLER. Pp. xiv + 719. San Francisco: W. H. Freeman and Co. 1972. Price $14.50.

A more appropriate title to this book would be "An Introduction to Quantitative Inorganic Analysis," but one can understand any attempt to avoid producing yet another book having this title.

The book aims to provide an intensive training in certain of the fundamental techniques of quantitative chemical measurements. Much of it is devoted to a rather elementary treatment of gravimetric and titrimetric analysis, the latter occupying almost half of the book. Despite the great impact of complexometry over the past 25 years, this method receives scant treatment. It does, however, include the Ringbom curve, an item often omitted when presenting this topic.

Forty-eight pages cover laboratory equipment and operations and feature, with appropriate diagrams, how to hold a glass stopper while pouring liquid from a reagent bottle and how to insert a glass tube into a stopper. Optical and electrical methods, again treated at an elementary level, occupy the final 63 pages. As in so many American books, there is a profusion of numerical problems and questions. Detailed experimental procedures are given throughout, each being followed by an elaborate system of notes.

There is little to fault in the treatment of the subject matter as such. In fact, it is dealt with in a most thorough manner and conforms to high educational standards. What is far more difficult is to justify the scope of the book, particularly if one has in mind U.K. analytical chemistry courses. At the lower end it assumes virtually no chemical background on the part of the student, and at the other end it stops short of giving a balanced course at a reasonable level.

One novel feature of the book is the inclusion of mass titrations carried out with a polythene wash-bottle and a top-pan balance.

W. J. WILLIAMS

PMR SPECTROSCOPY IN MEDICINAL AND BIOLOGICAL CHEMISTRY. By A. F. CASY. Pp. xvi + 425. London and New York: Academic Press. 1971. Price £7·30; $23.

Dr. Casy has set out to write a book that assumes a familiarity with nuclear magnetic resonance theory, which many of his potential readers will not possess. It is a pity that he does not provide more background theory to support the many applications discussed. On the few occasions when some theory is presented, it is quite inadequate. For example, in the section on aromatic ring current effects (p. 93), a clear qualitative picture of the origin of these effects does not emerge from the text. The book contains a clear detailed discussion of the analytical aspects of nuclear magnetic resonance and a useful chapter on the nuclear magnetic resonance spectral features of nitrogen-containing compounds. Dr. Casy discusses many interesting examples of the application of nuclear magnetic resonance techniques to the study of compounds of pharmacological and biological interest and, although little attempt has been made to assess the papers critically, the book will serve as a useful reference source. An appendix on solvent and hydrogen-bonding effects contains many useful practical hints.

It is unlikely that many scientists will buy their own copy of this book but, because of its reference value, laboratories interested in this type of work will need to purchase a copy.

J. FEENEY

ANALYTICAL CHEMISTRY: KEY TO PROGRESS ON NATIONAL PROBLEMS. *Proceedings of the 24th Annual Summer Symposium on Analytical Chemistry, held at the National Bureau of Standards, Gaithersburg, Maryland, June* 16–18, 1971. Edited by W. WAYNE MEINKE and JOHN K. TAYLOR. *National Bureau of Standards Special Publication* 351. Pp. x + 470. Washington: U.S. Department of Commerce. 1972. Price $3.50.

This book is a record of six papers delivered by invitation in order to direct attention to analytical problems in important areas of current everyday interest. Unusually, the volume is prefaced by the complete re-publication of a paper presented in 1933 by Dr. G. E. F. Lundell and subsequently published the same year in *Ind. Engng Chem., Analyt. Edn*, entitled "The Chemical Analysis of Things as They Are." This paper deals with basic points relating to such matters as sampling and accuracy and is still quoted today. The chapters that follow relate basically to the American scene and are devoted in turn to the consideration of analytical problems in biochemical research and clinical chemistry, agricultural science, air pollution control, water pollution control, oceanography and in solid-state research and electronics. A panel discussion concludes each chapter; each covers a wide range of individual topics. "Problems in Agricultural

Science," for example, includes fumigation, nutrition and amino-acid analyses, fats and fatty acids, fibrous compounds, seed and plant constituents, meat quality and the composition of meat and dairy products, the sensory characteristics of food, veterinary chemicals, mycotoxins, plant growth regulators, pesticides, nitrosamines and pollutants. While it is not possible to treat all of the problems that arise in these areas in depth, the areas discussed clearly relate to a wide field of stimulus for analytical research. This is also true for other chapters, especially perhaps that on biomedical research and clinical chemistry, which is illustrated with both diagrams and cartoons. The text throughout is supported by references to the original literature. A comprehensive index adds to the value of the book and helps to draw together common analytical interest from a very wide variety of sources. H. EGAN

THE ANALYTICAL CHEMISTRY OF SULFUR AND ITS COMPOUNDS. Part II. Edited by J. H. KARCHMER. *Volume 29 in Chemical Analysis: A Series of Monographs on Analytical Chemistry and its Applications*. Pp. xviii + 835. New York, London, Sydney and Toronto: Wiley-Interscience. 1972. Price £21·25.

This volume deals with the analytical chemistry of sulphides, disulphides and polysulphides, thiophenes, sulphur analogues of carbonyls, carboxylic and carbonic acids and quadrivalent and sexavalent sulphur compounds. In conjunction with the first volume, the most commonly encountered sulphur compounds are covered. In each of the chapters there is a general pattern and in covering the analytically significant properties, most techniques have been dealt with. For each group of compounds there is a relatively large number of pertinent references, so that the whole can probably become a source book for the analytical chemistry of sulphur.

Although there is excellent coverage, it is inevitable that some specialists may feel disappointed that a particular chapter has not been devoted to their particular speciality. However, by judicious use of the excellent index they will, I am sure, be able to find enough of relevance to interest them.

This is a well written book and the authors of the various chapters, and the editor, have filled a gap in analytical chemistry. L. S. BARK

THE DETERMINATION OF HYDROXYL GROUPS. By STIG VEIBEL. *An International Series of Monographs, No. 1*. Pp. xviii + 159. London and New York: Academic Press. 1972. Price £3·50; $10.50.

The term "Determination" in the title of this text goes beyond the normal use of the word. This text includes methods for the detection of the hydroxyl group and methods for characterising hydroxy-compounds as well as methods for measuring the hydroxyl group. Twenty-four pages are devoted to detection methods, thirty-nine to characterisation and eighty pages to measurement.

The chemical methods are described completely in the text, and they are compared and evaluated. The instrumental methods for dealing with the hydroxyl group are only lightly treated. This is not detrimental to the text as someone who is interested in wet methods is rarely also interested in instrumental methods. The text includes not only the common, well accepted methods but also some of the less common methods.

The book is authoritative and well joined together to present a unified picture of the subject area. It is obvious from the text that Dr. Veibel is well versed in the material of which he speaks.

This book should interest both students and practitioners in the field of organic chemistry and organic analysis. S. SIGGIA

APPOINTMENTS VACANT

Imperial Ethiopian Government

CHIEF ANALYST

Chief Analyst required for geochemical laboratory attached to Geological Survey. Present Staff of 15 Ethiopian and expatriate chemists and assistant chemists but intention to recruit additional staff after appointment of Chief Analyst. Major equipment includes 5 Atomic Absorption spectrometers and one X-Ray Fluorescence Spectrometer. Rocks, soils and waters being analysed for major and minor elements. Applicants should have experience in organising high productivity laboratories and knowledge of appropriate instrumentation.

Laboratory situated Addis Ababa with ideal climate. Readily available European style housing and good facilities. Salary up to Eth. $30,000 p.a. (Eth. $5.2 approx. £1). Appointment will be on a 3 year contract, renewable, although a shorter first contract would be considered if desired. Return airfares for candidate and dependants will be provided. Annual leave of 30 days plus up to 15 days sick leave.

Applications to Minister of Mines, Ministry of Mines, Box 486, Addis Ababa, Ethiopia. Interviews will be held in London.

LECTURES & COURSES

TRENT POLYTECHNIC, NOTTINGHAM
Department of Chemistry and Biology
LIQUID CHROMATOGRAPHY WORKSHOP

The Workshop specialising in high performance liquid chromatography will be held on

Tuesday	September 4th	9.30 am – 5.30 pm
Wednesday	September 5th	9.30 am – 5.30 pm
Thursday	September 6th	9.30 am – 3.30 pm

Course fee £24

The course is an extended version of earlier workshops. Further details may be obtained from Head of Department of Chemistry and Biology, Burton Street, Nottingham NG1 4BU.

The Determination of Tin and Antimony in Lead Alloy for Cable Sheathing by Atomic-absorption Spectroscopy

A method has been evolved for the rapid determination of tin and antimony at levels of about 0·4 and about 0·2 per cent., respectively, in lead alloy used for sheathing electric cables.

The sample is dissolved in a mixture of fluoroboric acid and hydrogen peroxide and the determination is completed by atomic-absorption spectroscopy with the use of an air - acetylene flame for antimony and a nitrous oxide - acetylene flame for tin. The method of dissolving the sample avoids the precipitation reactions that are likely to arise from lead, antimony or tin if conventional acid dissolution processes are used and hence permits a direct and rapid analysis by the atomic-absorption technique.

Calibration for antimony must be effected with a solution containing the dissolution mixture and, in calibration for tin, lead must additionally be present.

TERESA M. QUARRELL, R. J. W. POWELL and H. J. CLULEY

The General Electric Company Limited, Central Research Laboratories, Hirst Research Centre, Wembley, Middlesex, HA9 7PP.

Analyst, 1973, **98**, 443–449.

Replacement of Platinum Vessels with a Pressure Device for Acid Dissolution in the Rapid Analysis of Glass by Atomic-absorption Spectroscopy

The rapid analysis of glass is made possible by replacing the crucibles in which time-consuming fusion is carried out by a device for quantitative acid dissolution under pressure and subsequent atomic-absorption spectroscopic determinations of the elements.

The sample is decomposed by hydrofluoric acid at 105 °C in a decomposition vessel consisting of a crucible-shaped stainless-steel container fitted with a removable PTFE crucible and a stainless-steel screw-cap with a PTFE disc inserted in the metal body. Subsequent addition of boric acid forms the analysis matrix of fluoroboric acid - boric acid for the atomic-absorption determinations of silica, alumina, iron, titanium, magnesium, calcium, sodium and potassium.

This procedure obviates the use of platinum vessels, prevents losses of constituents due to alloying, reduction and volatilisation, does not introduce extraneous cations, and is reliable, simple and rapid to perform.

Y. HENDEL

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Analyst, 1973, **98**, 450–451.

Thermometric Assay of Some Sulphonamides of Pharmaceutical Importance

The thermometric determination of several sulphonamides used in pharmaceutical preparations is described. The sulphonamide is dissolved in the minimum amount of dilute sodium hydroxide solution and the pH adjusted to 8·9 with thymolphthalein as indicator. The solution is then made up to 10 cm^3 with an appropriate buffer solution (pH 8·0 or 9·18). In these controlled alkaline conditions, the sulphonamide is titrated directly with silver nitrate solution, the equivalence point being determined thermometrically. The effects of several matrix ingredients in common use in pharmaceutical preparations have been determined. The time of the titration is approximately 1 minute and the accuracy is within ± 2 per cent.

L. S. BARK and J. K. GRIME

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Analyst, 1973, **98**, 452–455.

Nitrogen Contents of Raw Fish

Report prepared by the Fish Products Sub-Committee.

ANALYTICAL METHODS COMMITTEE
9/10 Savile Row, London, W1X 1AF.

Analyst, 1973, **98**, 456–457.

The Determination of Small Amounts of Zinc in Organic Matter by Atomic-absorption Spectroscopy

Report prepared by the Metallic Impurities in Organic Matter Sub-Committee.

ANALYTICAL METHODS COMMITTEE
9/10 Savile Row, London, W1X 1AF.

Analyst, 1973, **98**, 458–460.

REPORTS OF THE ANALYTICAL METHODS COMMITTEE

The Reports of the Analytical Methods Committee listed below may be obtained direct from The Society for Analytical Chemistry, Book Department, 9/10 Savile Row, London, W1X 1AF (not through Trade Agents), at the price of 10p. to members of the Society and 15p. to non-members. Remittances must accompany orders and be made payable to "Society for Analytical Chemistry."

Certain Reports published before 1946 have been omitted from this list, but are still available.

Additives in Animal Feeding Stuffs Sub-Committee:

Report of the Antibiotics Panel: The Determination of Penicillin, Chlortetracycline and Oxytetracycline in Diet Supplements and Compound Feeding Stuffs.
Report of the Hormones Panel: The Determination of Stilboestrol and Hexoestrol in Compound Feeding Stuffs.
Report of the Prophylactics Panel: The Determination of Nitrofurazone in Compound Feeding Stuffs.
Report of the Vitamins (Water-soluble) Panel: The Determination of Water-soluble Vitamins in Compound Feeding Stuffs.
Report of the Vitamins (Fat-soluble) Panel: The Determination of Fat-soluble Vitamins in Diet Supplements and Compound Feeding Stuffs.
Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Amprolium in Animal Feeding Stuffs.
Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Sulphaquinoxaline.
Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Acinitrazole.
Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Ethopabate in Feeds.
Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Furazolidone in Feeds.
Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Dimetridazole in Animal Feeds: Revised Method.
Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Dinitolmide (Zoalene) in Animal Feeds.
Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Amprolium, Sulphaquinoxaline and Ethopabate when Present Together in Animal Feeds.
Report of the Prophylactics in Animal Feeds Sub-Committee: The Determination of Carbarsone in Animal Feeds.

Analytical Standards Sub-Committee:

Sodium Carbonate as a Primary Standard in Acid - Base Titrimetry.
Sulphamic Acid as a Primary Standard in Acid - Base Titrimetry.

Essential Oils Sub-Committee:

Report No. 15. Determination of Linalol in Essential Oils.
Application of Gas - Liquid Chromatography to Essential-oil Analysis: Interim Report on the Determination of Citronellol in Admixture with Geraniol.
Spectral Characteristics of Eugenol.
Application of Gas - Liquid Chromatography to the Analysis of Essential Oils. Part 1: Determination of Cedrol.

Fish Products Sub-Committee:

Nitrogen Factor for Cod Flesh.
Nitrogen Factor for Coal Fish.

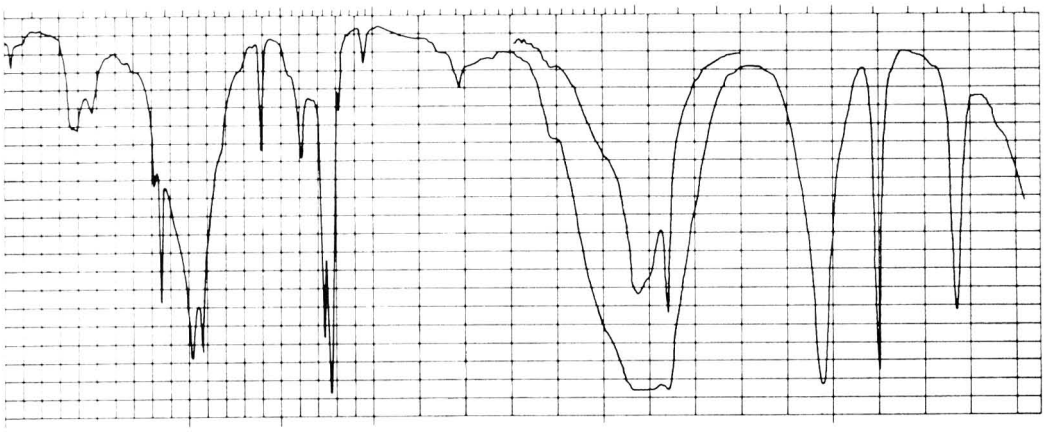
Meat Products Sub-Committee (formerly Meat Extract Sub-Committee):

Analysis of Meat Extract.
Determination of Gelatin in Meat Extract and Meat Stocks: Interim Report.
Nitrogen Factors for Pork *and* Nitrogen Content of Rusk Filler (as one reprint).
Nitrogen Factors for Beef.
Nitrogen Factors for Chicken.
Nitrogen Factors for Liver.
Nitrogen Factor for Veal.
Nitrogen Factors for Turkey.
Nitrogen Content of Rusk Filler.
Nitrogen Factor for Kidney.
Nitrogen Factor for Tongue.
Nitrogen Factor for Barley.
Nitrogen Factor for Blood.

Metallic Impurities in Organic Matter Sub-Committee:

Methods for the Destruction of Organic Matter.
The Determination of Small Amounts of Arsenic in Organic Matter.
The Determination of Small Amounts of Copper in Organic Matter.
The Determination of Small Amounts of Mercury in Organic Matter.
The Determination of Small Amounts of Tin in Organic Matter. Part 1. Amounts of Tin up to 30 μg.
The Determination of Small Amounts of Zinc in Organic Matter.
The Use of 50 per cent. Hydrogen Peroxide for the Destruction of Organic Matter.
The Determination of Small Amounts of Tin in Organic Matter. Part 2. Amounts of Tin from 30 to 150 μg.
The Determination of Small Amounts of Cadmium in Organic Matter.
The Determination of Small Amounts of Copper in Organic Matter by Atomic-absorption Spectroscopy.

RS solvents for UV and IR spectrophotometry



Acetone UV and IR
Acetonitrile UV and IR
Benzene UV and IR
Carbonium sulfide
UV and IR
Carbonium tetrachloride
UV and IR
Chloroform UV and IR
Cyclohexane
UV and IR

N-N-Dimethylformamide
UV and IR
Dichloroethane IR
Dimethylsulfoxide UV
Dioxane UV
Ethyl acetate IR
Ethyl alcohol UV
Ethyl ether UV
n-Heptane UV
n-Hexane UV
Isooctane UV and IR

Isopropyl alcohol UV
Methylene chloride
UV and IR
Methyl alcohol UV
n-Pentane UV
Potassium bromide IR
Tetrachloroethylene IR
Tetrahydrofuran
UV and IR
Toluene IR
Trichloroethylene IR

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