DETERMINATION OF TRACE ELEMENTS

by

PAUL YOUNG, Dip.Tech., A.C.T. (Birm)

A thesis submitted for the degree of

DOCTOR OF PHILOSPHY

in the University of London.

Department of Chemistry,

Imperial College of Science and Technology,

LONDON, S.W.7.

May, 1966.

ABSTRACT

The analyses of four elements by a variety of spectrophotometric procedures have been investigated.

A simple and rapid colorimetric method for the determination of aluminium in plain carbon steels down to 0.001% is described. The determination is based upon the formation of the yellow aluminium - 8 - hydroxyquinolate complex; interfering ions are removed by solvent extraction or masked with complexing agents.

4 -(2-Pyridylazo) - resorcinol forms a red-coloured complex with lead (II) in alkaline solutions and provides the basis for a colorimetric determination of lead in steel, brass and bronze alloys. Selectivity is obtained by solvent extraction, precipitation and masking techniques.

Lead has also been determined by atomic-absorption spectrophotometry. The technique is very sensitive and is virtually free from all cation and anion interferences. The method has been applied to the determination of lead in steel, brass and bronze alloys and compared with the colorimetric method.

The adaptation of an atomic-absorption spectrophotometer to the measurement of cadmium atomic-fluorescence in an air-acetylene flame is described. This new analytical technique is compared with the more conventional method of atomic-absorption for the determination of cadmium, and is seen to be more sensitive and equally free from foreign ion interferences.

The application of a colorimetric method to the determination of tin in steels down to 0.003% is described. The procedure is based upon reaction with Catechol violet in the presence of gelatin to give a blue-coloured complex.

Interferences are removed by the use of solvent extraction procedures.

The determination of tin by the application of atomic-absorption spectrophotometry is also investigated.

ACKNOWLEDGEMENTS

The work recorded in this thesis was carried out in the Chemistry Department of Imperial College of Science and Technology between October 1963 and May 1966. It is entirely original except where due reference is made and no part has been previously submitted for any other degree.

I wish to express my gratitude to my supervisors, Professor T. S. West and Dr. R. M. Dagnall for their unfailing assistance and advice given throughout this project, and to other members of the Analytical Research Team for many helpful discussions and suggestions.

I am also grateful to the British Welding Research Association and to United Daries Limited for finanical support which enabled me to carry out this work.

Thanks are also due to Mr. B. Bagshawe of the Brown-Firth Research Laboratories and to Mr. F. Coe of the British Welding Research Association for providing steel and bronze samples used in this project.

Finally I would like to thank Mr. W. T. Elwell of Imperial Metal Industries for providing the lead and camium hollow-cathode lamps.

CONTENTS

FOREWORD

During recent years there has been a steadily growing interest in the constituents of certain materials, present only in trace amounts. Such an interest is shown in the rapidly expanding area of metallurgy where there has been considerable research into the significance of trace elements. It is undoubtedly with this knowledge that the British Welding Research Association made provision for the research scolarship held by the author during the first academic year.

Absorption spectrophotometry is undoubtedly one of the most serviceable and versatile techniques of trace metal analysis and it was decided at the outset of this programme to concentrate on this technique.

A survey of the literature and discussion with the Research Association revealed that there was a particular need for new methods of analysis for aluminium, lead and tin present in steel and other metal alloys.

Following the development of solution-based spectrophotometric procedures for the determination of aluminium, lead and tin it seemed logical to extend investigations into the analytical technique of atomic-absorption spectrophotometry in flame media. The technique is as sensitive as absorption spectrophotometry in solution and requires less chemical manipulation and pre-handling of the sample. This will become particularly evident from a comparison of Chapters II and III where methods for the determination of lead traces are developed by both techniques.

In direct consequence of the work carried out in atomic absorption spectrophotometry an investigation into the very new analytical technique of atomic-fluorescence spectrophotometry was undertaken, which led to the determination of a fourth element, cadmium.

INTRODUCTION

The major part of the work reported in this thesis is concerned with the development of some methods for the determination of trace elements in steels and other metal alloys.

The term, "trace", was first used to designate a minute quantity of substance known to be present in a sample but not quantitatively determined. This was usually because the amount was below that readily determinable with the existing titrimetric or gravimetric methods. Today the determinations of constituents making up only a fractional percentage of the sample are frequently required, and the term, "trace", has come to represent amounts which constitute less than 0.01 per cent of the matrix.

Some methods for the determination of four elements, aluminium, lead, cadmium and tin, have been developed and will be dealt with in this order.

ALUMINIUM

Aluminium is added as a deoxident during the latter stages of steel making toreduce soluble iron oxide. The insoluble alumina thereby formed is normally dispersed through the metal in the form of very hard inclusions which, during subsequent processing, can give beneficial effects in respect of grain growth and impact strength. Normally at least 50 per cent in excess of the stoichiometric amount required to deoxidise the steel is added in order to ensure that the alumina inclusions are randomly dispersed and not segregated at grain boundaries. Thus, part of the aluminium content in steel is "metallurgically soluble" and part "insoluble" thereby doubling the analytical problems.

The existing official, standardised methods [1 to 4] of chemical analysis for aluminium in ferrous metals are often lengthy, require many separations and, because of the necessity to have an appreciable amount of aluminium, large sample weights must be taken.

Most methods require preliminary separations from interfering elements such as iron, chromium, titanium and zirconium. The separations are of two main types:-

(a) Those in which the interfering elements are separated from the aluminium;

(b) Those in which the aluminium is separated from the interfering elements.

Type (a) includes the mercury-cathode electrolytic separation [5,6], precipitation with cupferron [7,8] from acid solution, precipitation of hydroxides of iron (III), chromium and titanium with sodium hydroxide and precipitation with hydrogen sulphide [9]. Large amounts of iron may be separated by solvent extraction of hydrogen tetrachloroferrite [10] into a variety of solvents such as diethyl ether, iso-propyl ether, iso-butyl acetate or amyl acetate. Smaller amounts of iron may be removed by extraction as its cupferrate.[11] Older methods of type (b) mostly depend on the hydrolysis of aluminium salts to insoluble hydroxide with various reagents such as sodium bicarbonate [2,3], sodium thiosulphate [12], potassium iodide-iodate [12] and pyridine.[13] Alternatively, basic aluminium succinate [14], aluminium phosphate [5,15] or aluminium acetate may be preciptated at controlled pH . The solvent extraction of aluminium cupferrate at pH 4.5 into chloroform gives a rapid and simple separation of aluminium after the removal of iron.[16]

The gravimetric determination of aluminium may be completed by precipitation of the hydroxide and ignition to the oxide [2]., Precipitated aluminium - 8 - hydroxyquinolate may be dried and weighed directly or dissolved in acid and titrated with potassium bromate - bromide solution.

Aluminium may be determined titrimetrically by the fluoride method after suitable preliminary separations [17 to 21].

All these methods are based upon neutralisation of the aluminium solution with sodium hydroxide solution in the presence of sodium potassium tartrate, usually to a phenolphthalein end point, and after addition of neutral potassium fluoride the liberated potassium hydroxide is titrated as a measure of the aluminium present with standard acid solution.

The reaction may be represented by the following equations:-

$$Al^{3+} + 3\,OH^{-} \rightleftharpoons Al(OH)_3$$

$$Al(OH)_3 + 6.KF \rightleftharpoons K_3Al.F_6 + 3KOH.$$

In fact, the reaction does not go to completion, but stops about 10 per cent before the stoichiometric equivalence point and standards must therefore be used.

Several methods for the colorimetric determination of aluminium have been described based on the use of organic reagents which form coloured lakes with aluminium hydroxide. Of these, aluminon (aurin tri-carboxylic acid) is probably the most well-known [22,23] other reagents which have been used similarly include solochrome cyanine - R, (Eriochrome cyanine - R) [24 to 28], Alizarin - S[29], Haematoxylin [22 30] and Stilbazo [31].

In recent years there have been many fluorimetric reagents described for the determination of very small amounts of aluminium, examples of which include Morin [32], Quercetin [33], Pontachrome blue-black R[34], 2 - Hydroxy, 3 - Naphthoicacid[35], 8 - Hydroxyquinoline[36] and Salicylidene ortho amino phenol[37 38].

Several methods have been described for the spectrophotometric determination of aluminium in steels[39 to 44]. Generally these methods suffer from disadvantages, such as the length of time required for their completion or from the necessity for complicated separation processes based on multiple extractions with different complexing agents at various pH values. Many of the methods based on repetitive solvent extractions are potentially subject to several errors, such as incomplete and variable recovery of aluminium or of interfering elements, incomplete removal of the organic reagents and phase separation problems. Generally those methods which include a preliminary separation by mercury-cathode electrolysis are probably more reliable, but relatively tedious and expensive. Furthermore solvent extraction procedures still have to be used to remove elements that are either not separated or incompletely separated by electrolysis.

The object of the work carried out and reported in Chapter I of this thesis was to develop a reliable and yet more rapid and simple spectrophotometric method for determining aluminium in plain carbon steels.

LEAD

There are many procedures available for the selective separation of lead from commonly encountered and commercially important substances in which the usual interferences such as that of iron are encountered.

Typical methods for the separation of lead include precipitation, electrodeposition and solvent extraction. Other methods which have been used are the evaporation of volatile lead iodide, ion-exchange and chromatography.

Precipitation methods which have been used include both many inorganic and organic precipitants. Examples of the inorganic methods are typified by the time - honoured lead sulphate [45] and lead sulphide [2,3,46,47] precipitations, or as lead molybdate from dilute nitric acid [48,49] and as the insoluble lead chromate [50]. Examples of organic precipitants include thiourea [51], thionalid [52], mercaptobenzthiazol [53] and salicylaldoxime [54].

There are many examples of solvent extraction techniques for the separation of lead of which the most commonly encountered are based on reaction with dithizone [5,55,56], or with diethyl dithiocarbamates [55,57,58]. Other solvent extraction procedures which have been used include extraction of the lead rhodizonate into chloroform [59] and the iodide into methyl iso-propyl ketone [60].

Electrolytically, lead may be separated by deposition as the dioxide [56,61,62] or as metallic lead [63], usually onto a platinum electrode.

There are many gravimetric finishes for the determination of lead, a full list of which is given by Kolthoff and Elving [59] in their treatise on analytical chemistry, and includes those methods given under separation by precipitation. These will not be discussed further since they have little relevence to the present programme.

Lead may be determined titrimetrically by means of precipitation and complex formation reactions. It may also be determined indirectly by precipitation followed by an oxidation - reduction titration. One of the most widely used precipitation titration methods is that with standard molybdate solution. The classical procedure uses ammonium molybdate as titrant and tannic acid as external indicator. A better external indicator, potassium thiocyanate plus stannous chloride, has been described, the red potassium molybdothiocyanate, $K_3\,[Mo(SCN)_6\,]4H_2O$, forming at the end point.

The equation for titration with molybdate may be expressed as:-

$$(NH_4)_6\,Mo_7O_{24} + 4H_2O + 7.Pb(NO_3)_2 = 6.NH_4NO_3 + 7.PbMoO_4 + 8.HNO_3.$$

Other precipitation titration methods include titration with chromate using 2,6 dichlorophenol-indophenol as an absorption indicator [65] and with phosphoric acid using diphenylcarbazide as indicator.[66]

The only reagent widely used for complexometric titration of lead is ethylenediamine tetra-acetic acid, EDTA., for which there are a wide variety of organic indicators such as Eriochrome Black T, Xylenol orange, 1-(2-pyridylazo) 2-naphthol and 4-(2-pyridylazo)-resorcinol.

Lead may be determined polarographically as it possesses particularly favourable electrochemical characteristics. References may be found in Kolthoff and Lingane's treatise on polarography [67]. Once again, however, this particular aspect of trace analysis will not be expanded since it is not directly relevant to the present programme.

A few colorimetric reagents for the determination of small amounts of lead exist of which the most widely used is dithizone [5 68 to 73]. Others include Solochrome red B [74], tetra methyldiaminodiphenylmethane (following electrodeposition as the dioxide onto platinum) [56 75], diethyldithio - carbamate after the addition of copper [76], diphenyl - carbazone [66 77 78] and 4-(2-pyridylazo)- resorcinol [79 to 82].

Procedures for the determination of lead in ferrous materials by measurement of the absorption due to colloidal lead sulphide have also been described[83,84].

Other methods of determination include flame photometry, for which Dean [85] reports emission sensitivities of lead at 4058, 3684 and 3600 Å of 14, 21 and 41 ppm for 1 per cent transmission respectively in oxy-acetylene flames, and by spectrography using the 2833 Å emission line.

Atomic-absorption has been used for the determination of lead and this technique will be dealt with in detail later.

The addition of lead to steel during its manufacture has been shown to improve its later machinability, and is becoming a frequently encountered alloying element. Standard methods [2,3,46] of analysis have, therefore, been developed for lead content in the order of about 0.01 per cent. Usually lead is separated from the bulk of the iron matrix by sulphide precipitation from dilute hydrochloric acid, but if the lead content is less than 0.1 per cent the solution must be allowed to stand for at least 4 hours. After redissolving the sulphide in nitric acid, lead is reprecipitated as the molybdate from an ammoniacal - tartrate medium and the filtered precipitate ignited and wieghed as lead molybdate. The procedure is reliable to about only ± 0.01 per cent on a 10g. sample and is subject to interference from tin and tungsten.

Where the lead content of a steel is less than 0.01 per cent it is normally present as an accidental impurity, and the existing classical analytical estimation becomes even more time consuming.

Since its introduction dithizone [87] has undoubtedly become the most widely used reagent for the spectrophotometric determination of traces of lead in steels [5,88]. Although the formation of lead dithizonate provides one of the most sensitive methods for determining lead, ($\varepsilon_{520m\mu}$ = 65,000)[89] the method suffers many disadvantages arising from non-selectivity, photodecomposition of dithizone solutions and insolubility of complex in aqueons media.

Steels containing about 0.1 per cent of lead have been analysed polarographically [90]. Extremely small concentrations of lead of the order of 0.0001 per cent have also been determined polarographically in cast iron, but preliminary separations of iron by extraction as ferric chloride and of lead as diethyldithiocarbamate must be carried out.[91]

The presence of trace amounts of lead in bronzes and associated materials has undesirable effects. For example, in aluminium bronze, lead has a low solubility in the α-phase (the aluminium-bronze matrix) and therefore separates to the grain boundaries where it forms films. These films have low melting points and so contribute to grain boundary weakening during high temperature service of the component.

Lead may be determined in copper-based alloys by methods similar to those used for steel analyses. For example dithizone extraction procedures have been described by Milner and Townsend [92] who extract the lead dithizonate from an ammonia-ammonium chloride buffered solution containing large amounts of cyanide and sulphite, and by Young and Leibowitz [93] who use a preliminary separation by coprecipitation with ferric hydroxide followed by removal of iron by ether extraction. Lead is then extracted from an alkaline cyanide medium and co-extracted bismuth removed by a back extraction before the lead is determined with dithizone.

Copper and aluminium alloys containing 0.001 to 2 per cent of lead have been analysed by a procedure using the extraction of lead diethyldithiocarbamate [94].

The development of a new and more reliable spectrophotometric procedure for the determination of lead in steels and copper-based alloys is described in Chapter II of this thesis.

ATOMIC-ABSORPTION SPECTROPHOTOMETRY

Atomic-absorption spectrophotometry provides a simple, sensitive and rapid technique for the determination of traces of metals. Because of the freedom from inter-elemental interference the technique may be applied directly to the determination of trace amounts of metals in steels and other metal alloys.

The technique of atomic-absorption spectrophotometry has been used by the author for the determination of three elements methods for which are reported in this thesis. It is, therefore, of value to include here a brief description of the basic theory involved and of the apparatus required.

If we consider the emission of a spectral line due to the transition from an excited state to the ground state of lowest energy, the intensity of emission is proportional to the number of atoms present in the excited state, neglecting effects of self-absorption and induced emission.

The ratio of the number of atoms in the excited state, N_j of excitation energy E_j, to the number of atoms in the ground state, N_o, is given by the equation:-

$$\frac{N_j}{N_o} = \frac{p_j}{p_o} \quad \exp. \quad \left({}^{-E_j}/_{kT} \right).$$

Where p_j and p_o are the statistical weights for the excited and ground state weights, k is a constant and T the absolute temperature.

In most instances, excepting extremely high temperatures, the number of atoms in the lowest excited state is very small compared with the number in the ground state and so the ratio Nj/No will be very small.

The number of atoms in the ground state can therefore be regarded as being approximately equal to the total number of atoms, N. Thus whilst the number of excited atoms varies exponentially with temperature, the number of atoms in the ground state remains virtually constant.

If we now consider a parallel beam of radiation of intensity I_o of frequency ν passing through an atomic vapour of thickness l, then if I_ν is the intensity of transmitted radiation, the absorption coefficient K_ν is given by:

$$I_\nu = I_o \exp^{(-K_\nu l)}.$$

The integrated absorption, $\int K_\nu . d\nu$ is given by the equation:-

$$\int K_\nu . d\nu = \frac{\pi e^2}{mc} N_\nu f$$

Where e is the electronic charge, m the electronic mass, c the velocity of light, N_ν the number of atoms capable of absorbing radiation of frequency ν and f is the oscillator strength.

It is, therefore, seen that for a transition from the ground state, where N_ν approximates to N (the total number of atoms), the integrated absorption is proportional to the concentration of free atoms and independent of temperature.

Thus, in so far as effects observed in emission are due to variation in the distribution of atoms in the various excited states, there is no counter part in absorption.

There is, however, the problem of measurement of the integrated absorption. At temperatures between 2,000 and 3,000 °K the width of an absorption line is about 2.10^{-2} Å, (compared with a natural line width of about 10^{-4} Å), resulting from Doppler broadening, pressure broadening and stark broadening. To measure the profile of an absorption line accurately would require a monochromator with a resolution of 500,000, which is beyond the capacity of most spectrographs. However, by using a sharp-line source with a much smaller half-width than the absorption line, the absorption coefficient at the centre of the line can be determined.

A typical instrumental arrangement comprises a hollow-cathode lamp for supplying a sharp-line source, a long and narrow air-acetylene flame fed by an atomiser with spray chamber, (which may be the barrel of the burner), a prism monochromator, a photomultiplier detector tube and a galvanometer or pen recorder. When flame emission from thermal excitation could be troublesome, the light from the emitter source may be modulated either by a mechanical chopper or by using the lamp on alternating current. The signal amplifier is then tuned to receive only at the frequency of the emitted light. Alternatively an optical system of defocussing the thermally excited radiation may be used. Double beam instruments are sometimes used to compensate for drift in the emitted radiation.

Radiation from the source is passed through the flame and, after being monochromated, its intensity measured at a selected wavelength. The element under investigation is vapourised into flame through a spray chamber. The atomic vapour of the element produced in the flame, absorbs radiation from the sharp-line source and the reduction in intensity determined.

As mentioned earlier, a sharp-line source should emit resonance radiation of the element under investigation with a line half-width considerably less than the Doppler width of the absorbing line, and with a sufficiently intense and stable radiation to enable measurement to be made accurately.

Emission sources which have been used include vapour discharge lamps and hollow-cathode lamps. The latter have become the most widely used source as they can be made to cover a wide range of elements. A general discussion of the construction and characteristics of hollow-cathode lamps for atomic absorption spectrophotometry have been given by Jones and Walsh [95] and by Elwell and Gidley [96].

Various lens and diaphragm systems have been designed for passing the radiation from the source through the best part of the flame as inhomogeneity in the flame causes premature curvature of working curves [97] as well as loss in sensitivity.

Atomiser requirements are similar to those for the more widely-known technique of flame emission spectrophotometry. The unit must incorporate a system for ensuring a reproducible supply of consistently fine droplets of solution. A detailed study of atomiser characteristics for both emission and absorption spectrophotometry has been given by Hermann [98]. Most workers appear to use conventional atomiser-burners for atomic absorption spectrophotometry, as the introduction of cold vapours causes little variation in the flame temperature and does not significantly influence absorption characteristics.

In most instances a good ultraviolet monochromator is necessary for selecting the required wavelength, but where a source emits a resonance line in the visible region with high intensity, a simple coloured glass or gelatin filter may be used. Also where the resonance line is in the visible or near U.V. region interference filters may be used as selectors provided no lines, other than the resonance line, are within the bandwidth of the filter.

For instruments using either interference or coloured filters for wavelength selection, it is possible to use a simple barrier-layer photocell and galvanometer for intensity measurements, but in most other cases photomultiplier detectors are the most useful.

In emission spectroscopy the extent of emission of one element may be influenced to a considerable extent by the presence of other elements. It was an attempt to devise a spectrochemical procedure free from interelemental effects that first led Walsh [99] to examine possible causes of interferences and consequently to the development of the new technique of atomic-absorption spectrophotometry. Since the introduction of atomic-absorption spectrophotometry [99, 100] as an analytical tool many advances have been made, several of which have been discussed by Elwell and Gidley [96], Gilbert [101, 102] and Scribner and Margoshes [103].

The determination of comparitively large amounts, (0.08 to 3.2 per cent), of lead in copper-based alloys and steels has been described by Elwell and Gidley [104] and other applications to metallurgical analyses by Gidley [105] and Stumpf [106], but there is no record of the application of the method to traces of lead in steels. However applications of atomic absorption to the analyses of trace amounts of lead in non-metallic products have been discussed elsewhere [107 to 110].

The development of a simple and rapid procedure for the determination of lead by atomic-absorption spectrophotometry is given in Chapter III. The application of the method to the analyses of steel samples is also given.

CADMIUM

(By Atomic-Absorption and Fluorescence Spectrophotometry)

During the development of the solvent extraction procedures for the separation of lead it was observed that the only elements passing right through the procedure together with the lead were cadmium and the more uncommon element ruthenium.

It was, therefore, decided to investigate the possible utlisation of the development as a means of isolating cadmium prior to its determination.

It was also decided to investigate the determination of cadmium by the new technique of atomic-fluorescence spectrophotometry and to compare the technique with the more conventional means of atomic-absorption spectrophotometry.

In atomic-fluorescence spectrophotometry, A.F.S., atoms are excited by the absorption of radiation of the proper frequency followed by the emission of radiation resulting from deactivation of the atoms. The frequency of the emitted radiation is characteristic of the absorbing atoms and the intensity is proportional to their concentration.

The experimental arrangement used in A.F.S. is basically similar to that of solution spectrofluorimetry, but the individual components are similar to those used in atomic emission and absorption spectrophotometry. A typical experimental arrangement consists of an intense source of radiation directed onto a suitable sample cell containing the atomic vapour of the element under investigation. The fluorescent radiation at right angles to the exciting beam is passed into a monochromator, and the amplified signal from a photomultiplier detector displayed on a galvanometer or recorder. In the event of the sample emitting thermally excited radiation of the same frequency as the fluorescent radiation the incident radiation from the excitation source may be chopped and the a.c. amplifier turned to the same frequency.

Early studies involving the measurement of atomic fluorescence have been summarised by Mitchell and Zemansky [111]. Most of the early studies utilized quartz or glass cells for the confinement of atomic vapours, but these methods were extremely inconvenient. Later the use of a stable flame proved to be a much more convenient "sample cell." The first fluorescence of species in flames were reported by Nichols and Howes [112] who obtained weak fluorescence from sodium, lithium, calcium, strontium and barium. More recently Robinson [113] noted a weak fluorescence of the magnesium 2852 line in hydrogen-oxygen flames when excited with a magnesium hollow-cathode lamp.

The introduction of A.F.S. as a means of chemical analysis has been made by Winefordner and his coworkers during the last two years [114 to 117]. These papers include studies of theoretical considerations and experimental parameters which are sufficiently new to be included in summary here.

Atomic-fluorescence spectrophotometry is an emission method based on radiational rather than thermal activation of an atomic vapour. In most cases the absorbance and emitted radiation are of the same frequency, ie. resonance fluorescence is observed. The energy of the fluorescent radiation, E_f, is directly proportional to the energy of the resonance radiation absorbed, E_a, i.e.

$$E_f \propto E_a \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\text{or} \qquad E_f = \phi \cdot E_a \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where the proportionality constant, ϕ, is a measure of the quantum effiency of the process.

In practical cases where the fluorescent radiation originates throughout a finite body, e.g. a flame, a term must be included in the equation (2) to account for self absorption.

FIGURE 1.

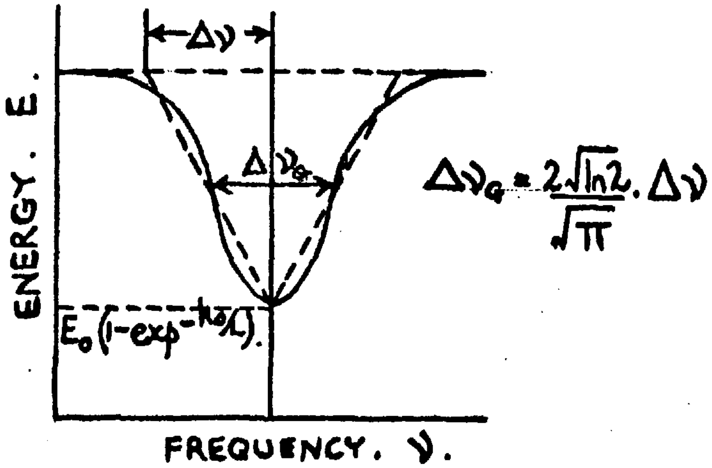


Figure 1 shows an idealised absorption line, Guassian in shape, on which is superimposed a triangle of equivalent area. The area under either curve represents the total energy absorbed by the line.

The area of the triangle is given by the peak absorption times the half-width of the triangle, and it therefore follows that:-

$$E_a = E_o\left(1 - \exp^{-k_oL}\right).\Delta\nu \quad .... (3)$$

Where E_o = energy of incident radiation,

k_o = atomic absorption coefficient at the line centre,

L = average path length of radiation passing through the flame

and $\Delta\nu$ = half the base width of the triangle.

Willis [118] has shown that the half-width of the triangle is related to the half-intensity width of the gaussian curve $\Delta\nu_G$ by the equation:

$$\Delta\nu = \frac{\sqrt{\pi}}{2\sqrt{\ln 2}}\,\Delta\nu_G \quad ....(4)$$

In flame spectrophotometry the absorption line does approximate to the Gaussian curve and so $\Delta\nu$ can be evaluated from the half-intensity line width, and the total absorption of the line calculated from equation (3). The value of k_o =

$$\frac{\sqrt{\ln 2}\cdot\lambda^2\cdot p_j}{4\pi^{3/2}\,p_o\cdot\Delta\nu_D}\cdot N_o\cdot A_t\cdot\delta \;\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Where $\Delta\nu_D$ = Doppler half-width of the absorption line,

p_j and p_o = Statistical weights in the upper, j, and lower, o, states,

No = Number of absorbing species in the ground state,

λ = Wavelength at the absorption line centre,

A_t = Transition probability from the j to O state.

δ is defined so:-

$$\sqrt{\ln 2}\left(\frac{\Delta\nu_L + \Delta\nu_H + \Delta\nu_N}{\Delta\nu_D}\right).$$

where $\Delta\nu_L$ = Lorentz half-width

$\Delta\nu_H$ = Holtsmark half-width

$\Delta\nu_N$ = Natural half-width

and $\Delta\nu_D$ = Doppler half-width

From equation (3) it follows that the energy emitted as fluorescent radiation is given by:

$$E_F = \phi\cdot E_o\cdot\Delta\nu\left(1-\exp^{-k_oL}\right)\exp^{-k_o.L/2}\cdot\cosh\left(k_oL/2\right) \;\ldots\ldots \quad (6)$$

where the product $\exp^{-koL/2} . \cosh (koL/2)$ approximately accounts for self-absorption of fluorescent radiation. Equation (6) can be rewritten in terms of intensity by dividing E_f by the area of the flame cell, A_f, from which the fluorescent radiation is emitted, and by 4Π steradians:-

$$I_F = \frac{\phi . E_o . \Delta\nu}{4\pi . A_f} . \left(1-\exp^{-k_oL}\right) \exp^{-k_oL/2} . \cosh\left(k_oL/2\right) \ldots\ldots (7)$$

when ko is small, as when the limit of detection is approached, equation (7) may be simplified to give:

$$I_F = \frac{\phi . E_o \Delta\nu k_o L}{4\pi A_f} \quad \ldots\ldots\ldots\ldots (8)$$

substituting for ko gives:

$$I_F = \left(\frac{\sqrt{\ln 2}\, \phi . \Delta\nu . L . \lambda^2 . p_j A_t . \delta}{16\pi^{5/2} . A_f . \Delta\nu_D . p_o}\right) . E_o . N_o \ldots\ldots\ldots\ldots (9)$$

For a given line in a constant flame the bracketed term is constant and may be represented by C, therefore:

$$I_F = C . E_o . N_o . \quad . \ . \ . \ . \ . \ . \ . \ . \ (10).$$

We finally see from the above equation that, providing the incident source is constant, the fluorescent radiation varies linearly with the number of ground state atoms, i.e. concentration.

Unlike A.A.S. it will be seen possible to increase sensity by increasing the intensity of the incident radiation. It is also possible to increase the sensitivity by increasing the term C, which includes the length of fluorescent path and cross section area of the flame cell.

The application of A.F.S. to the determination of very small amounts of cadmium in oxy-acetylene [115] and oxy-hydrogen [115 117] flames has been described by Winefordner and coworkers.

The objects of the studies undertaken and reported in chapter IV of this thesis were to investigate the possible modification and use of an existing commercially available flame photometer for the measurement of cadmium fluorescence in air-acetylene flames.

Following investigations into the determination of cadmium by A.F.S. it was decided to compare the technique with the more conventional means of A.A.S. using the same instrument.

Several references have been made to the determination of cadmium by A.A.S. [96, 97, 99, 119, 120] and analytical procedures have been described for cadmium in zinc samples using propane-butane-air flames [121] and in biological materials using air-coalgas flames [104].

The results obtained from investigations into the determination of cadmium by atomic-absorption spectrophotometry are given in Chapter V.

TIN

Tin is present as an accidental impurity in steel resulting from the use of tin-plate scrap. Knowledge of the amount present in alloy steels is of importance as tin can increase the hardenability of the steel which can give rise to forging difficulties. Methods for the determination of trace amounts of tin in steel are, therefore, required for routine analyses.

The existing standard, "classical" methods [1 to 4] are very lengthy and time consuming.

Tin can be separated from other elements in solution by precipitation as sulphide, [122] as metastannic acid [122], as phosphate, with tannin [123 124] or by displacement using excess metallic zinc. It can be distilled as the chloride [125] or as the bromide [126]. Under proper conditions tin may be quantitatively distilled from sulphuric acid with hydrobromic acid [127 128] or with a mixture of hydrochloric and hydrobromic acids [129 130 131]. Subsequent determination of the tin titrimetrically involves reduction to the stannous state, usually by the addition of metallic aluminium, antimony, nickel or iron, followed by titration with iodide or iodate. Reduction and subsequent titration is usually carried out in an inert atmosphere, usually carbon dioxide.

Tin can be determined gravimetrically by ignition to the oxide, after sulphide separation with subsequent purification by volatilisation using ammonium iodide. The method is satisfactory for small amounts of tin and affords separation from elements other than members of the hydrogen sulphide group. Tin precipitated from a solution containing large amounts of iron, nickel and cobalt is best redissolved and reprecipitated, since stannic sulphide tends to carry down these elements. The gravimetric determination of tin by precipitation from dilute hydrochloric or sulphuric acid with cupferron has been described[128]. The method has been applied to the determination of tin in copper ~~and~~ based alloys. It is also applicable, after preliminary separation by distillation, to many other materials containing non-volatile elements [127].

Tin has been determined in ores by indirect precipitation with mercuric chloride and is based upon the reaction between stannous chloride and mercuric chloride [122 132].

$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$$

A large number of colorimetric finishes are available using a wide variety of reagents, examples of which include toluene - 3,4 - dithiol [131 133 134 135], phenylfluorone [136 137], dinitro-diphenylamine sulphoxide [138], cacotheline [139] and xylenol orange [140]. The application of colorimetric procedures is usually limited by the interferences encountered from other elements.

The titrimetric procedures usually prove more satisfactory than the gravimetric ones for the determination of tin in ferrous materials, but the preliminary separations required are lengthy and care must be taken in the presence of large amounts of phosphorus.

A search of the literature showed that although there are numerous colorimetric reagents for tin few give high sensitivity. However, Malat has recently described [141 142] the use of pyrocatechol violet as a rather sensitive reagent for tin in the presence of gelatin and has prepared a calibration curve over the range 0.1 to 0.6 μg Sn per ml using 2 cm. cuvettes. No application of the method has been made to steel analysis. The selective extraction of Sn (IV) by a non-polar solvent, benzene, from a perchloric acid - perchlorate - iodide medium has been described by Gilbert and Sandell [137], and was the basis of gaining selectivity used by Malat.

It was decided to utilise this selective iodide separation of tin to isolate it from steel samples and subsequently determine the tin spectrophotometrically with pyro-catechol-violet.

The development of a simple and rapid procedure for the determination of tin in steels is given in Chapter VI of this thesis together with investigations into the nature of the complex and possible use of alternative dispering agents to gelatin as used by Malat.

CHAPTER I

THE DETERMINATION OF ALUMINIUM IN PLAIN CARBON STEEL

SUMMARY.

A simple and rapid method is described for the spectrophotometric determination of aluminium in plain carbon steel down to about 0.001 per cent.

In the developed procedure [143] the sample is dissolved in hydrochloric acid and the bulk of the iron removed as hydrogen tetrachloroferrite by extraction with amyl acetate. Remaining trace elements are complexed by 1,10-phenanthroline and potassium cyanide in the presence of hydroxylammonium chloride at pH.5.5. The aluminium is then extracted with a chloroform solution of 8-hydroxyquinoline. Any co-extracted elements, such as titanium or zirconium, are stripped from the extract by shaking it with an ammonia buffer solution of pH 9.2. A small amount of sulphide ion is incorporated in the buffer solution which also strips out any trace elements that may not have been completely complexed at pH 5.5.

The absorbance of the extract is then measured at 385 mμ in a spectrophotometer against a reagent blank solution taken through the procedure and compared with standard amounts of aluminium taken through the procedure.

The method provides a simple and rapid means of determining

aluminium in steel, it does not involve repetitive extraction with different organic reagents and avoids the necessity for a mercury-cathode electrolysis by using a preliminary extraction to remove the bulk of the iron.

INTRODUCTION

It is well known that aluminium is an element lacking outstanding reactions suitable for separation and determination.

Probably the most widely used method for the separation of aluminium from the bulk of interfering metals present in steels is by mercury-cathode electrolysis. Large quantities of cobalt, copper, iron, nickel and zinc and many other metals can be effectively separated from aluminium. Some elements remain in solution with aluminium examples of which include beryllium, magnesium, phosphorus, scandium, thorium, titanium, vanadium and zirconium, the alkaline earths and rare earths. Solvent extraction techniques, therefore, still have to be used for the removal of remaining minor constituents which could interfere with the final aluminium determination. In particular, niobium, titanium and zirconium must be removed before the determination stage, usually by a cupferron extraction following a complicated precipitation procedure after electrolysis.

Aluminium may be then determined either:- (1) gravimetrically; examples include direct ignition to the oxide, or precipitation and direct weighing of aluminium 8-hydroxyquinolate, (2) titrimetrically; following oxine precipitation aluminium may be determined by titration with a bromate-bromide solution in acid medium. Liberated bromine reacts quantitatively with 8-hydroxyquinoline precipating the 5,7-dibromo compound. The excess bromine may then be determined by liberation of iodine which is then titrated with sodium thiosulphate.

(3) photometrically; there are many colorimetric and fluorimetric reagents for aluminium determination following mercury-cathode electrolysis or other separations. Examples include formation of the Solochrome Cyanine and 8-hydroxyquinoline complexes. Other reagents are given in the general introduction.

The object of the study reported in this first chapter was to develop a reliable, simple and yet more rapid spectrophotometric method for the determination of trace amounts of aluminium in steel following solvent extraction procedures for the separation of aluminium from interferences.

EXPERIMENTAL

Apparatus

Spectrophotometer :-	Beckman D.B., with 1 cm silica or glass cuvettes.
pH Meter :-	Vibron, model 39A.

REAGENTS

All reagents were of analytical grade.

Hydrochloric acid	Sp. gr. 1.18.
Nitric acid	Sp. gr. 1.42.
Sulphuric acid	Sp. gr. 1.84
Acetic acid	Glacial
Hydrofluoric acid	40 per cent (w/w).
Ammonia solution	Sp. gr. 0.88
Iso-amyl acetate	
Chloroform	
Hydroxylammonium chloride	10 per cent (w/v) aqueous
1,10-Phenanthroline	0.2 per cent (w/v) aqueous.
Potassium cyanide	10 per cent (w/v) aqueous.
Sodium sulphide	10 per cent (w/v) aqueous.
8-Hydroxyquinoline	0.5 per cent (w/v) in Chloroform.
Potassium Hydrogen Sulphate.	
Electrolytic Iron powder.	

Aluminium Solution, 0.01N :-

Dissolve 4.7441 g of $Al_2(SO_4)_3 . K_2SO_4 . 24H_2O$ in small volume of hydrochloric acid and dilute the solution to 1 litre.

Buffer Solution, pH 9.2 :-

Mix 50 ml of ammonia solution and 27 ml of acetic acid and dilute the mixture to 1 litre with distilled water. Check the pH with a pH-meter and adjust with ammonium hydroxide or acetic acid if necessary.

RECOMMENDED PROCEDURE

1. Preparation of Calibration Curve:-

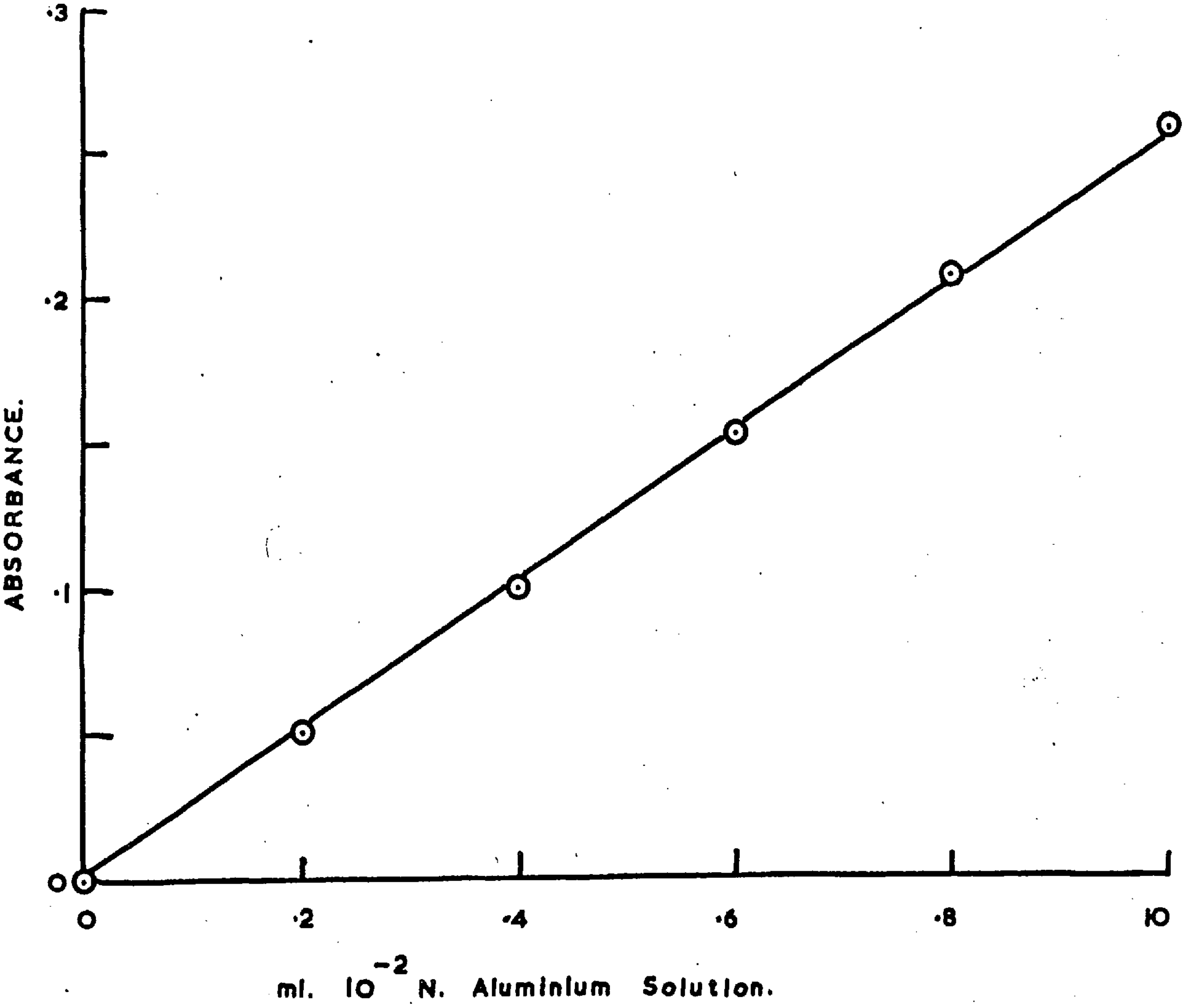
Dissolve 0.5g. samples of electrolytic iron powder in 10 ml. portions of conc. hydrochloric acid contained in 250-ml beakers, warming to assist solution. Transfer by pipette 0.2 to 1.0 ml. aliquots of standard aluminium solution into the beakers. Oxidise the iron by the dropwise addition of nitric acid, and transfer the solutions to 250-ml separating funnels with the aid of a further 25 ml of conc. hydrochloric acid. Add 50 ml of amyl acetate to each funnel and shake each for one minute to remove the bulk of ferric iron. Run the lower extracted phases into different 250-ml separating funnels containing 30 ml of amyl acetate, and shake these funnels for a further minute. Run the equeous phases into 50-ml volumetric flasks. To the first series of separating funnels add 10 ml. of conc. hydrochloric acid and shake for one minute. Run the aqueous phases into the second series of funnels and repeat the procedure. Add the aqueous phases to the 50-ml volumetric flasks and dilute them to their marks with distilled water.

Transfer, by pipette, 5 ml aliquots of these solutions into 250-ml. beakers containing 20 ml of water and 5 ml of 10 per cent hydroxylammonium chloride solution to reduce trace amounts of Fe (III). Add 5 ml. 0.2 per cent 1,10 - phenanthroline solution, 5 ml of ammonia solution and 1 ml of 10 per cent potassium cyanide solution to each beaker. Adjust the pH of the solutions to 5.5 with acetic acid utilising a pH meter. Transfer the solutions to 250-ml separating funnels with minimum amounts of water. To each funnel pipette 10 ml. of 0.5 per cent 8 - hydroxyquinoline-chloroform solution and shake each for 2 min. Run the lower chloroform solutions into different separating funnels containing 20 ml of buffer solution (pH 9.2) and add 2 ml of 10 per cent sodium sulphide solution. Shake the funnels for one min. and, after phase separation, run the chloroform extracts through 7-cm. Whatman No. 1 filter papers into 25 ml. volumetric flasks. To the first series of separating funnels add further 10 ml amounts of 8 - hydroxyquinoline solution and after shaking the funnel for one minute run the extracts into the second series of separating funnels. After shaking these funnels for one minute run the chloroform extracts through the filter papers into the 25 ml. volumetric flasks and diute them to their marks with dry chloroform.

Measure the absorbance of each solution at 385 mµ in 1-cm. cuvettes against a reagent blank solution taken through the procedure.

The graph of absorbance plotted against the amount of aluminium taken is a straight line passing through the origin (Fig. II).

FIG. II.



2. Determination of Aluminium in Plain Carbon Steels.

Dissolve a suitable weight of sample (usually 0.1 to 2.0 g) containint about 50 to 270 μ-g of aluminium in 10 ml of concentrated hydrochloric acid in a 250 - ml beaker. After oxidising the iron with concentrated nitric acid transfer the solution, with the aid of 20 ml of concentrated hydrochloric acid, through a small pulp pad into a 250 - ml separating funnel. The pulp pad must be first washed with concentrated hydrochloric acid to replace any water in the pulp and in the stem of the funnel so as to maintain the high acidity of the filtered solution.

Transfer the pulp pad and residue, which contains undissolved alumina, to a platinum crucible and ignite it at about 900°C. Continue the determination as described in the next paragraph.

Meanwhile, add 50 ml of amyl acetate to the filtrate and shake the funnel for one minute. Transfer the lower extracted phase to a second separating funnel and repeat the extraction with 30 ml of amyl acetate. Run the aqueous solution into a 50 - ml volumetric flask. Wash the remaining organic phase in the first separating funnel with 10 ml. of concentrated hydrochloric acid and then run the washings into the second funnel repeating the operation. Finally run the lower aqueous solution into the 50 - ml volumetric flask, but do not yet dilute it to its mark.

To the platinum crucible and residue add a few drops of concentrated sulphuric acid and 40 per cent hydrofluoric acid. Heat the crucible to volatilize any silicon tetrafluoride, and continue heating to dryness. Fuse the residue with a small amount of potassium hydrogen sulphate in the usual manner and, after it has cooled, extract the fused residue with distilled water. Add the extract to the 50 - ml volumetric flask and dilute to the mark. The small amount of iron introduced at this stage will be accounted for by masking agents at a later stage. High silicon steels may cause introduction of larger than usual amounts of iron and in such cases the subsequent addition of larger amounts of hydroxylammonium chloride and masking agents will be required.

Finally continue the determination as in the preparation of calibration curve at the paragraph beginning, "Transfer by pipette 5 ml aliquots . . . . . ", measuring the absorbance against a reagent blank solution taken through the procedure. Aliquotslarger than 5 ml may be taken when very low amounts of aluminium (< 0.005 per cent) are encountered.

The amount of aluminium present may then be determined from the calibration curve.

RESULTS

The results obtained by applying the recommended procedure to the analysis of a number of various British Chemical Standard Certificated steels and analysed samples obtained from the British Welding Research Association are shown in Tables I and II respectively.

TABLE I

Analysis of B.C.S. Certificated Mild Steels

Sample No. B.C.S.	Aluminium Found (Average) per cent	Certificate Value Per cent.
271	0.008	0.008
273*	0.060	0.06
275*	0.022	0.02
327	0.016	0.020 (0.016)
328	0.047	0.048 (0.047)
329	0.052	0.056 (0.052)

* Aluminium is a non-standardized element.

The certificate values given in Table I represent the average results of inter-laboratory analyses carried out independently by various procedures. It is worth noting that the results obtained from the recommended procedure for sample numbers 327, 328 and 329 are in very close agreement with those obtained by Rooney's [16] polarographic procedure, (bracketed values).

TABLE II

Analyses of Commercial Samples *

Sample No.	Type of Sample	Aluminium Found (Average) per cent	Reported Value per cent
B.W. 1	Mild-steel Welding Wire	0.007	0.005
B.W. 4	Mild-steel Weld Metal	0.028	0.021
B.W. 5	" " " "	0.010	0.009
B.W. 8	Copper coated mild steel wire	0.161	0.17
B.W. 9	Mild-steel Weld Metal	0.040	0.05
B.W. 10	Copper coated mild steel wire	0.136	0.14
B.W. 11	Mild-steel weld metal	0.040	0.05
B.W. 12	Copper coated mild steel wire	0.622	0.59
B.W. 13	Mild-steel weld metal	0.218	0.23
B.W. B.	Plate	0.008	0.008
B.W. C.	"	0.003	0.003
B.W. D.	"	0.010	0.009
B.W. E.	Mild-steel plate	0.004	0.004
B.W. 2A.	Copper coated mild steel wire	0.008	0.008

*Samples obtained from F.Coe.

These results are slightly lower than most of those obtained by the spectrophotometric procedure using Solochrome Cyanine. This may, perhaps, be explained by the known tendency of Solochrome Cyanine to react metallochromically with many trace elements.

The certificate value for B.C.S. numbers 273 and 275 are only approximations in the sense that aluminium is a non-standardized element.

The values obtained by the recommend procedure given in Tables I and II are the average of two or more results. In order to gain an idea of the reproducibility of the procedure a further series of repeated analyses of three samples was carried out. The results are shown in Table III.

TABLE III

Repetitive Analyses of Some Steels for Aluminium Content

Sample No.	Aluminium Found per cent	Avg. per cent	Reported Value per cent
B.W. 2A	0.007. 0.008. 0.008. 0.009.	0.008	0.008
B.W. 10	0.135. 0.143. 0.133. 0.133. 0.126	0.134	0.14
B.W. 11	0.036. 0.042. 0.057. 0.040. 0.050	0.041	0.05

It will be seen that in the case of the higher concentrations of aluminium interpretation of the third decimal place should not be argued to much closer than ± 0.005 per cent absolute. It should, however, be noted that the samples listed in Table III are Weld-metals and may give an unfavourable impression of the method since such samples are subject to segregation.

The range of values obtained by the recommended procedure compares favourably with the range reported by various laboratories for the certificated samples, and in this respect, since the latter are undoubtedly the mean results from a series of analyses, the precission of the recommended method is as satisfactory as those accepted for standard procedures.

Development of Proposed Method

The preliminary studies carried out on the determination of trace quantities of aluminium in steels followed directly from previous work on this subject reported by M, Herrero - Lancina.[144]

It was proposed to reproduce the previously established method of determination. The method consisted in the removal of iron from a hydrochloric acid solution of the steel sample by an amyl acetate extraction. This was followed by extraction with a chloroform solution of 2-methyl, 8-hydroxyquinoline for the removal of interfering metal ions. The aluminium was then extracted as its 8-hydroxyquinolate into chloroform, and after evaporation of the chloroform the remaining complex was destroyed by heating with mixed strong acids. Finally, the aluminium was determined spectrophotometrically with Solochrome Cyanine in an aqueous buffered solution.

Despite a careful and close adherance to this procedure erratic results were obtained.

Initial discrepancies were found to result from the particular sample of Solochrome Cyanine used. Replacement with a fresh sample obtained from an alternative manufacturer gave more stable and promising results, and a satisfactory calibration curve was prepared for mixtures of standard aluminium and Solochrome Cyanine solutions buffered at pH 5.8.

An examination of the 8-hydroxyquinoline solvent extraction procedure revealed that prior to the extraction, the pH of the aqueous solution was lower than that required for an efficient extraction [145, 146]. The pH of further experiments was therefore carefully controlled, but inconsistent results were still obtained.

Following extraction of the aluminium-oxinate, the complex is destroyed by a nitric-perchloric acid mixture and then determined spectrophotometrically with Solochrome Cyanine.

The inconsistent results were, therefore, thought to arise from incomplete or inconsistent breakdown of the aluminium - 8, hydroxyquinolate. An extensive examination of this particular stage was, therefore, undertaken.

A better and more controlled oxidative destruction was ultimately found with an acid mixture of sulphuric, perhloric and nitric acids. Organic substances containing nitrogen in a ring structure are notoriously difficult to breakdown, which therefore explains the necessity of a vigorous acid mixture.

Utilising this, however, did not solve all the problems as low results were still obtained.

Attention was therefore turned to the 2 - Methyl - 8, hydroxyquinoline stage for extraction of the interferences. As reported in the literature [43], this should remove most metal ions except aluminium.

However, low results were always found following an extraction with 2 - methyl, 8-hydroxyquinoline. It was found that, although aluminium does not precipitate or form a coloured species with 2 - methyl, 8-hydroxyquinoline, it was extracted to a certain extent by chloroform.

The results tended to contradict the literature and so a closer examination of the 2 - methyl, 8-hydroxyquinoline extraction procedure was undertaken. Results showed that appreciable amounts of aluminium could be extracted by a chloroform solution of 2 - methyl, - 8-hydroxyquinoline at certain pH values. Figures III, IV and V show the effect of a preliminary extraction with this reagent prior to determination with 8 - hydroxyquinoline at three different pH values of 5.9, 5.1 and 4.2. Curves IIIa, IVa and Va were prepared by diluting 0 to 10 ml of 10^{-4}M aluminium aliquots to 100 ml with water and after pH adjustment they were extracted with 10 ml of a 0.5 per cent chloroform solution of 8 - hydroxyquinoline. The absorbance of each extract was measured at 385 mμ in 1 cm cuvettes against a reagent blank.

Curves III b, IV b, and V b were prepared as above but following an extraction with 10 ml of 1 per cent 2-methyl,

FIG. III

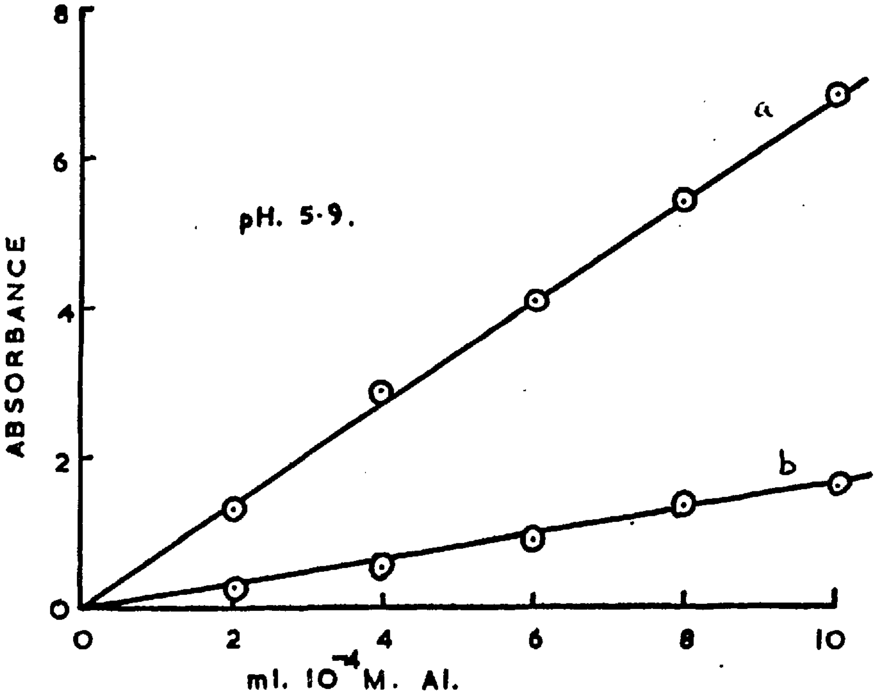


FIG. IV

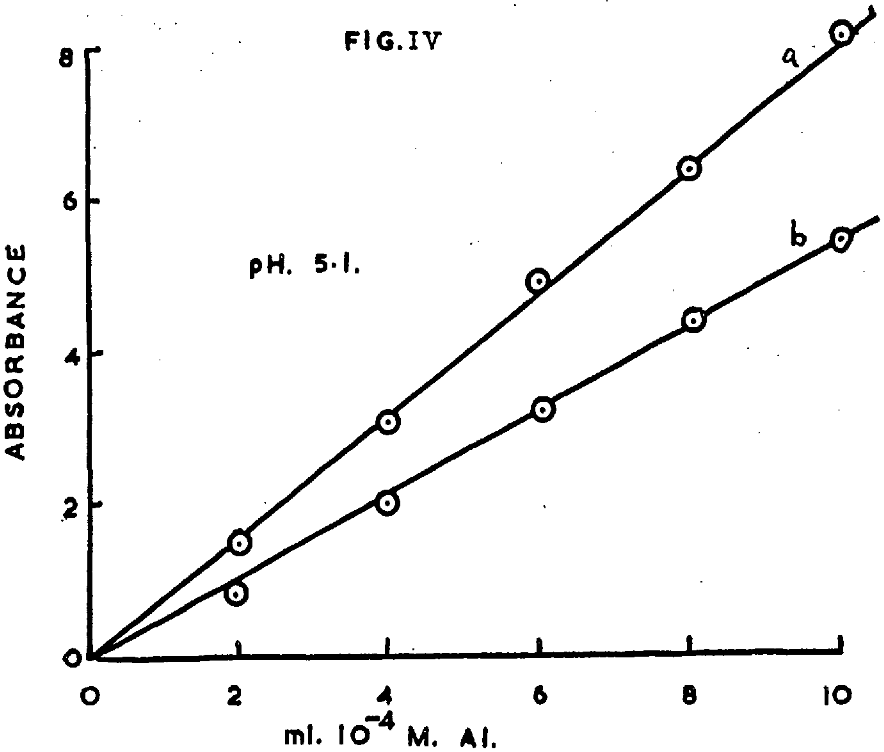
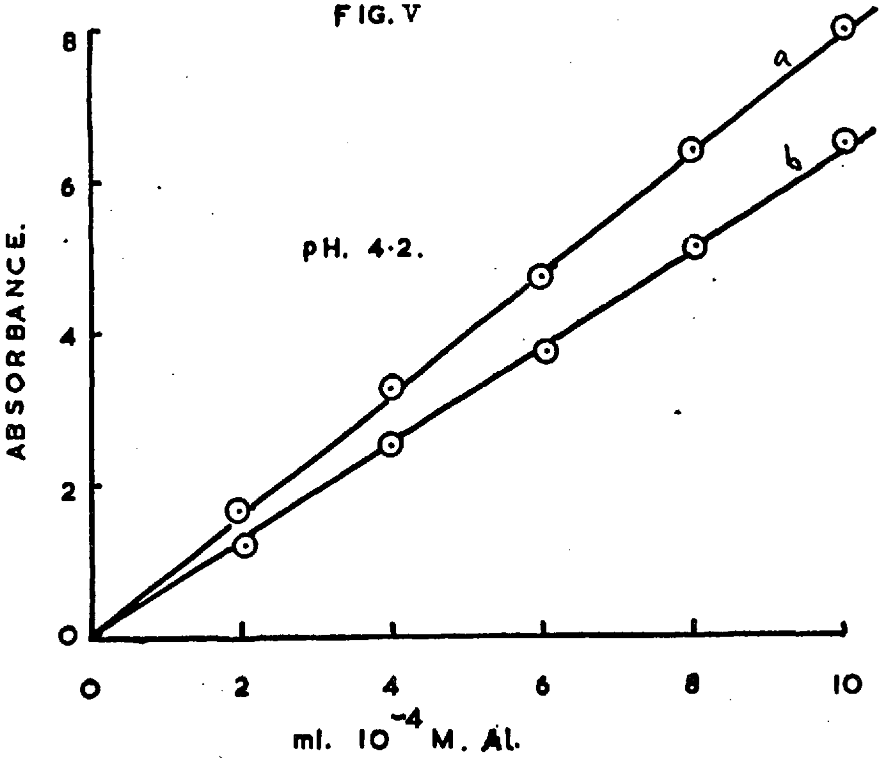


FIG. V



8-hydroxyquinoline solution and a chloroform wash of the remaining aqueous solution,

At pH 5.9 the effect of a preliminary extraction with 2 - methyl, 8 - hydroxquinoline is to reduce the molecular extinction coefficient from 7,000 to an apparent 1,650. At lower pH values the loss in sensitivity is less serious. For example at pH 5.1 the sensitivity drops from 8,000 to 5,500 and at pH 4.2 from 8,000 to an apparent 6,500. At lower pH values than 4.2 it was found that, in common with others[145] [146], the aluminium is incompletely extracted by 8 - hydroxyquinoline and consequently it was expected that the efficiency in forming the 2 - methyl, 8 - hydroxyquinolate complex would also be less.

In the present studies it was also shown that aluminium was being extracted by 2 - methyl, 8 - hydroxyquinoline into chloroform by submitting the extract to examination by a double - monochromating spectrofluorimeter. The extract showed characteristic strong excitation and emission peaks at 370 and 480mμ which compare with values of 380 and 515mμ for the corresponding 8 - hydroxyquinolate complex. The values are sufficiently different to remove any doubt of possible 8 - hydroxyquinoline content in the 2 - methyl, 8 - hydroxyquinoline used.

It therefore became apparent that any method based on a preliminary extraction of interfering metal ions with 2 - methyl, 8 - hydroxyquinoline would yield significantly low results, even at pH values most favourable for non-removal of aluminium.

Experiments conducted with other extractive reagents for the removal of interferences proved somewhat unsatisfactory as it was sometimes found difficult to remove the excess of reagent which could itself interfere with the aluminium - 8 - hydroxyquinolate determination. A particular example of this was observed with cupferron which was investigated in connection with the possible removal of titanium and zirconium. The use of high molecular weight amines used in conjunction with different solvents for removal of titanium and zirconium was also investigated, but without any success.

Attention was therefore turned to the possibility of using selective masking agents to hold back undesirable metal ions.

It was found, in common with others, that cyanide successfully masked cobalt, copper, iron and nickel over a wide range of pH values from extraction by oxine, but manganese, titanium and zirconium were still extracted. At pH 5 to 6 manganese was successfully masked with 1,10 - phenanthroline.

The addition of hydroxylammonium chloride at pH values between 5 and 6 proved beneficial, because it favoured the formation of both ferrocyanide and tris 1, 10 - phenanthrolinium - iron (II), both of which are more stable than the corresponding ferric iron complexes.

E.D.T.A. gave dissappointing results for masking manganese, titanium and zirconium and, moreover, had a definite depressing action on the aluminium - 8 - hydroxyquinolate extraction.

Although others [44] have reported that E.D.T.A. can be used as a masking agent to prevent the extraction of other elements with aluminium - 8 - hydroxyquinolate, it was observed that the use of E.D.T.A. does give low aluminium recoveries.

The reaction between aluminium and E.D.T.A. is known, but kinetically it is very slow. However in the presence of large amounts of electrolyte it may be possible to obtain a quantitative recovery of aluminium by 8 - hydroxyquinoline extraction from solutions containing E.D.T.A. However, a procedure including the use of E.D.T.A. is theoretically unsound and this was found to be so in practice.

Other masking agents investigated for possible prevention of titanium and zirconium extraction by 8 - hydroxyquinoline include sulphosalicylic acid, mandellic acid and pyrophosphate, but no complete or satisfactory masking was obtained.

Eventually, pH studies showed that owing to progressive hydrolysis of their 8 - hydroxyquinolates, titanium and zirconium were not extracted at pH 9.2. It was shown possible that an extraction made at pH 5.5. containing aluminium, titanium and zirconium could be stripped of the titanium and zirconum by shaking the extract with an aqueous solution buffered at pH 9.2. Furthermore, the addition of sulphide to the pH 9.2 buffer solution proved useful for removal of any traces of iron still present in solution.

Although it was possible to determine aluminium in steel down to 0.001 per cent by the measurement of the 8 - hydroxyquinolate, it was also observed that after evaporation of the chloroform extract and wet-ashing the residue with a sulphuric-perhloric - nitric acid mixture, a more sensitive determination with Solochrome Cyanine could be made. However, the time and extra operations involved would not justify their inclusion for routine purposes.

THE DETERMINATION OF ALUMINIUM IN STAINLESS STEELS

Following the satisfactory development and application of the spectrophotometric determination of aluminium in plain carbon steels an extension of the procedure to include stainless steels was investigated.

In general, stainless steels differ from plain carbon steels in chromium and nickel content. A typical stainless steel, for example, contains 18 per cent chromium and 8 per cent nickel.

At first sight it appeared that there would be little difficulty in the direct application of the developed procedure to cover stainless steels. From the literature [146] chromium should not be extracted by 8 - hydroxyquinoline into chloroform at room temperatures. The increased nickel content should give no problem as it may be easily masked with excess cyanide.

Preliminary attempts to analyse stainless steels, however, met with failure. Values ranging from 2 to 8 times the reported aluminium content were obtained.

It was eventually shown that, despite reports in the literature, some chromium was in fact being extracted together with the aluminium by 8 - hydroxyquinoline in chloroform.

Attempts to minimise the chromium extraction, by cooling the solutions in ice baths to less than 10°C, met with only partial success. It therefore became apparent that the chromium must either be masked from extraction or removed from solution prior to the 8 - hydroxyquinoline extraction.

The removal of some of the chromium was obtained at the steel-dissolution stage by evaporation of the volatile chromyl chloride from a perhloric - hydrochloric acid medium. However, complete removal by this technique could not be obtained.

Attention was then turned to the possibility of chromium separation by precipitation as the insoluble lead chromate.

Before precipitation as lead chromate the chromium must first be oxidized from its existing state as chromium (III) up to chromium (VI). This was successfully obtained by boiling an ammoniacal solution of the sample with hydrogen peroxide. After decomposing the excess of peroxide by boiling, the solution was adjusted to pH 3.5 and excess lead nitrate solution added. The solution was then boiled, cooled and filtered to remove lead chromate. The excess lead remaining in solution was then removed by precipitation and filtration of the insoluble sulphate. The chromium free solution was finally analysed by the recommended procedure, but again high and inconsistent results for the aluminium content were obtained.

These inconsistencies were eventually shown to stem partly from the incomplete removal of excess hydrogen peroxide, which subsequently oxidesed the 8 - hydroxyquinoline to the yellow N-oxide species.

Complete destruction of the excess hydrogen peroxide was successfully obtained by boiling the solution in the presence of platinum metal, but inconsistent results were still obtained.

The use of sulphur dioxide to remove excess peroxide chemically was investigated, but similar results were found.

The precipitation of chromium (VI) with barium in place of lead also met with the same inconsistencies.

As a consequence of the above work solvent extraction techniques for chromium removal were then investigated.

The extraction of chromium (VI) with tri-benzylamine into chloroform from 1 to 5 N hydrochloric acid solution has been described by Fasola and his coworkers [147]. Attempts were therefore made to utilise this procedure for the separation of chromium from aluminium.

Synthetic mixtures of aluminium (III) and chromium (VI) were made 2N in hydrochloric acid and extracted with 10 ml of 5 per cent tri-benzylamine in chloroform. After washing the extracted phase with pure chloroform, the aqueous solutions were adjusted to pH 5.5 and extracted with 8 - hydroxyquinoline in the usual way.

Low and variable results were obtained using this procedure, but variation of acidity to 1N did appear to give more consistent results.

When the tribenzylamine extraction procedure was used following the peroxide oxidation stage low and variable results were yet again obtained.

The extraction of chromium as perchromic acid from sulphuric acid - hydrogen peroxide solution at a reduced temperature into a butanol - ether mixture was investigated but no satisfactory application to complete chromium removal from aluminium was obtained.

It was finally decided to postpone extension of the aluminium procedure to include stainless steels until a satisfactory method for the complete removal of chromium was obtained.

CHAPTER II

PART I THE DETERMINATION OF LEAD IN STEEL AND COPPER-BASE ALLOYS.

SUMMARY

4-(2-Pyridylazo) - resorcinol forms a red-coloured complex with lead (II) in an ammonia-ammonium chloride medium at pH 10. Maximum colour is developed immediately and it is stable for at least 24 hours. The reaction is sensitive, $\epsilon_{520\,m\mu} = 40,000$, but many metal ions interfere. Selectivity is achieved by extracting the lead into *iso*-butyl methyl ketone, from an iodide solution, followed by back-extraction into an ammoniacal solution. Those metals which would also extract as iodides are removed by a preliminary extraction of their thiocyanates.

The procedure has been applied to the determination of lead down to 0.001 per cent in iron, mild steels - and alloy steels and to the analyses of brass and bronze alloys. Ferrous alloys require a preliminary separation of the bulk of the iron by an *iso*-amyl acetate extraction; copper-base alloys are treated by a preliminary concentration of lead on freshly precipitated calcium carbonate.

INTRODUCTION

Undoubtedly the most widely used spectrophotometric procedures for the determination of trace amounts of lead are those based upon reaction with dithizone [5, 68 to 73]. Although the formation of lead dithizonate provides one of the most sensitive methods for determining lead ($\mathcal{E}_{520 m\mu} = 65{,}000$)[89], the method suffers many disadvantages arising from non-selectivity, photodecomposition of the dithizone and insolubility of the complex in aqueous media.

In the present studies a search was, therefore, made for a more reliable method. From a preliminary investigation of a large number of possible metallochromic reagents for lead, 4-(2-pyridylazo)-resorcinol appeared to be the most suitable.

The use of 4-(2-pyridylazo)-resorcinol, (P.A.R.), as a possible analytical reagent for the photometric determination of lead has been described independently by Pollard and coworkers [79, 80, 81] and by Kristiansen and Langmyhr [82], but they disagree about the nature of the complex, and the method they described would not be directly applicable to solutions containing other metal ions in addition to the lead.

The present studies were, therefore, directed to resolving the disagreement and to extend the scope of the procedure by use of selective separations and masking agents to cover steel and other metal alloy analyses [148, 149].

EXPERIMENTAL

Apparatus

Spetrophotometer,	Beckman D.B. with 1-cm cuvettes.
pH Meter	E.I.L Vibron pH Meter, Model 39A.

Reagents

All the reagents were of analytical grade, except for the organic solvents which were of (G.P.) reagent grade. Distilled water from an all-glass still was used throughout.

Hydrochloric acid;	Sp.gr. 1.18 and 5 per cent ($^{v}/v$) in water.
Nitric acid:	Sp. gr. 1.42.
Ammonia Solution:	Sp. gr. 0.88
iso-Butyl Methyl Ketone;	
Calcium Chloride Solution;	5 per cent ($^{w}/_{v}$) aqueous.
Sodium Carbonate Solution;	10 per cent ($^{w}/_{v}$) aqueous.
Ammonium Thiocyanate Solution;	Aqueous saturated solution.

Potassium Iodide solution;	Aqueous saturated solution.
Potassium Cyanide solution;	10 per cent ($^{w}/_{v}$) aqueous.
10^{-3}M Lead Nitrate Solution;	Dissolve 0.3312 g of lead nitrate in water and dilute to 1 litre.
10^{-2}M P.A.R. Solution;	Dissolve 0.273g P.A.R. (mono sodium salt) in water and dilute to 100 ml.
Buffer Solution, (pH 10);	Dissolve 26 g of ammonium chloride in 900 ml water and add sufficient ammonia ($^{\underline{ca}}$85 ml) to obtain pH 10. Dilute to 1 litre.

RECOMMENDED PROCEDURE

1. Removal of Major Component

(a) Determination of Lead in Steel

Dissolve a suitable weight of sample (containing 10 to 200 μg of lead) in 10 ml of concentrated hydrochloric acid in a 100 - ml beaker, warming to assist solution, and oxidise the iron present to iron (III) by the dropwise addition of concentrated nitric acid. For steel samples containing greater than 0.04 per cent of lead, take 0.5 g of sample, dissolve according to the procedure, dilute to 100 ml with concentrated hydrochloric acid and take a suitable aliquot for further analysis. Transfer the solution to a 250 - ml separating funnel with the aid of a further 15 ml of concentrated hydrochloric acid. Add 25 ml of iso-amyl acetate and extract the bulk of iron (III) by shaking the funnel for 30 sec. Allow the phases to separate and run the lower (aqueous) phase into a second 250-ml separating funnel. Repeat the extraction with a further 25 ml of iso-amyl acetate and discard the organic extract. Run the aqueous phase into a 100 - ml beaker and evaporate the solution to dryness. Baking to a hard dryness should be avoided as this will cause low recoveries.

(b) Determination of Lead in Brass and Bronze Alloys

Dissolve a suitable weight of sample, (containing 10 to 200 μ g of lead), in a small quantity of concentrated nitric acid in a 100-ml beaker, warming to assist solution. Add 10 ml of 5 per cent calcium chloride solution and make ammoniacal with concentrated ammonia solution. Add 10 ml of 10 per cent sodium carbonate solution and stir well to obtain intimate mixing. Allow the solution to stand for 5 minutes and then filter through a small pulp pad. Alternatively, where large amounts of gelatinous precipitates are encountered, the use of a centrifuge is much more superior with respect to speed and ease of manipulation. Wash the precipitated carbonates with distilled water and discard the filtrate and washings. Redissolve the carbonates in 25 ml of 20 per cent ($^{v}/_{v}$) nitric acid and run the solution back into the original beaker. Make the solution ammoniacal (ca 10 ml of conc. ammonia solution), and add 1 ml of 10 per cent potassium cyanide solution. Reprecipitate the calcium and lead carbonates by adding 10 ml of 10 per cent sodium carbonate solution. Allow the solution to stand for 5 minutes and then filter on a small pulp pad and wash the residue thoroughly with water. Redissolve the residue in 25 ml of 20 per cent ($^{v}/_{v}$) nitric acid solution and run the solution back into the original beaker. Finally, evaporate the solution to dryness on a hot-plate.

2. Extractive Separation and Determination

After evaporation to dryness, redissolve the residue in 10 ml. of 5 per cent ($^{v}/_{v}$) hydrochloric acid and 1 ml of saturated thiocyanate solution. Transfer the solution to a 250-ml separating funnel with aid of a further 10 ml. of 5 per cent hydrochloric acid. Extract the solution with 20 ml of *iso*-butyl methyl ketone and run the aqueous phase into a second 250-ml separating funnel. From a pipette add 2.5 ml of saturated potassium iodide solution and 20 ml of *iso*-butyl methyl ketone. Shake the funnel for 1 minute to extract the lead. Discard the extracted aqueous phase and wash the organic phase with 10 ml of 5 per cent hydrochloric acid containing 1.25 ml of saturated potassium iodide solution; discard the washings. To the organic phase add 15 ml of pH 10 buffer solution and 1 ml of 10 per cent potassium cyanide solution. Shake the funnel to back-extract the lead into the aqueous phase. Pipette 1 ml of 10^{-2}M P.A.R. solution into the funnel and shake for 30 seconds to obtain intimate mixing. After phase separation run the lower aqueous phase into a 50-ml volumetric flask. Wash the remaining organic phase with 10 ml of water and add the washings to the volumetric flask. Dilute to the mark with distilled water and measure the absorbance of the solution in a 1-cm cuvette at 520 mμ against a reagent blank taken through the procedure.

A calibration curve should be prepared from 0.1 to 1.0 ml aliquots of standard 10^{-3}M lead nitrate solution taken through the procedure.

RESULTS AND DISCUSSION

The results obtained by application of the proposed procedure to the analysis of a variety of certificated British Chemical Standard (B.C.S.) steel and copper-base alloys are shown in Tables IV and V, respectively.

TABLE IV

Analysis of Lead in B.C.S. Certificated Steels

Sample No.	Lead Found Per cent	Average Per cent	Average Certificate Value Per cent	Range in Certificate Per cent
B.C.S. 326	0.013 0.014	0.013_5	0.014	0.012-0.017
327	0.012 0.011	0.011_5	0.010	0.009-0.012
328	0.015 0.016 0.014	0.015	0.015	0.012-0.018
329	0.048 0.049	0.048_5	0.05-	0.042-0.053
330	0.004 0.004	0.004	0.003	0.002-0.004
271	0.004 0.004	0.004	0.002_5	0.001_5-0.003
273*	0.004 0.004	0.004	0.003	-
275	0.005 0.006 0.007	0.006	0.005	0.003-0.006
277*	0.008 0.008 0.008	0.008	0.006_5	-

* Lead is a non-standardised element in these steels.

TABLE V

Analysis of Lead in B.C.S. Certificated Copper-Base Alloys

Sample No.	Lead Found Per cent	Average Per cent	Average Certificate Value Per cent	Range in Certificate Per cent
B.C.S. 179/1	0.208 0.216 0.188	0.206	0.19	0.17 -0.22
180/1	0.009 0.009	0.009	0.009	0.003-0.010
183/1	3.50 3.52	3.51	3.51	3.40 -3.63
207/1	0.073 0.069 0.070	0.071	0.079	0.073-0.084

The reproducibility of the method was verified by the repetitive analysis of steel sample No. B.C.S. 328. The data obtained showed that the method is capable of yielding results reproducible within ±0.001 per cent, absolute, Table VI.

TABLE VI

Repetitive Analysis of B.C.S. 328

Lead Found Per cent	Average Per cent	Average Certificate Value Per cent	Range in Certificate Per cent
0.015 0.016 0.015 0.016 0.014 0.015 0.014 0.016 0.015 0.016 0.016	0.015	0.015	0.012-0.018

It will be seen from the data in Tables IV, V and VI that the values obtained by the PAR procedure, with the exception of those for B.C.S. 271 and 207/1, are within the spread of results reported in the certificate. It is not possible to compare the results on B.C.S. 273 and 277 because lead in these samples was a non-standardised element, and was determined by a polarographic procedure following an extensive separation process.

Table VII shows the results obtained by application of the procedure to a number of commercial stainless and tungsten steels. It will be noted that slightly higher results than the reported values were found for the tungsten steels. Originally the high results were thought to be due to the presence of tungsten, but the results from the analysis of a synthetic mixture of iron, lead and tungsten showed no such interference.

TABLE VII

Analysis of some Commercial Steels*

No.	Type	Major Components Per cent	Lead Found Per cent	Average Per cent	Reported* Per cent
1.	Stainless Steel	Ni.Co.Mo.Ti. 18 8 5 0.5	0.007 0.007	0.007	0.008
2	"	Cr. NiMo 18 10 2.5	0.002_5 0.003	0.003	0.002_5
3.	"	Ni.Co.Mo.Ti. 18 8 5 0.5	0.010 0.011	0.010_5	0.012
4.	Sponge Iron	-	0.002 0.001	0.001_5	0.001
5.	Tungsten Steel	W 3	0.004 0.003	0.003_5	0.002
6.	"	W 18	0.004 0.004	0.004	0.002_5

*Samples and results supplied by B. Bagshawe.

DEVELOPMENT OF PROCEDURE

PRELIMINARY INVESTIGATIONS

Twenty-five possible metallochromic reagents for the determination of traces of lead were examined with regard to colour, pH and approximate sensitivity of reaction. Table VIII indicates the spectral characteristics of the free reagents and their lead complexes over the pH range 1 to 11.5. Where no colour change between reagent and complex were detected no values given.

From these reagents eight were chosen for closer examination, viz. Alizarin Complexan, P.A.R., Xylenol Orange, Solochrome Fast Violet, Bromopyrogallol Red, pyro-Catechol Violet, 1-(2 pyridylazo)-naphthol and methyl thymol blue. Each of these reagents and their lead complexes were examined for colour stability in the presence of six common complexing agents. Absorption spectra for each reagent and its lead complex were plotted and 4(2-pyridylazo)-resorcinol appeared to be the most suitable.

TABLE VIII

Preliminary Spectral Investigations

Reagent.	pH 1		pH 4.1		pH 5.8		pH 6.9		pH 10.7		pH 11.5	
	a	b	a	b	a	b	a	b	a	b	a	b
Acid Alizarin Black	•	•	•	•	Gy	V	B	V	•	•	•	•
Alizarin Complexan	y	O	y	O	R	V	R	V	•	•	•	•
Bromophenol Blue	•	•	•	•	•	•	•	•	•	•	•	•
Catechol Violet	•	•	•	•	y	Gn	y	T	V	B	•	•
Bromopyrogallol Red	•	•	R	V	R	V	R	V	P	V	•	•
Glycine Thymol Blue	•	•	•	•	y	Gy	y	V	•	•	•	•
Methyl Thymol Blue	•	•	O	V	O	V	Gn	B	•	•	•	•
Pattan Reader Indicator	•	•	•	•	•	•	•	•	•	•	P	B
Naphylazoxime	•	•	Pk	O	Pk	O	Pk	O	•	•	•	•
P.A.R.	•	•	y	R	y	R	y	R	O	R	•	•
Rhodiozonic Acid	y	R	y	R	O	R	O	P	•	•	•	•
Solochrome Black	•	•	•	•	B	P	B	P	•	•	•	•
Xylenol Orange	y	O	y	R	y	P	R	P	•	•	•	•
Sandox X	•	•	•	•	y	O	y	O	•	•	•	•
" II	•	•	•	•	O	P	O	P	•	•	•	•
" III	•	•	•	•	O	P	O	P	O	P	•	•
" IX	•	•	•	•	B	P	B	P	•	•	•	•

Contd/ overleaf.

Table VII Contd/..

Solochrome Fast Violet	.	.	.	.	P	R	P	R	y	P	y	P
Chrome Fast Grey	.	.	.	.	R	P	R	P	.	.	.	.
Omega Chrome Red	.	.	.	.	y	O	y	O	y	O	y	R
Chrome Fast Red	.	.	.	.	y	O	O	y	.	.	.	.
Pyrogallol Red	.	.	.	.	R	P	R	P	.	.	.	.
Diphenylcarbazone	.	.	.	.	y	Pk	y	R	y	R	.	.
Gallocyanine	.	.	.	.	B	P	B	P	.	.	.	.
1-(2-pyridylazo)naphthol	.	.	y	R	y	R	O	R	.	.	.	.

a = free reagent

y = yellow

O = orange

R = red

Pk= pink

P = purple

b = lead complex

V = violet

Gn = green

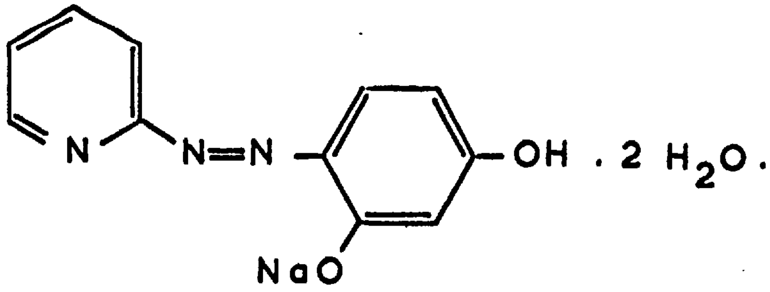
Gy = grey

T = turquoise

4-(2-Pyridylazo)-resorcinol

4-(2-Pyridylazo)-resorcinol is usually obtained as the mono sodium salt and contains two molecules of water.

Structure



The sample used in these studies was obtained from Hopkin Williams Limited, Chadwell Heath, England. Its purity was established from potentiometric titration and from organic elemental analysis, both of which showed the sample to be virtually 100 per cent pure.

Results from Organic Analysis

Element	Theoretical Value	Value Found
C	48.4 per cent	49.98
H	4.43 " "	4.18
N	15.4 " "	13.10
Na	8.4 " "	8.14

PRELIMINARY ABSORPTION SPECTA

Figure VI shows the absorption spectra for P.A.R. (curve a) and its lead complex (curve b). It will be seen that the absorbance of the reagent, ($\mathcal{E}_{max}$ = 412mμ), is very small at the wavelength of maximum absorption of its lead complex, ($\mathcal{E}_{max}$ = 520m μ).

Curve (a) was prepared by diluting 1 ml of a 10^{-2}M P.A.R. solution and 15 ml of buffer pH 10 solution to 50 ml and measuring the absorbance against distilled water in 1 cm cuvettes. Curve (b) was prepared by diluting 1 ml of a 10^{-2}M P.A.R. solution and 1 ml of a 10^{-3}M lead solution plus 15 ml of buffer pH 10 solution to 50 ml measured against distilled water in the same manner.

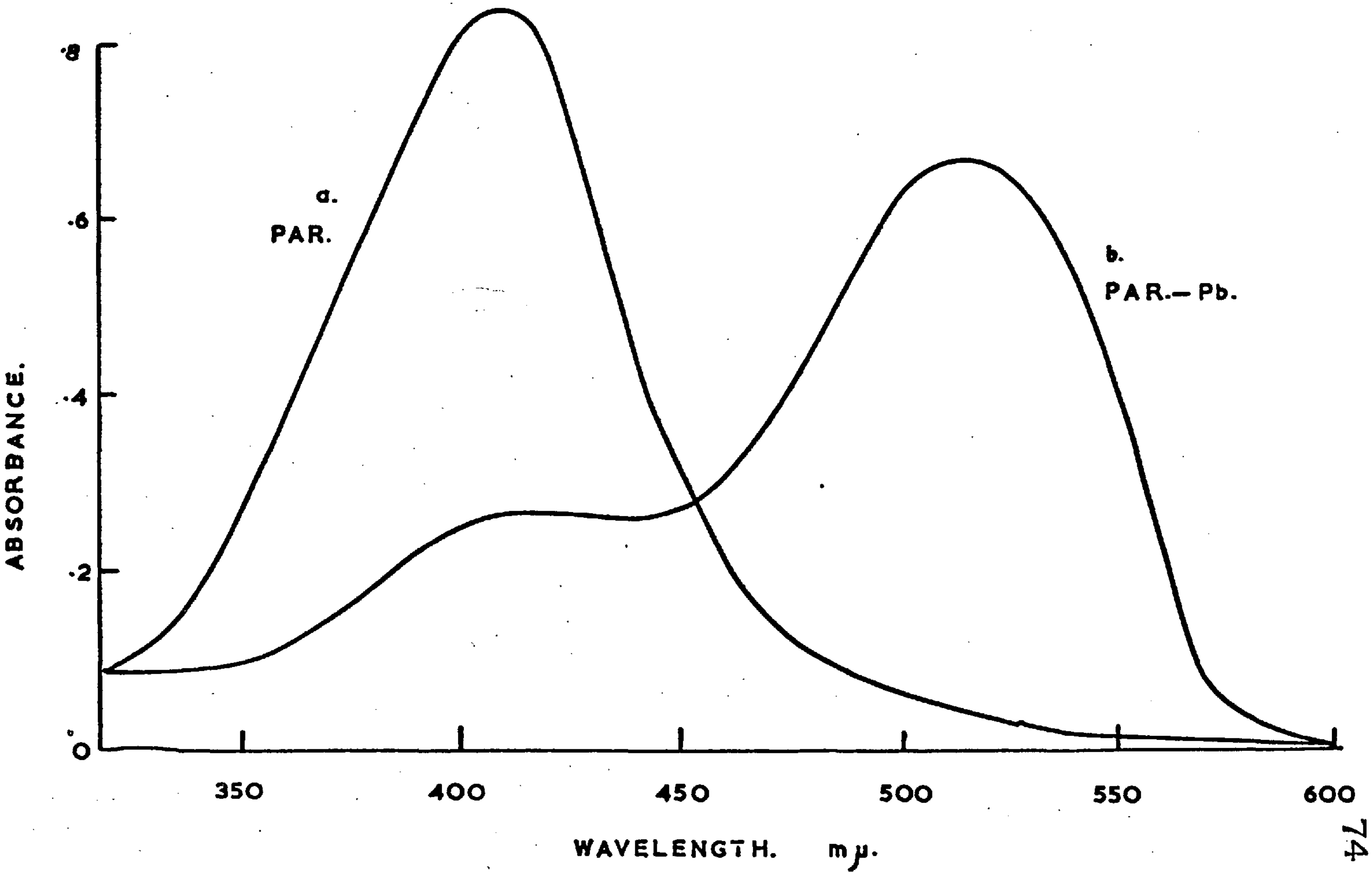
Subsequent measurements were, therefore, made at 520 mμ, the maximum wavelength of absorption of the lead-P.A.R. complex.

OPTIMISATION OF CONDITIONS FOR MAXIMUM SENSITIVITY

1. pH

Standard amounts of lead and P.A.R. solutions were buffered at varying pH values. The final pH of each solution was measured with a pH meter and the absorbance was subsequently measured at 520 mμ in 1-cm cuvettes. A plot of absorbance against pH, (Fig. VII), gave a maximum absorbance at pH 10.

FIG. VI



·8
·6
·4
·2
0
ABSORBANCE.
a.
PAR.
b.
PAR.— Pb.
350
400
450
500
550
600
WAVELENGTH. mμ.

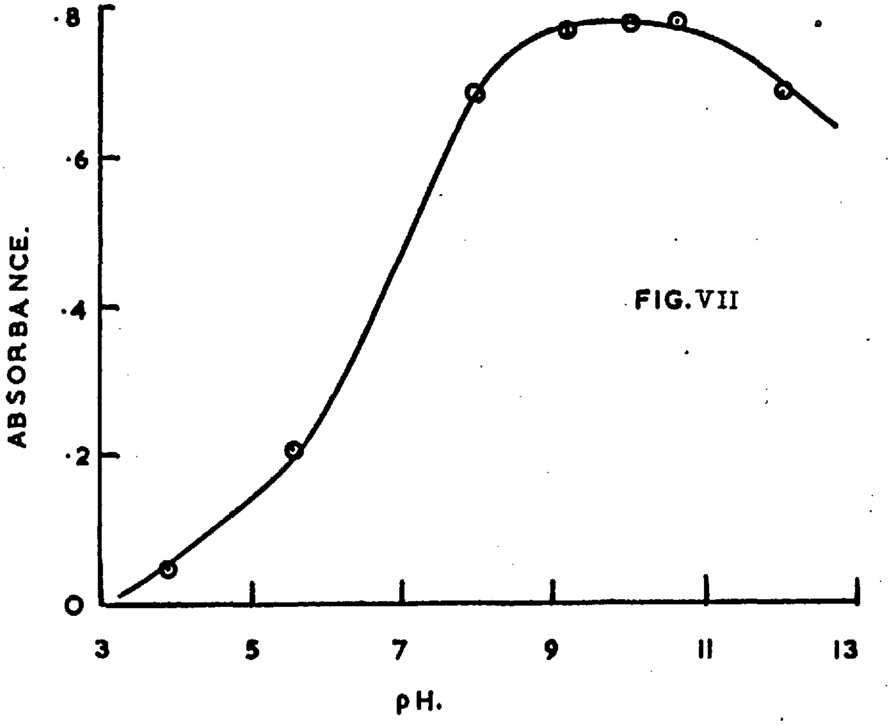


FIG. VII

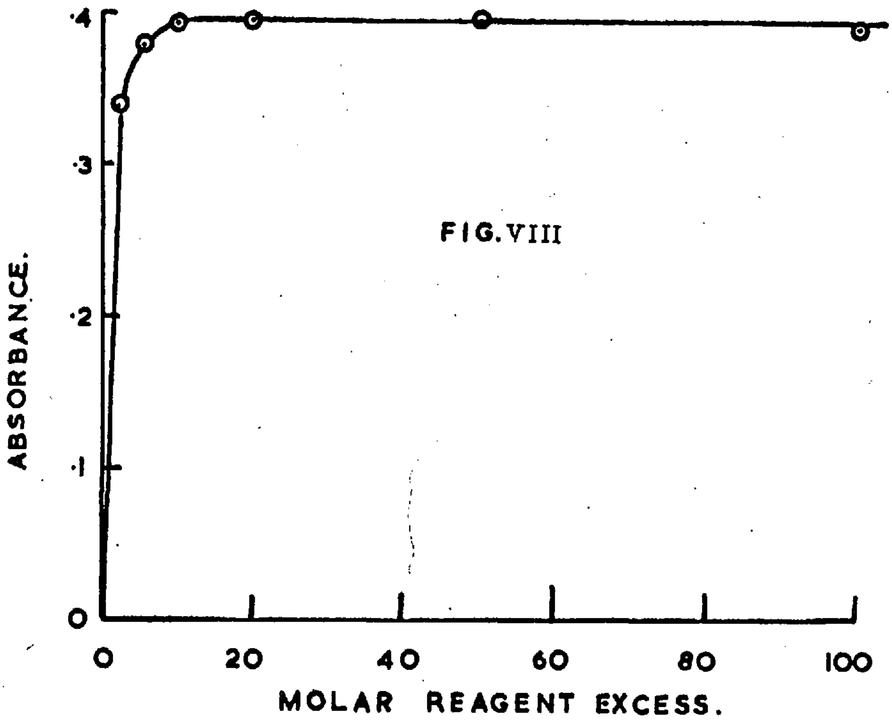


FIG. VIII

This is in agreement with the value given by Pollard, Hanson and Geary [79]. Subsequent determinations were, therefore, carried out at this pH.

2. Reagent Excess.

The absorbance of a series of solutions containing standard amounts of lead and a 2 to 100-fold molar excess of P.A.R. buffered at pH 10 were measured against the same excess of P.A.R. Maximum absorbance was obtained at about an eight-fold molar excess of P.A.R. with respect to lead and it remained constant up to *ca* 50-fold excess. Above this value a slight decrease in absorbance was observed. Figure VIII shows a reagent excess plot prepared from 0.5 ml of 10^{-3}M aliquots of lead plus 0.1 to 5.0 ml of 10^{-2}M. P.A.R. Each solution was buffered at pH 10 and diluted to 50 ml with distilled water.

3. Development Time.

The maximum colour of the P.A.R. lead complex was obtained immediately and was stable for at least 24 hours.

LAMBERT-BEER LAW CHECK

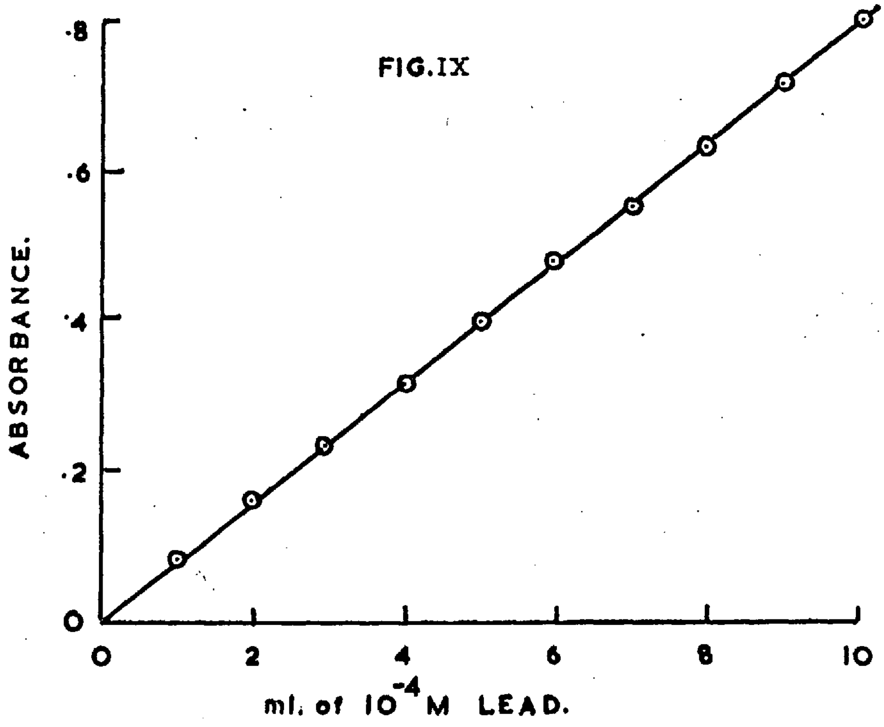
A calibration curve was prepared using the above optimum concentrations. Beer's law was obeyed between 10 and 207 μg of lead, and gave a molecular extinction coefficient for the complex of 40,000 at 520 mμ.

Figure IX shows a calibration curve prepared by using 1 to 10 ml of a 10^{-4}M lead solution plus 5 ml of a 10^{-3}M P.A.R. solution, buffered at pH 10 and diluted to 50 ml with distilled water. Each solution was measured in a 1-cm cuvette against a reagent blank at 520 mμ.

NATURE OF COMPLEX

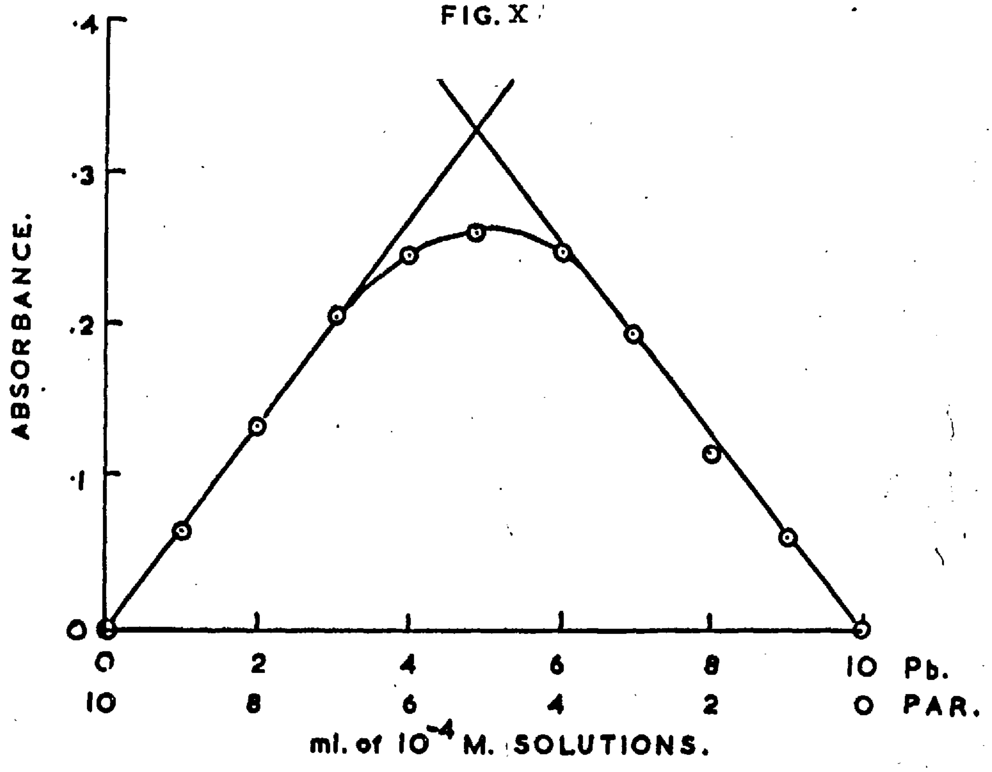
A Job continuous variation plot measured at three different wavelengths (500,520 and 540 mμ), exhibited clear indication only of a 1:1, P.A.R.:lead complex, no other species being detected. Figure X shows a continuous variation plot measured at 520 mμ. The curve was prepared from 0 to 10 ml of a 10^{-4}M lead solution to which was added 10 to 0 ml of a 10^{-4}M P.A.R. solution, so as to maintain a constant total molarity of lead and P.A.R. Each solution was buffered at pH 10 and diluted to 50 ml with distilled water. The absorbances were then measured against reagent blanks containing similar amounts of P.A.R.

FIG.IX



ABSORBANCE.
·8
·6
·4
·2
0
0
2
4
6
8
10
ml. of 10^{-4}M LEAD.

FIG. X



ABSORBANCE.
·4
·3
·2
·1
0
0
2
4
6
8
10 Pb.
10
8
6
4
2
0 PAR.
ml. of 10^{-4} M. SOLUTIONS.

Figure XI shows a Yoe and Jones [150] mole-ratio plot prepared from 1 ml aliquots of a 10^{-4}M lead solution to which were added 0 to 2 ml of a 10^{-4}M PAR. solution. A clear break in the curve is seen and a 1:1 complex is indicated. A Harvey - Manning [151] slope-ratio plot was also prepared and is shown in Fig. XII. Curve (a) was prepared from 1 ml aliquots of a 10^{-3}M lead solution plus 0.1 to 0.4 ml of a 10^{-3}M PAR. solution and curve (b) from 1 ml aliquots of a 10^{-3}M PAR. solution, plus 0.1 to 0.4 ml of a 10^{-3}M lead solution. Each solution was buffered to pH 10 and, after diluting to 50 ml with distilled water, it was measured against an appropriate reagent blank. A 1:1 ratio of PAR: lead is again observed.

Potentiometric titrations also confirmed a 1:1, PAR: lead complex. The results obtained from the potentiometric titration of PAR. plus various amounts of lead are shown in Fig. XIII. Curve (a) was prepared by diluting 5 ml of a 10^{-2}M PAR. solution

to 50 ml with water and titrating with N/10 sodium hydroxide. Curve (b) shows the titration of 5 ml of a 10^{-2}M lead solution which had been diluted to 50 ml with water. Curves (c), (d) and (e) were prepared from the titration of 5 ml aliquots of a 10^{-2}M solution of PAR. plus 5 ml, 2.5 ml and 10 ml of a 10^{-2}M lead solution respectively after dilution to 50 ml with distilled water. This value of 1:1 differs from the 2:1, PAR: lead reported by Pollard and coworkers [79 80 81], but is in agreement with that found by Kristiansen and Langmyhr [82].

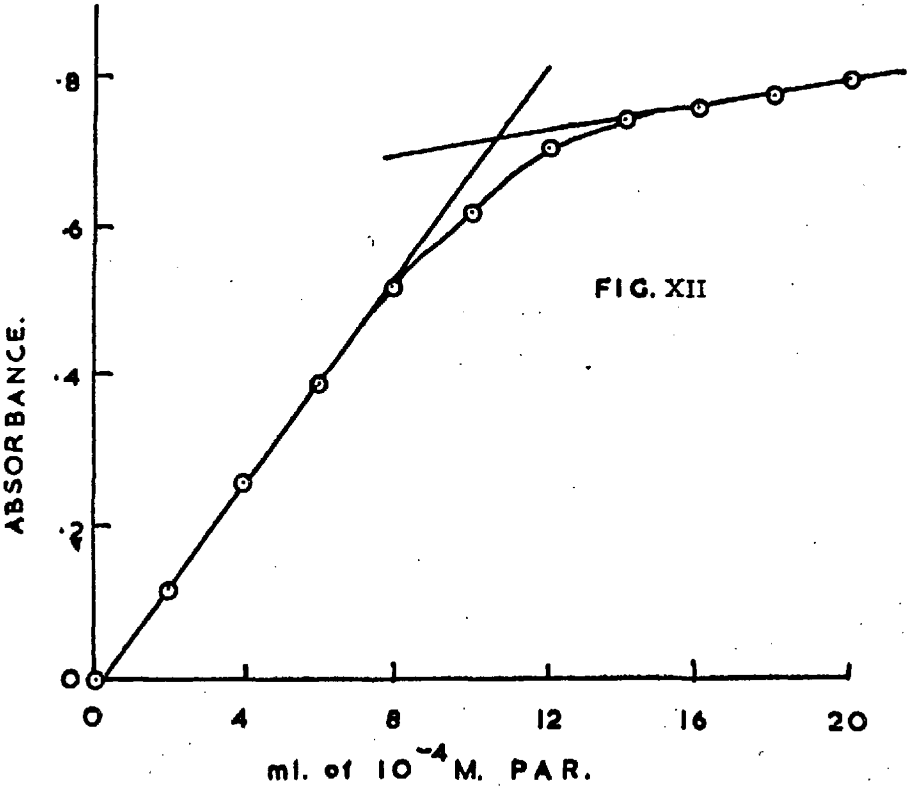


FIG. XII

FIG. XII

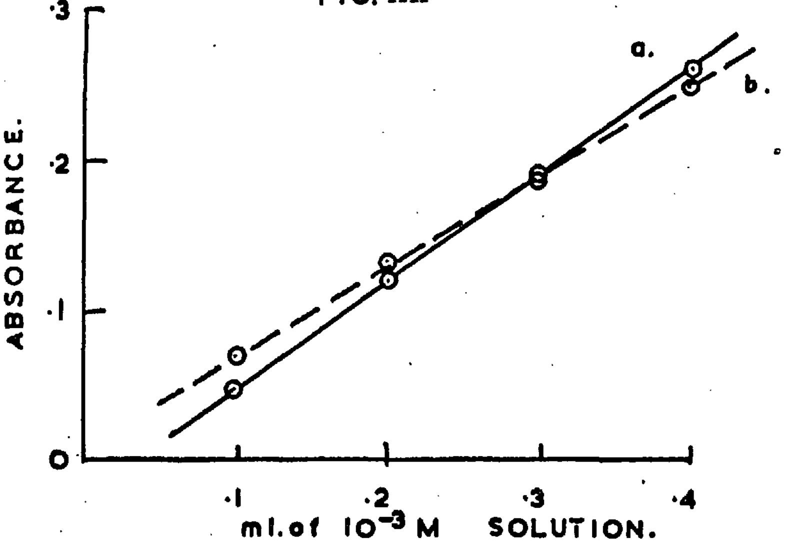
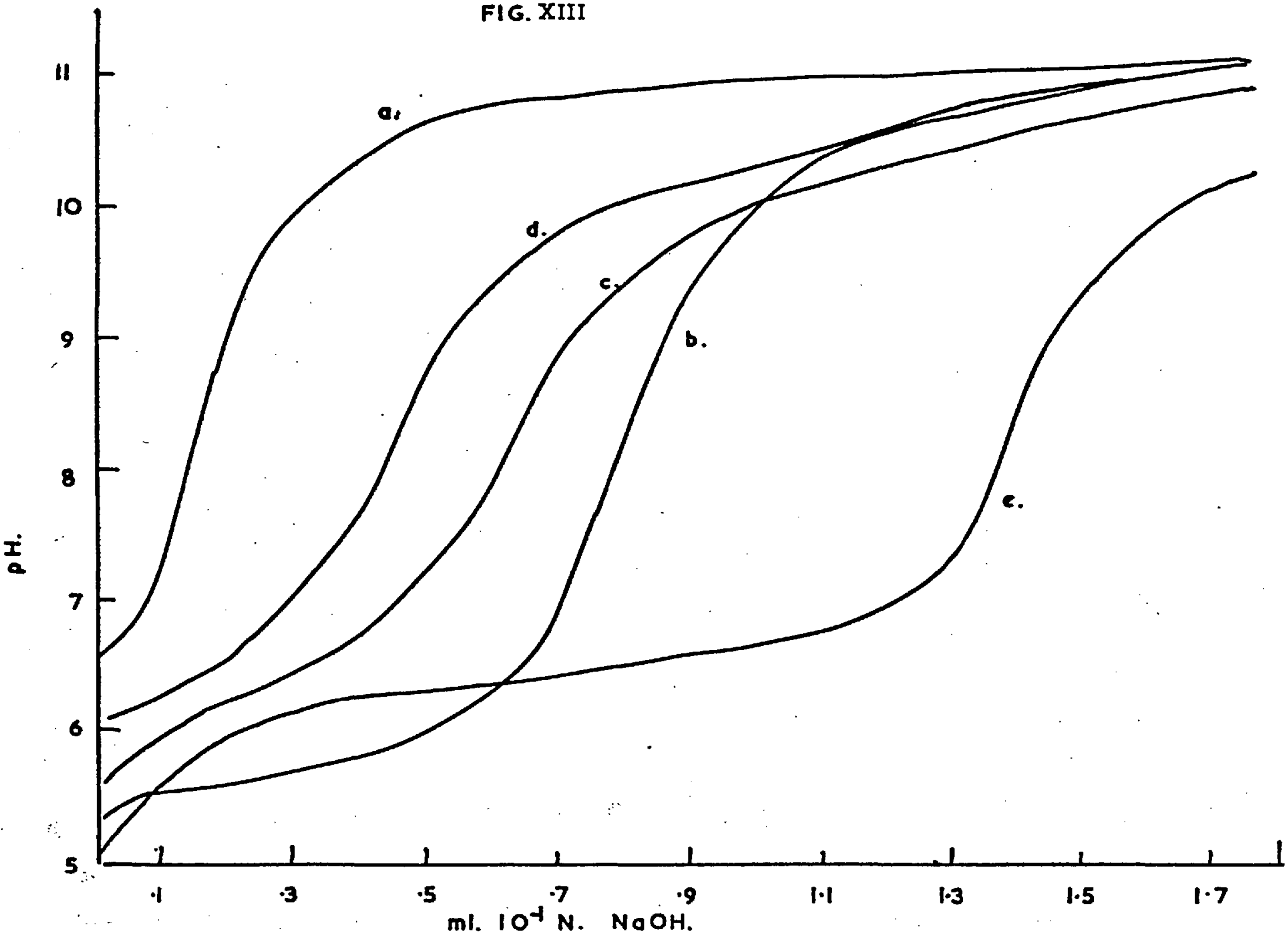


FIG. XIII



EFFECT OF FOREIGN IONS ON THE COLOUR SYSTEM

Most of the 25 common metal ions examined showed interference, of which only seven could be successfully masked with cyanide, viz. Ag, Cd, Co (II) Cu (II) Hg (II), Ni and Zn. A number of the interfering metal ions investigated gave high results, but a large number gave low results by coprecipitating lead on their hydroxides. Consequently, it is necessary to separate lead from most metal ions.

SEPARATION

The solvent extraction of lead iodide by _iso_-propyl methyl ketone from dilute hydrochloric acid has been described by West and Carlton [152]. It was therefore decided to utilise their recommended procedure. Extraction was made from 5 per cent hydrochloric acid solution as the complex lead iodide into _iso_-propyl methyl ketone. The extract was evaporated to dryness and the residue redissolved in a minimum of nitric acid. After buffering the solution to pH 10 the PAR. complex was developed. Poor recoveries and high blank values were obtained and thought to stem from the presence of, or impurities in, the _iso_-propyl ketone. Subsitution of _iso_-butyl methyl ketone was investigated and found to give more promising results.

Optimum conditions for extraction of the lead iodide into this solvent were then established.

1. OPTIMUM ACID CONCENTRATION

To a series of separating funnels each containing 0.5 ml of a 10^{-3}M lead solution were added 10 ml of distilled water and 5 ml of saturated potassium iodide solution. 1 to 10 ml of concentrated hydrochloric acid were then added, and each solution dilluted to 25 ml with distilled water. The solutions were then extracted with 10 ml amounts of *iso*-butyl methyl ketone by shaking the funnel for about one minute. The separated organic phases were then stripped of their lead by equilibration with an ammoniacal aqueous solution buffered at pH 10. The P.A.R. lead complex was then developed and the absorbance of each solution was measured against its own reagent blank.

A graph of percentage recovery against acid concentration showed a maximum at 5 per cent hydrochloric acid, (Fig XIV). This value was therefore, used in subsequent extractions.

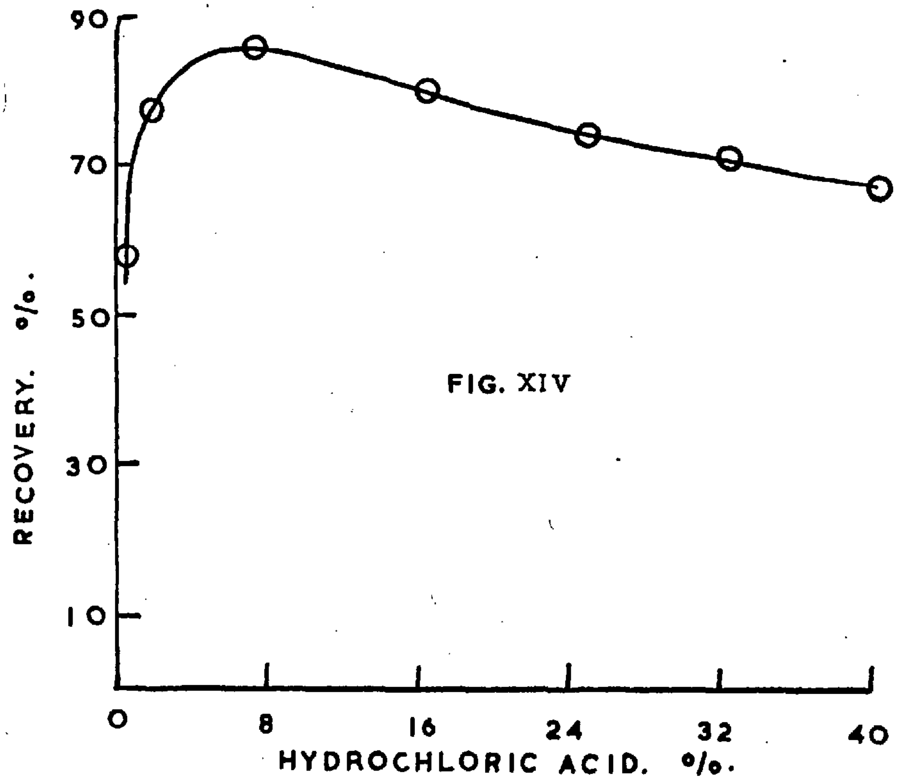


FIG. XIV

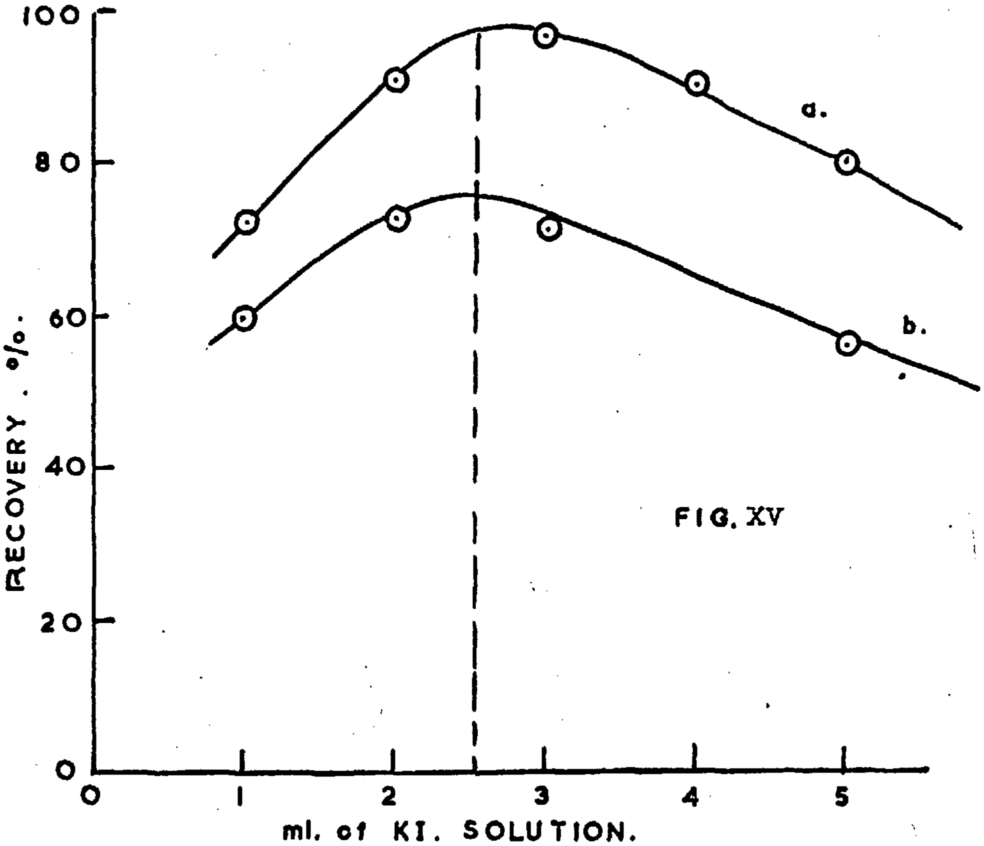


FIG. XV

2. OPTIMUM IODIDE CONCENTRATION

Lead iodide was then extracted from 5 per cent hydrochloric acid in the presence of varying amounts of iodide. Maximum extraction was obtained from 25 ml of solution containing 7 per cent ($^{w}/_{v}$) of potassium iodide, i.e. 2.5 ml saturated potassium iodide solution diluted to 25 ml.

According to West and Carlton [152] a number of metal ions are wholly or partially extracted with lead as their iodides, but all except cadmium and ruthenium may be removed from a 5 per cent hydrochloric acid solution as their thiocyanates by a prior extraction with *iso*-propyl methyl ketone or *iso*-butyl methyl ketone. When this preliminary separation was used in these studies, a successful separation of lead from the interfering ions was obtained, but low results were encountered. It was thought that excess thiocyanate remaining in the aqueous solution might affect the optinum iodide concentration, but experiments showed that it did not. Figure XV shows the recovery of lead after extraction as the iodide, curve (a), and following both a preliminary thiocyanate extraction and an iodide extraction, curve (b).

It was, therefore, concluded that if a preliminary thiocyanate extraction for the removal of interferences was to be employed, a 20 per cent loss of lead would have to be tolerated at this stage.

West and Carlton [152] did not observe this loss following a thiocyanate extraction, but such a loss was consistently and reproducibly observed during these investigations. The loss in presumably due to the extraction of lead thiocyanate, which is known to be insoluble in more concentrated media.

The possibility of back-extraction into a pH 10 ammoniacal buffer solution was investigated and satisfactory results were obtained. Thus, the need for evaporation of the organic extracts to dryness was eliminated. Potassium cyanide was added to the back extracted solution to mask any cadmium which might pass through the procedure together with the lead. Standard P.A.R. solution was finally added and the absorbance of the P.A.R lead complex measured at 520 mμ.

APPLICATION TO STEEL ANALYSIS

With the above separation and spectrophotometric determination techniques attempts were made to analyse synthetic iron-lead mixtures. It soon became apparent that the presence of large amounts of iron caused low and variable recoveries of lead. It was, therefore, necessary to separate the traces of lead from the bulk of ferric ion.

During the development of the spectrophotometric determination of aluminium in steels, use was made of the iso-amyl acetate extraction of hydrogen tetrachloroferrite. It was decided to utilise this same extraction procedure for isolating lead from the bulk of iron in steel samples. For the complete extraction of iron (III) into iso-amyl acetate a concentrated hydrochloric acid medium containing the sample is required. As only a 5 per cent final concentration of hydrochloric acid is required for the thiocyanate and iodide extractions, a considerable dilution would be required thereby resulting in a large and unmanageable volume. Preliminary attempts were made to neutralise part of the excess acid, but low recoveries of the lead were always obtained, presumably because of increased electrolyte strength.

Attempts were, therefore, made to remove the excess acid by evaporation. After the removal of iron (III) by solvent extraction, the remaining aqueous acid phase was evaporated to dryness. The residue was redissolved in 5 per cent ($^{v}/_{v}$) hydrochloric acid and thiocyanate and iodide extractions made. Satisfactory recoveries of lead were obtained. A calibration curve was then prepared from synthetic mixtures containing 0.5 g of electrolytic iron powder and 0.1 to 1.0 ml of a 10^{-3}M lead solution.

Preliminary attempts to analyse steel samples met with only partial success. Slightly high results were sometimes encountered which were eventually shown to be caused by interference from manganese remaining in the small quantity of aqueous solution adhering to the funnel walls. This interference was easily overcome by washing the ketone extract with an aqueous solution containing 5 per cent hydrochloric acid and 7 per cent iodide.

The separation and spectrophotometric procedures described were then successfully applied to a large number of steel samples.

APPLICATION TO THE ANALYSIS OF COPPER-BASE ALLOYS

Attention was next turned to the possible extension of the scope of the procedure to include the analyses of brass and bronze alloys.

Again it was shown necessary to separate the lead from the bulk of the major component.

Initial attempts were directed to the use of solvent extraction with diethybdithiocarbamate into carbon tetrachloride. After extraction of the lead into the carbon tetrachloride the organic extract was evaporated to dryness and the complex destroyed with hot concentrated nitric acid. The residue was then redissolved in a minimum of concentrated nitric acid and buffered to pH 10. After the addition of cyanide the

P.A.R - lead complex was developed. Erratic results were always obtained and attention was, therefore, turned to an alternative means of separation.

It was decided to utilise the carbonate coprecipitation technique for the separation of lead from the copper base alloy. As copper carbonate would precipitate in acid and neutral solutions, separations can only be obtained in ammoniacal solution in which the copper is complexed as the soluble cuprammonium ion. Small amounts of lead carbonate are partially soluble in ammoniacal solution and it is therefore necessary to use a coprecipitant such as calcium carbonate.

In this way, lead can be successfully separated from copper, nickel etc., but it will still require separation from coprecipitated carbonates such as aluminium, chromium (III), iron (III), manganese, tin (IV) and zinc. It has been shown that it is possible to isolate the insoluble carbonates from an ammoniacal solution of a copper-base alloy and to then isolate the lead from coprecipitated elements by utilising the thiocyanate and iodide extractions into iso-butyl methyl ketone.

A number of copper-base alloys were successfully analysed for lead using this procedure.

PART II DIPHENYLCARBAZONE AS A SPECTROPHOTOMETRIC REAGENT FOR LEAD

INTRODUCTION

Diphenylcarbazide and diphenylcarbazone react with many heavy metals such as cadmium, copper, lead and mercury to yield chelate complexes having blue, violet or red colours [5]. The products can be extracted into benzene, chloroform and other solvents. It appears that the reaction of diphenylcarbazide first involves oxidation to diphenylcarbazone. It is this latter compound which is the active species in the reaction with the metals mentioned above.

In 1939 Evans [66] noted that the addition of an acetone solution of diphenylcarbazide to a lead nitrate solution, containing pyridine, produced a pink colour. On standing a dark red solution was produced and after 20 hours a stable colour was obtained which was proportional to the lead concentration. Evans noted that his stock solutions of diphenylcarbazide, prepared in ethanol or acetone, darkened on standing. This was suspected to be due to the production of diphenylcarbazone as a result of atomospheric oxidation. It was also observed that freshley prepared solutions of diphenylcarbazide required long development times of the lead complex. Solutions, could be aged by the addition of dilute bromine water or peroxide again indicating that there is a preliminary need for oxidation to the diphenylcarbazone.

Vasserman and Supronovitsch [78] observed that many metal-diphenylcarbazone complexes were precipitated from aqueous solution and could be extracted into organic solvents. These workers were able to determine lead, mercury and zinc gravimetrically with diphenylcarbazone but they found that a colorimetric determination gave untrustworthy results.

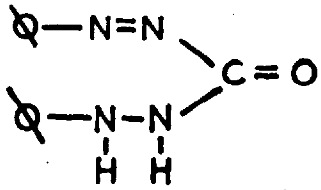
In the present work an investigation into the spetrophotometric determination of lead with diphenylcarbazone was undertaken.

The reaction was found to be sensitive, $\epsilon_{520m\mu} \stackrel{\frown}{=}$ 80,000, but evaluation of an exact extinction coefficient was not possible because of a continual fading in colour. This fading was shown to result from atomospheric oxidation of the diphenylcarbazone. Attemps to prevent such oxidation were only partially successful. The instability of the system has shown that, despite the fact that diphenylcarbazone is a sensitive reagent for lead, its use as an analytical spectrophotometric reagent would not be practicable.

EXPERIMENTAL

REAGENTS

Diphenylcarbazone:-



$\phi = C_6H_5$

A sample of pure reagent was prepared by recrystallising a commercial sample (B.D.H. Ltd., Poole, England), from an aqueous - ethanol solution. The orange needles obtained melted at 152-4 °C which agrees with values reported in the literature [153].

10^{-2}M solutions of diphenylcarbazone were preprared by dissolving 0.240g in 100 ml of a variety of organic solvents including chloroform and xylene. 10^{-3}M solutions were prepared by appropriate dilution.

Ammonia solution,	Sp.gr. 0.88
Potassium Cyanide solution,	10 per cent ($^w/_v$) aqueous
10^{-3}M Lead solution,	Dissolve 0.3312 g. of lead nitrate in water and dilute to 1 litre. 10^{-4}M solutions were prepared by appropriate dilution.

APPARATUS.

Spectrophotometer,	Beckman D.B. with 1 - cm cuvettes.
pH meter	E.I.L., Vibron (Model 39A).

PRELIMINARY SPECTRA

The absorption spectra of diphenylcarbazone and its lead complex were prepared by shaking 10 ml of a pH 10.5 buffer solution and 10 ml of buffer plus 0.5 ml of a 10^{-4}M lead solution with 10 ml aliquots of a 10^{-2}M xylene-diphenylcarbazone solution. The absorption spectrum of each solution was measured in 1-cm cuvettes against pure xylene.

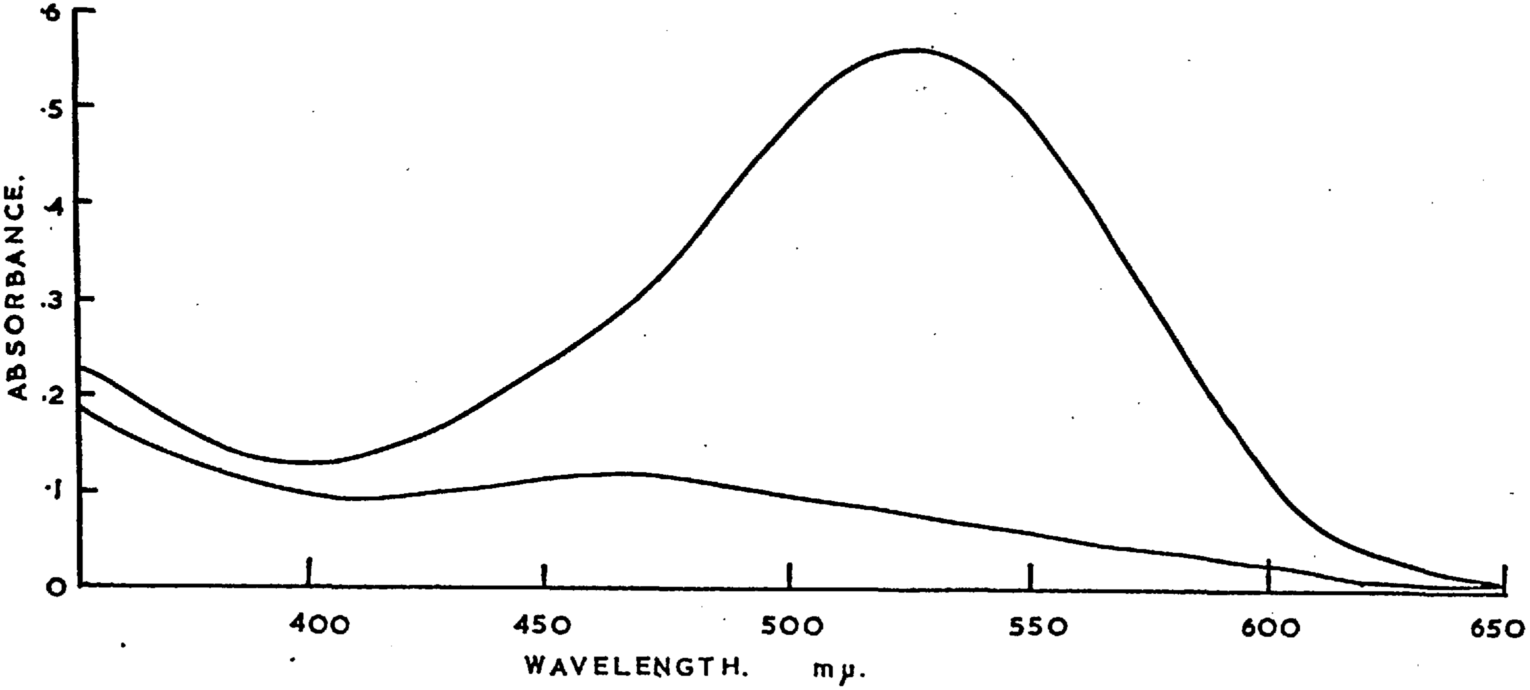
Maximum absorption of the complex was found to occur at 520 $m\mu$, (Fig XVI). This wavelength was therefore, used in subsequent measurements.

OPTIMISATION OF CONDITIONS FOR COLOUR DEVELOPMENT

pH

To a series of separating funnels were added 10 ml of buffer solution ranging from pH 7 to 13, each pH having been accurately determined with pH meter. To each funnel was added

FIG. XVI



0.2 ml of a 10^{-3}M lead solution and the solutions extracted with 10 ml of a 10^{-3}M diphenylcarbazone solution in xylene. A maximum absorption at pH 10.5 was observed, Fig XVII.

ORGANIC SOLVENT

An examination of ten common organic solvents was undertaken, viz: chloroform, carbon tetrachloride, benzene, toluene, xylene, iso-amyl acetate, ether, tert-butyl phosphate, iso-butyl methyl ketone and ethyl acetate.

To about 20 ml of each solvent in 100 - ml beakers were added 0.012 g amounts of diphenylcarbazone. The mixtures were heated over a steam-bath to obtain complete dissolution. The solutions were then diluted to 50 ml with pure solvents to give concentrations of 2.10^{-3}M diphenylcarbazone.

The absorbance of each solution was measured in 1 - cm cuvettes against solvent blanks.

Those solvents not containing oxygen produced purple or red-coloured solutions, while those containing oxygen produced yellow solutions. The difference in colour may be due to the existence of two forms of diphenylcarbazone, i.e. the keto or enol forms.

A series of solutions containing 10 ml of pH 10.5 buffer solution or buffer solution plus 0.5 ml of 10^{-4} lead

FIG. XVII

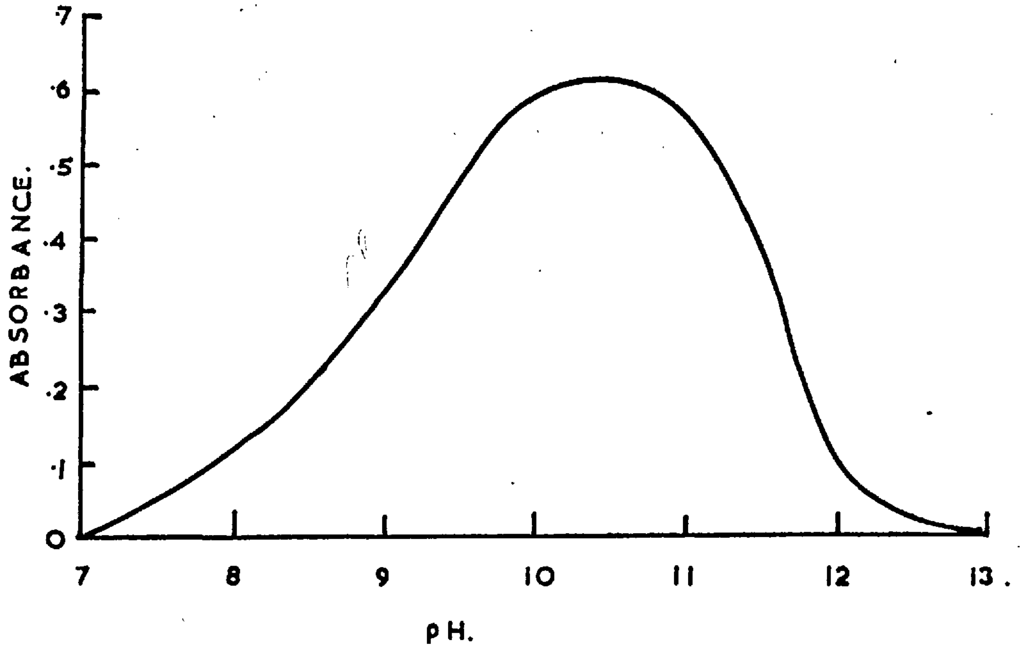
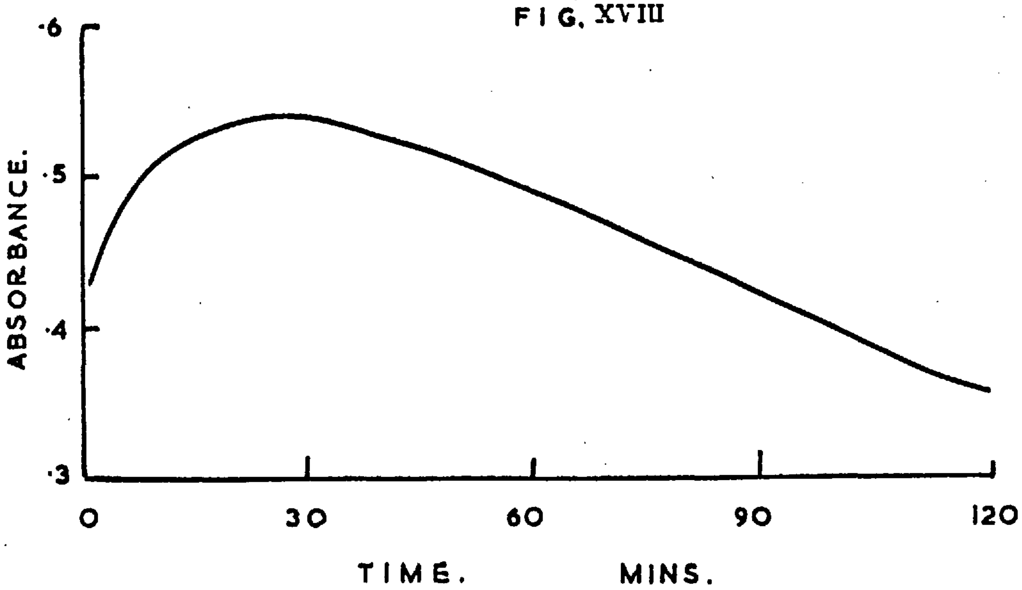


FIG. XVIII



solution were equilibrated with 10 ml aliquots of each solvent-dye solution. The absorbances of the organic extracts were measured immediately against reagent blank solutions.

From these results, and measurements made on the same solutions after a few minutes, carbon tetrachloride, amyl acetate, ether, tert-butyl phosphate and iso-butyl methyl ketone were found to give unstable systems. In addition diphenylcarbazone dissolves in carbon tetrachloride and ether only with difficulty. Benzene, toluene and xylene gave the highest absorbances for the lead complex, and of these xylene produced the lowest blank value. This latter solvent was, therefore, chosen for further studies.

STABILITY MEASUREMENTS.

10 ml of a pH 10.5 buffer solution plus 0.2 ml of a 10^{-3}M lead solution were extracted into 10 ml of a 10^{-2}M diphenylcarbazone-xylene solution. The absorbance of the solution was measured immediately against a reagent blank at 520 mμ , and again over the following two hours.

An initial increase in absorbance was followed by a steady decrease. The graph of absorbance plotted against time is shown in Fig. XVIII, however, because of the non-reproducibility of the system, no great significance should be associated with this graph. It was also noted that, at times, streaky bands of colour developed in the cuvettes as measurements were being made, thereby giving erroneous results. It was found with an unstoppered cuvette that the fading of the solution became more apparent, thus indicating that atmospheric oxidation of the system was taking place.

The possibility of de-oxygenating all solutions used, by bubbling nitrogen through them was investigated, but it produced no great benefit, although more promising results were obtained.

The addition of sodium sulphite to the aqueous phase in order to remove remaining oxygen after degassing was investigated next, but unstable and unreproducible results were again obtained.

The addition of other reducing agents to the aqueous phase was also investigated. Neither ascorbic acid nor hydroxylamine hydrochloride completely solved the problem, but with addition of hydroxylamine less fading was observed.

The extraction of lead with xylene solution of freshly recrystallised diphenylcarbazone from an aqueous buffered solution containing hydroxylamine and potassium cyanide, after degassing with nitrogen, gave quite promising results.

A Lambert-Beer law check was therefore made and a straight line graph obtained between 0.2 to 0.8 ml of 10^{-4}M lead solution in 10 ml final xylene solution, giving a molecular extinction coefficient of $\underline{c^{a}}$ 72,000 at 530 mμ .

Attempts to reproduce the calibration curve, however, met with failure. Although a straight line graph was obtained the slope of the graph was not in agreement with the previous attempt.

The replacement of ammonia solution with pyridine for obtaining a pH of 10.5 was investigated. Together with hydroxylamine, potassium cyanide and the degassing process a calibration curve was prepared over the same concentration range of lead. A molecular extinction coefficient of 87,000 was given under these conditions, however, attempts to reproduce the curve consequently met with failure.

It was thought that, in the process of degassing with nitrogen, some of the ammonia or pyridine may be lost thereby giving a variable concentration. This could have affected the pH of the solution and so produce the variance in results. A check on the pH was therefore made after degassing and it was found to be as expected, no loss of ammonia or pyridine being observed.

It was therefore concluded that despite the fact that diphenylcarbazone is a sensitive reagent for lead its application in spectrophotometric analyses would be impracticable because of the marked instability of its lead complex.

CHAPTER III

THE DETERMINATION OF TRACE AMOUNTS OF LEAD IN STEELS, BRASS AND BRONZE ALLOYS BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

SUMMARY

Lead is determined in steels, brass and bronze alloys down to 0.001 per cent by atomic-absorption spectrophotometry.

Ferrous alloys are dissolved in concentrated hydrochloric acid and the bulk of iron removed by extraction into iso-amyl acetate. The aqueous solution is evaporated to dryness and the lead extracted into iso-butyl methyl ketone as its complex iodide. The organic extract is sprayed directly into an air-acetylene flame and the absorbance due to the lead is measured at 2833 Å.

Copper-base alloys are analysed by dissolution in nitric acid after which the lead is coprecipitated on calcium carbonate from an ammoniacal solution. The precipitate is redissolved in acid, evaporated to dryness and then extracted as the iodide and determined as before.

The procedure is precise, easy to operate and very rapid in comparison to spectrophotometric methods.

INTRODUCTION

Atomic-absorption spectrophotometry provides a simple, sensitive and rapid technique for the determination of trace amounts of lead. Because of its freedom from inter-elemental interference, it appeared logical to apply the technique directly to the determination of trace amounts of lead in steels and copper-base alloys.

The application of atomic-absorption spectrophotometry, to the determination of lead in metallurgical samples in the range 0.08 to 3.2 per cent, has been described by Elwell and Gidley [104], and also by Gidley [105] and Stumpf [106]. Applications of this technique have been reported for the determination of trace amounts of lead in petroleum spirit [107 108] and in urine[108 110].

The direct spraying of aqueous acid solutions of metal alloys frequently leads to difficulties such as corrosive attack upon the burner head, and subsequent introduction of metal ions into the flame. Neutralisation of the acid, on the other hand, may lead to clogging of the burner head because of the resulting high electrolyte concentration, and can reduce the efficiency of spraying by increase in viscosity.

As a result of this it appeared that it would be better to extract and concentrate the traces of lead into an organic solvent and spray it directly into the flame. This would have added advantage resulting from a higher input ratio through the aspirator-type of spray used in this work. This factor has been discussed recently by Dagnall and West [155] in relation to the determination of silver following its extraction from aqueous solution into organic solvents.

EXPERIMENTAL

APPARATUS

Absorbance measurements were made with an SP.900A atomic-absorption/flame-emmission spectrophotometer fitted with a lead hollow-cathode lamp, Unicam Cat. No. 103898 (Unicam Instruments Limited, Cambridge, England), and equipped with a 0-10 mV Honeywell-Brown recorder.

The burner head consisted of a stainless steel construction in which the gases were ignited through a line of 1 mm holes giving a resultant flame about 7 cm long and 0.3 mm wide.

Air was supplied from a rotary compressor (Newman Industries Limited, Bristol, England), via a regulator (Hymatic Eng. Co. Ltd., Worcester, England). Acetylene gas was obtained from a cylinder (British Oxygen Co.Ltd., London, England.)

REAGENTS

10^{-3}M Lead Nitrate solution,	0.3312 g $Pb(NO_3)_2$ dissolved in water and diluted to 1 litre.
Calcium Chloride solution,	5 per cent $(^{w}/_{v})$ $CaCl_2$ in distilled water.
Sodium Carbonate solution,	10 per cent $(^{w}/_{v})$ Na_2CO_3 in distilled water.
Potassium Iodide solution,	saturated solution of KI in distilled water.

All reagents were of analytical grade.

RECOMMENDED PROCEDURE

1. Removal of Major Component

(a) Determination of lead in steels:

Dissolve a suitable weight of sample (containing 10 to 300 μg of lead) in 10 ml of concentrated hydrochloric acid (AnalaR) in a 100 - ml beaker, warming to assist solution. Oxidise the iron present to Fe (III) by the dropwise addition of concentrated nitric acid (AnalaR). For steel samples containing greater than 0.08 per cent of lead, take a 0.5 g.

sample, dissolve according to the procedure and dilute to 100 ml with concentrated hyrochloric acid. A suitable aliquot may then be taken through the procedure. Transfer the solution to a 250 ml separating funnel with the aid of a further 15 ml of concentrated hydrochloric acid. Add 25 ml of iso-amyl acetate and extract the bulk of the ferric iron by shaking the funnel for 30 seconds. Allow the phases to separate and run the lower aqueous phase into a second separating funnel. Repeat the extraction with a further 25 - ml of iso - amyl acetate. Run the aqueous solution back into the 100 ml beaker and evaporate to dryness. Baking to a hard dryness should be avoided as this will cause low recoveries. The purpose of this separation is merely to remove excess acid and hence to facilitate the control of acidity subsequently for the H_2PbI_4 extraction.

(b) Determination of lead in Copper-base alloys:

Dissolve a suitable weight of sample (containing 10 to 300 μ g) in a small volume of concentrated nitric acid (AnalaR) in a 100 - ml beaker, warming to assist solution. For samples containing greater than 0.08 per cent, dissolve 0.5 g of sample in nitric acid and dilute to 100 ml with water. A suitable aliquot may then be taken.

To the solution add 10 ml of 5 per cent calcium chloride solution, make ammoniacal and add 10 ml of 10 per cent sodium carbonate solution. Stir well to obtain intimate mixing and allow the solution to stand for 5 minutes. Centrifuge the solution to collect the precipitate. Wash the precipitate thoroughly with water and redissolve it in a small quantity of nitric acid, transferring the solution back to the original beaker. Evaporate the solution to dryness observing the precautions mentioned above.

The presence of small amounts of copper ion in the calcium carbonate does not interfere with the method.

2. Extraction and Determination

After evaporating the solution to dryness, redissolve the residue in 10 ml of 5 per cent ($^{v}/_{v}$) hydrochloric acid. Samples containing appreciable amounts of titanium or tungsten however, cannot be redissolved at this stage. When these are present, subsequent extraction is made from a suspension of the residue in 5 per cent hydrochloric acid. The presence of sedimented material does not appear to affect lead recoveries.

Transfer the solution, with the aid of a further 15 ml of 5 per cent hydrochloric acid, to a 250 - ml separating funnel and add 2.5 ml of freshly prepared saturated potassium iodide solution. Pipette 20 ml of methyl *iso*-butyl ketone into the funnel and shake it for 30 seconds to extract the lead. Discard the lower aqueous phase.

The organic extract may now be passed directly into the atomic-absorption spectrophotometer using the instrumental settings and flame conditions summerised below.

The amount of lead present is determined by comparison with a calibration curve prepared by taking synthetic standard iron-lead mixtures or copper-lead mixtures (0.2 to 1.6 ml 10^{-3}M lead) through the procedure, Fig XIX. The appropriate standard solution should be taken through the procedure with each series of determinations to correct for any slight variation in instrumental response.

The following instrument settings and flame conditions were used on the SP.900A spectrophotometer:-

Analysing Slit width, = 0.20 mm.
Wavelength, = 2833 Å.
Lamp Current, = 6 mA.
Air Pressure, = 15 p.s.i.
Acetylene Pressure, The acetylene pressure was controlled such that a translucent flame just below the level of luminosity was obtained.

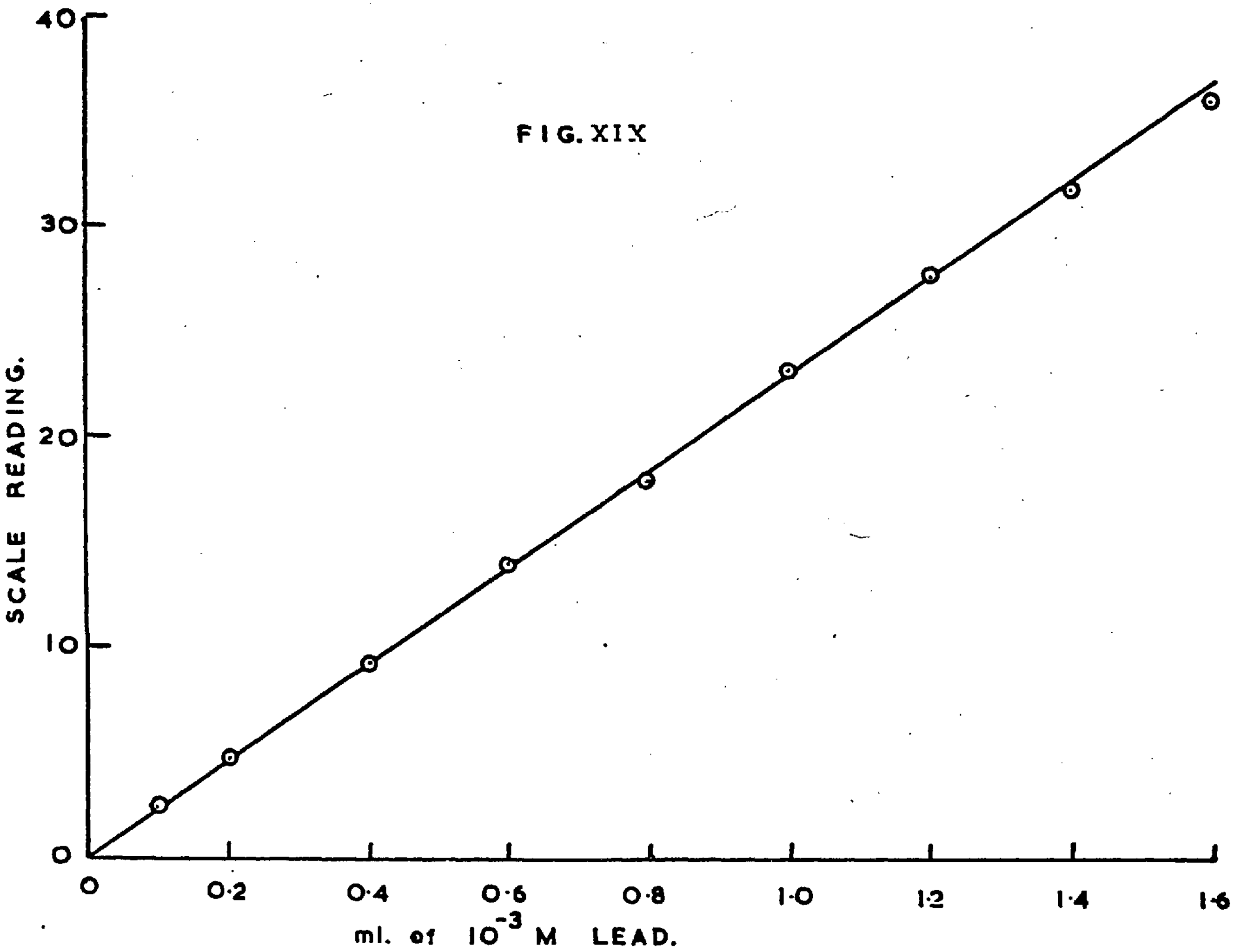


FIG. XIX

40
30
20
10
0
SCALE READING.
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
ml. of 10^{-3} M LEAD.

Light Path, The absorbance measurements were made low down in the flame just above the blue luminous cones of the flame.

RESULTS

The results obtained by application of the proposed procedure to the determination of lead in a variety of British Chemical Standard Certificated steel and copper-base alloys are shown in Tables IX and X.

TABLE IX

ANALYSIS OF LEAD IN B.C.S. CERTIFICATED STEELS

Sample No.	Type of Sample	Per cent Found	Average Per cent	Certificate value	Spread in Certificate
BCS 326	Mild steel	0.014_5 0.014_5 0.014	0.014	0.014	0.012-0.017
BCS 327	"	0.012 0.011_5	0.012	0.010	0.009-0.012
BCS 328	"	0.016_5 0.016 0.015_5	0.016	0.015	0.012-0.018
BCS 329	"	0.052 0.051 0.051	0.051	0.05-	0.042-0.053
BCS 330	"	0.004 0.004	0.004	0.003	0.002-0.004
BCS 271	"	0.003_5 0.003	0.003	0.002_5	0.001_5-0.003
BCS 273*	"	0.003_5 0.004	0.004	0.003	-
BCS 275	"	0.006 0.006	0.006	0.005	0.003-0.006
BCS 277*	"	0.008 0.007_5	0.008	0.006_5	-

* Lead is a non-standardised element.

ANALYSIS OF LEAD IN B.C.S. CERTIFICATED COPPER-BASE ALLOYS

TABLE X

Sample No.	Type of Sample	Per cent Found	Average Per cent	Certificate value	Spread in Certificat
BCS 179/1	High tensile brass	0.195 0.216 0.216	0.209	0.190	0.170-0.20
BCS 180/1	Cupro-nickel	0.008_5 0.008 0.008	0.008	<0.01	0.005-0.10
BCS 183/1	Bronze	3.60 3.58 3.40	3.53	3.51	3.44 -3.63
BCS 207/1	Bronze	0.087 0.093 0.081	0.087	0.079	0.073-0.84

Table XI shows the results obtained by application of the procedure to the determination of lead in a number of commercial stainless and tungsten steels.

TABLE XI

ANALYSIS OF LEAD IN COMMERCIAL STEEL SAMPLES*

Sample No.	Type of Sample	Per cent Found	Average Per cent	Given value
08917	Stainless steel	0.007 0.007	0.007	0.008
FMB	" "	0.003 0.002_5	0.003	0.002_5
40415	" "	0.011_5 0.011_5	0.011_5	0.012
41373	Sponge iron	0.001 0.001	0.001	0.001
G7471	Tungsten steel	0.003 0.003	0.003	0.002
MGS 186	" "	0.003_5 0.003_5	0.003_5	0.002_5

*Samples Supplied by B. Bagshawe.

The method has approximately the same sensitivity, is much more rapid and requires fewer operations than the method described for the spectrophotometric determination of lead in the same materials, using the reagent 4-(2-pyridylazo)-resorcinol as given in Chapter II. A comparison of the results obtained by the atomic-absorption and spectrophotometric method with P.A.R. is shown in Table XII.

TABLE XII

COMPARISON OF RESULTS BETWEEN THE ATOMIC ABSORPTION AND P.A.R. SPECTROPHOTOMETRIC PROCEDURES

Sample No.	Average per cent at. abs.	Average per cent P.A.R.	Given Value
BCS 326	0.014	0.013_5	0.014
BCS 327	0.012	0.011_5	0.010
BCS 328	0.016	0.015	0.015
BCS 329	0.051	0.049	0.05-
BCS 330	0.004	0.004	0.003
BCS 271	0.003	0.004	0.002_5
BCS 273	0.004	0.004	0.003
BCS 275	0.006	0.006	0.005
BCS 277	0.008	0.008	0.006_5
BCS 179/1	0.209	0.206	0.190
BCS 180/1	0.008	0.009	<0.01
BCS 183/1	3.53	3.51	3.51
BCS 207/1	0.087	0.071	0.079
08917	0.007	0.007	0.008
FMB	0.003	0.003	0.002_5
41373	0.001	0.001_5	0.001
G.7471	0.003	0.003_5	0.002
MGS 186	0.003_5	0.004	0.002_5

DEVELOPMENT OF PROCEDURE

1. WAVELENGTH

A complete emission spectrum of the lead hollow-cathode lamp was obtained over the range 10,000 down to 2,000 Å when operating at 6mA. The most suitable line for atomic-absorption measurements was obtained at 2833 Å corresponding to the $6p^2 . {}^3P_2 - 6p\ 7s . {}^3P_1$ transition [156]. This line agrees with the value reported by others in the literature.

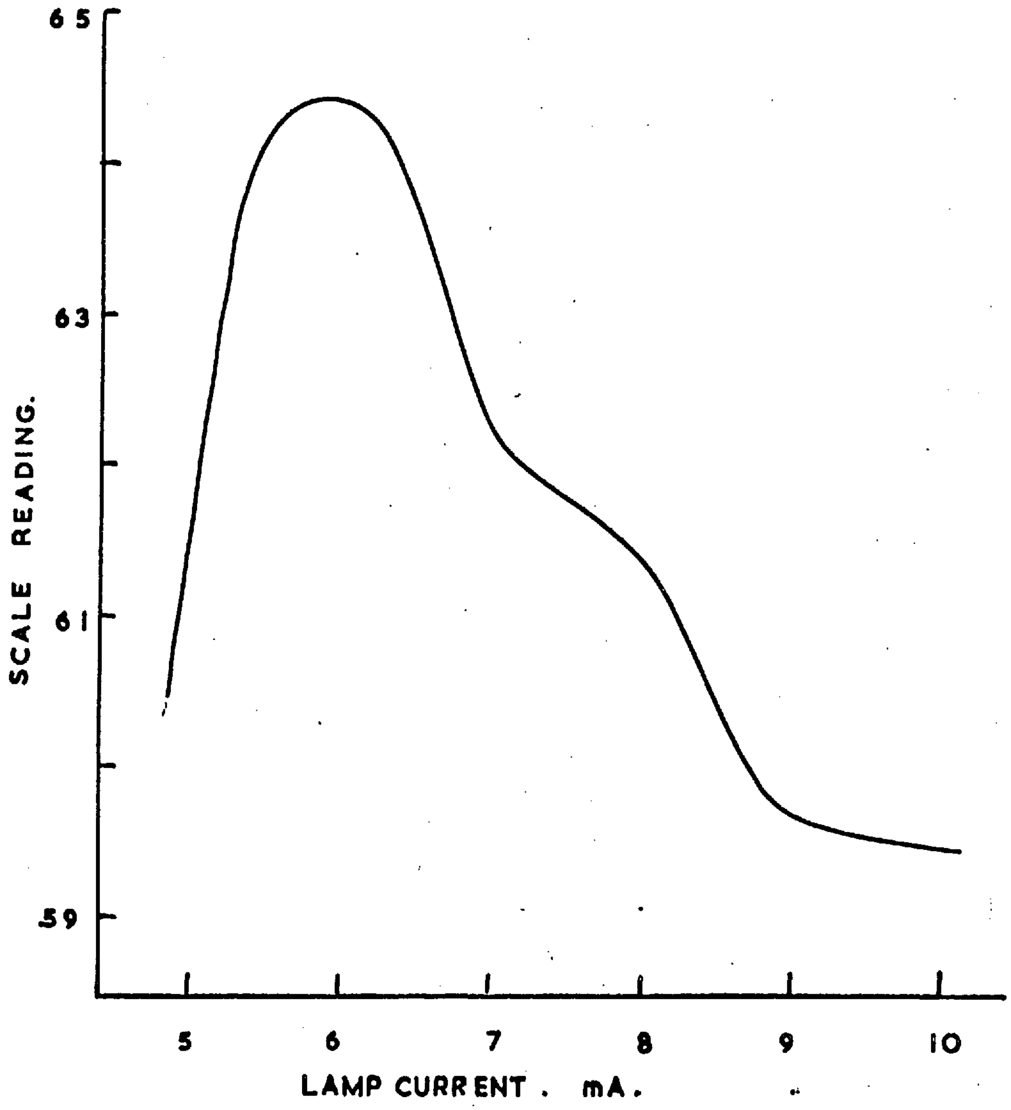
2. LAMP CURRENT

The optimum lamp current was obtained by plotting the change in absorbance with a standard lead nitrate solution. Fig XX shows the absorbance values obtained for an 8.10^{-4}M lead solution over the range 5 to 10 mA lamp current. An analysing slit width of 0.1 mm was used and air and acetylene were controlled at 15 p.s.i. and 13 cm manometer reading respectively.

3. AIR-ACETYLENE RATIO

A standard solution of lead nitrate was supplied to the spray chamber of the atomic-absorption spectrophotometer at a given air pressure of 15 p.s.i. An analysing slit of

FIG. XX



0.10 mm, and a lamp current of 6 mA were used while the acetylene gas pressure was varied to obtain a lean to fuel-rich range in flame conditions. The absorbance of a standard amount of lead atoms in the flame was measured at each gas pressure and plotted to find the point of maximum absorbance.

Fig. XXI shows such a plot while a 6.10^{-4}M aqueous lead solution was supplied to the spray chamber. It will be seen that maximum absorbance occurs just below the level of flame luminosity. These conditions were therefore used in subsequent determinations.

4. SLIT WIDTH

Little variation in the absorbance signal was found with differing monochromator entrance slit widths. A width of 0.20 mm was found to be convenient giving an adequate response with signal stability.

5. POSITION OF ABSORBANCE PATH

Maximum absorbance was found by plotting the change in signal when an iso-butyl methyl ketone solution of lead iodide, ($0.4.10^{-4}$M), was supplied to the spray chamber while the burner head assembly was raised or lowered. Maximum response occured when absorbance measurements were made just above the base of the flame, Fig.XXII.

FIG. XXI

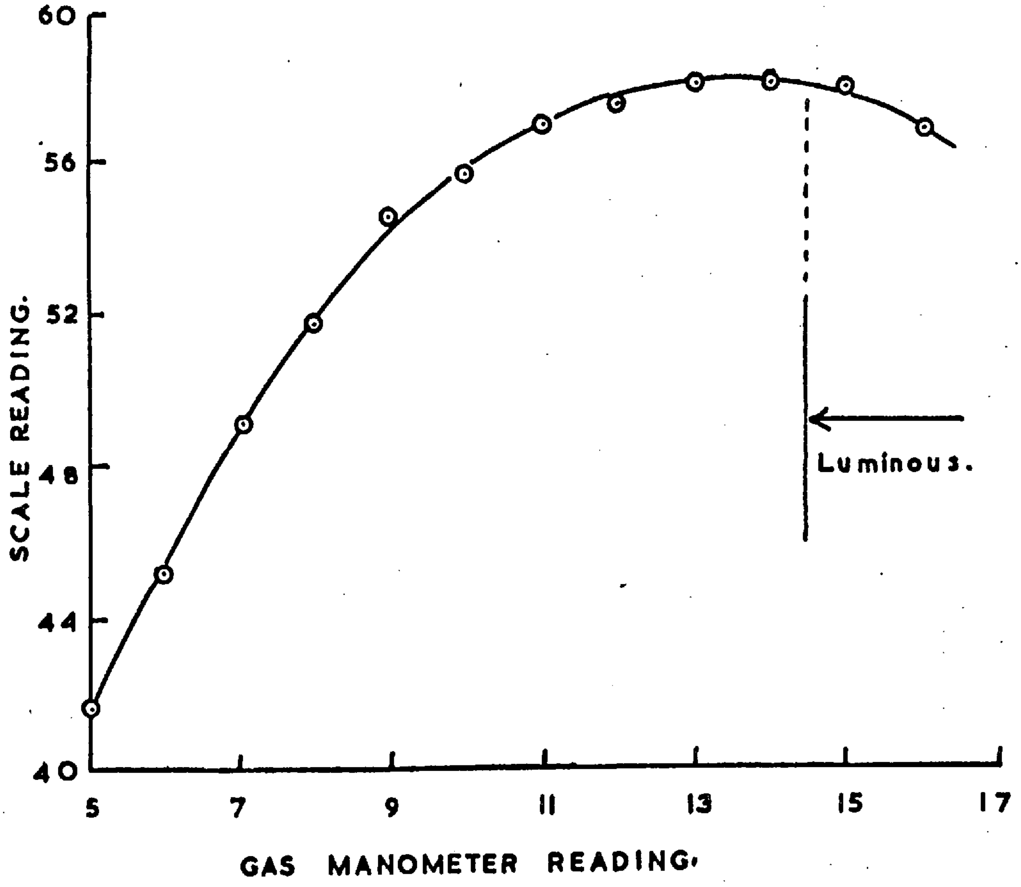
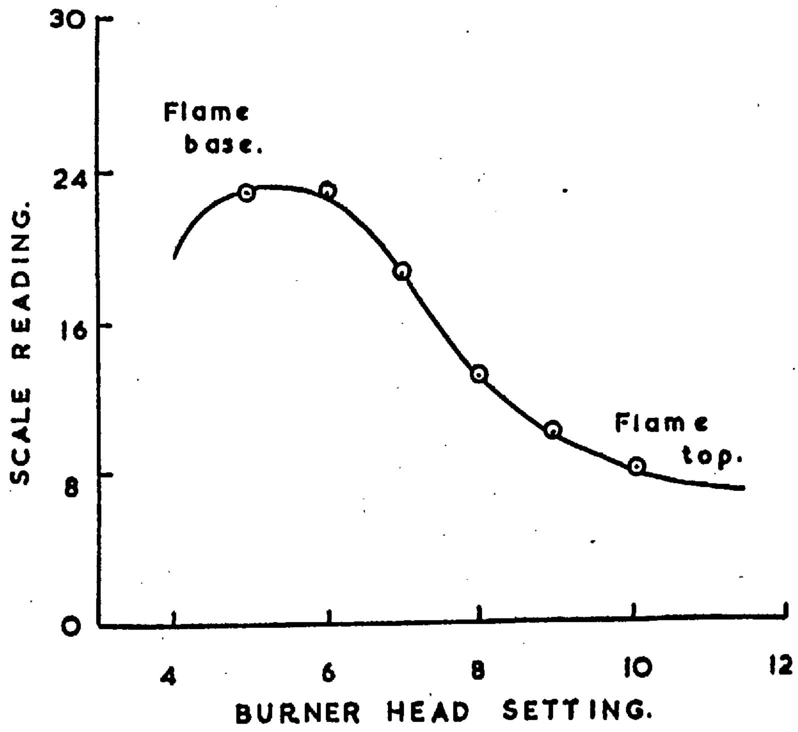

60
56
52
48
44
40
SCALE READING.
5
7
9
11
13
15
17
GAS MANOMETER READING.
Luminous.

FIG. XXII


30
24
16
8
0
SCALE READING.
Flame base.
Flame top.
4
6
8
10
12
BURNER HEAD SETTING.

6. EFFICIENCY OF SPRAYING ("ORGANIC SOLVENT EFFECT")

The enhancement in the absorbance obtained by use of iso-butyl methyl ketone containing lead in place of a standard aqueous lead solution was investigated. Firstly, a known volume of distilled water was partly converted into a fine spray by the aspiration spray chamber fitted to the apparatus and operating under the usual conditions (air pressure 15 p.s.i.). The total time for complete consumption of the water from the supply vessel was recorded, together with the volume of water not converted into a fine spray. The latter measurement was made by collecting the water from the waste outlet of the spray chamber. A similar experiment was then conducted with iso-butyl methyl ketone. The results obtained from the average of four runs of each solvent are shown in Table XIII. This shows that approximately five and a half times more ketone passes into the flame as a fine spray than an aqueous solution.

TABLE XIII

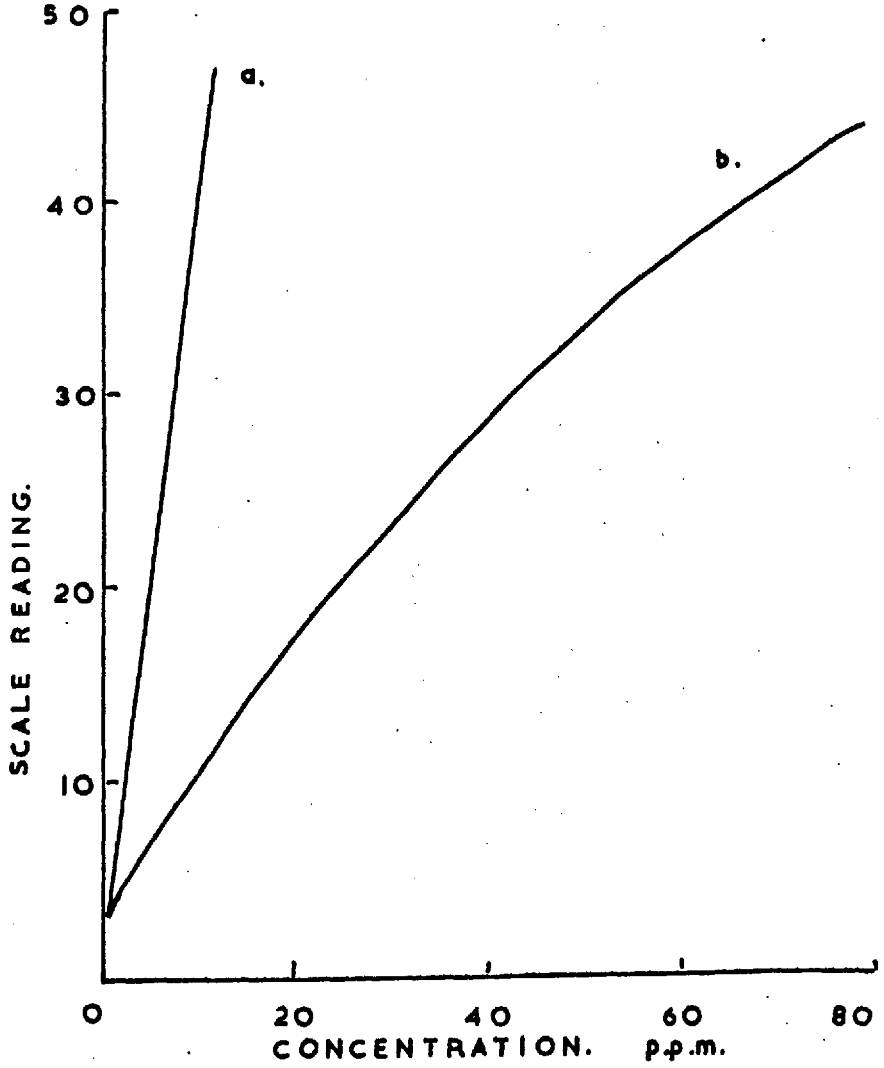
"ORGANIC SOLVENT EFFECT"

Volume used ml.	Volume recovered ml.	Volume Sprayed ml.	Time Taken	Rate of throughput ml/min.	Throughput ratio, relative to water
Distilled water					
25.0	24.0	1.0	6m 15s	0.21	1.00
25.0	23.5	1.5	6m 10s		
25.0	23.6	1.4	6m 1[illegible]		
25.0	23.7	1.3	6m 10s		
Ketone					
25.0	18.4	6.6	5m 17s	1.17	5.57
25.0	18.6	6.4	5m 11s		
25.0	19.2	5.8	5m 13s		
25.0	19.5	5.5	5m 07s		

7. CALIBRATION CURVE

A calibration curve was prepared by taking a series of synthetic iron-lead, (or copper-lead), solutions through the recommended method given under "Experimental Procedure".

FIG.XXIII



The organic ketone solutions were sprayed into the flame and the absorbances measured. Curve (a) in Fig. XXIII shows a calibration curve prepared from lead iodide-ketone solutions, while curve (b) shows that from aqueous solutions of similar concentration.

It will be seen that, relative to aqueous solutions of lead, about a five and half-fold increase in sensitivity was obtained with the ketone extract. As seen in the last section, this difference may be accounted for by the higher solvent input of the ketone extract.

The optimum conditions for the extraction of the lead iodide complex, H_2PbI_4, into iso-butyl methyl ketone were obtained from the results reported in Chapter II.

8. EXTRANEOUS IONS

A number of catious are wholly or partially extracted as their iodides from dilute acid solution with iso-butyl methyl ketone. The effect of these foreign ions was examined by preparing standard solutions of lead nitrate containing ca. 1000 fold molar excesses of these ions and subjecting the solutions to the recommended procedure.

Antimony (III), Arsenic (III), bismuth, cadmium, copper (II), gold (III), mercury (II), molybdenum (VI), tellurium (IV), thallium (I), tin (IV), zinc and also aluminium, chromium (III) and iron (III) were examined, but no interference was observed in any instance.

9. PRECISION OF METHOD

The precision of the method was investigated by determining the standard deviation from the multiple analyses of a series of solutions each containing 0.5 g of iron and 1.2 ml of 10^{-3}M lead nitrate solution by the recommended procedure.

The results are shown in Table XIV.

TABLE XIV

PRECISION DATA

Sample	Transmission decrease per cent	Deviation from mean	$(\text{Deviation})^2$
1	30.5	-1.5	2.25
2	31.0	-1.0	1.0
3	32.0	0.0	0.0
4	34.0	+2.0	4.0
5	31.5	-0.5	0.25
6	32.0	0.0	0.0
7	33.0	+1.0	1.0
8	32.5	+0.5	0.25
9	30.5	-1.5	2.25
10	31.0	-1.0	1.0
11	31.0	-1.0	1.0
Total	349.0		13.0
Average	32.0		

Variance = 1.3 Standard deviation = $\pm\sqrt{1.3} = \pm 1.14$

Percentage standard deviation = 3.55

CHAPTER IV

THE DETERMINATION OF CADMIUM BY ATOMIC-FLUORESCENCE SPECTROPHOTOMETRY

SUMMARY

The adaptation of a conventional atomic-absorption/flame-emission spectrophotometer to the measurement of atomic-fluorescence in an air-acetylene flame is described.

After optimisation of the experimental parameters to give maximum sensitivity, calibration curves over the range 10^{-5} to 10^{-6}M (1.0 to 0.1 ppm.) and 10^{-6} to 10^{-7} (0.1 to 0.01 ppm.) in aqueous solution are prepared. It will be seen from the calibration curves and from evaluation of detection limits, that, even with a very simple and inefficient means of exciting and measuring fluorescence, results can be obtained which indicate that atomic-fluorescence spectrophotometry is considerably more sensitive than atomic-absorption spectrophotometry or flame-emission photometry.

It will also be seen that, from the large number of foreign cations and anions investigated, atomic-fluorescence spectrophotometry is equally as free from interelemental interference as the complimentary technique of atomic-absorption spectrophotometry.

INTRODUCTION

Atoms may be excited from the ground state to a higher unstable energy level by the absorption of radiation of the proper frequency. As the excited atoms fall back to lower more stable energy levels they emit radiation, characteristic of the absorbing atoms.

It has been shown in the general introduction that the intensity of the emitted fluorescent radiation is directly propertional to the number of atoms in the ground state for a given experimental arrangement and constant source of energy i.e.

$$I_f = c.E_o. N_o.$$

where I_f = intensity of fluorescent radiation,

C = a constant of proportionality,

E_o = energy of incident radiation,

and N_o = the number of ground state atoms.

The experimental requirements to obtain and measure atomic-fluorescence therefore consist simply of a source of radiation directed onto a stable flame, into which the atoms under investigation are aspirated, and a means of monochromating and measuring the intensity of the emitted radiation.

Sources of incident radiation which may be used include vapour discharge lamps, hollow-cathode lamps and microwave excitation sources. A conventional atomic-absorption/flame-emission spectrophotometer provides a readily available means of monochromating and measuring the emitted radiation and also provides the means for aspirating the sample into the flame.

EXPERIMENTAL

The apparatus used consisted of a Unicam SP.900A atomic-absorption/flame-emission spectrophotometer equipped with a Honeywell-Brown 0-10 mV recorder.

The stainless steel burner head used was the Meker type in which the acetylene and air/sample mixture is combusted through a series of concentric rings of holes giving a flame about 6 cm high and 1.5 cm in diameter when operated at 15 p.s.i. air pressure and sufficient gas pressure to give a non-luminious flame.

Simple modification to the burner housing allowed the necessary radiation from a cadmium discharge lamp to pass through an adjustable slit-mechanism onto the flame. A hole was cut in the outer glass envelope of the lamp to allow passage of the 2288 Å line which was used in these studies.

The lamp itself was mounted in an upright position so that it subtended a right angle with the entrance slit of the SP900A spectrophotometer at the flame and was operated via a ballast unit.

It was found that a controlled forced constant draught of air directed onto the lamp increased and stabilised its output considerably when operated at the recommended current value. This may be due to an increased rate of convection of the atomic vapours inside the quartz discharge chamber (caused by cooling of the surface) and thereby increasing the availability of atomic vapour between the electrodes. Alternatively the effect of an increased rate of cooling of the lamp is to reduce the running temperature of the lamp and so reduce the vapour pressure of the metal vapour. This would therefore reduce Doppler-broadening and self-reversal, both of which would affect the sensitivity of method.

When too strong a current of air was used the discharge was cut down, presumably due to over cooling and condensation of the vapour on the walls of the chamber.

With the Unicam SB900A vapourisation unit, large droplets of sample solution are removed by centrifugal force in the expansion chamber and this minimises the scattering of light by large droplets and solid particles in the flame.

REAGENTS

10^{-3}M stock solutions of cadmium were prepared by dissolving 0.3662 g of cadmium iodide or 0.2563 g of cadmium sulphate in water and diluting to 1 litre. 10^{-4} to 10^{-9}M solutions were prepared by appropriate dilutions immediately before use. Both salts were of analytical grade.

OPTIMISATION OF CONDITIONS FOR MAXIMUM SENSITIVITY

1. PRELIMINARY SPECTRA

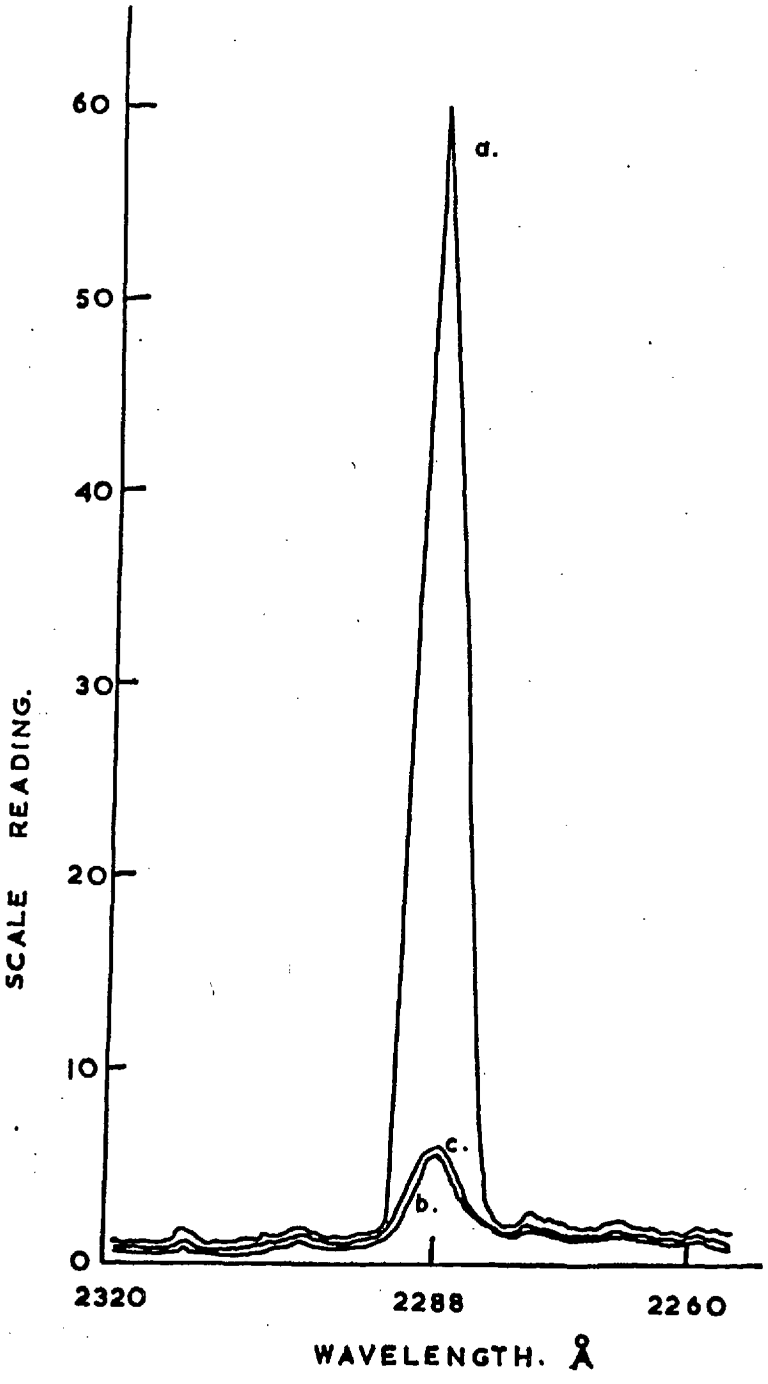
The ultraviolet region of the spectrum was scanned while a 10^{-4}M aqueous solution of cadmium iodide was sprayed into the flame which was being irradiated with the cadmium discharge lamp operating at its recommended current.

A sharp peak was obtained at 2288Å corresponding to the singlet $5\,^1S_0 - 5\,^1P_1$ resonance line.

Figure XXIV shows the flurorescent emission spectrum for 10^{-4}M cadmium iodide, (curve a), together with the scattered light blanks from distilled water (curve b), and a 10^{-1}M copper solution, (curve c).

The similarity between curves b and c shows that there is no appreciable scattered light when spraying a solution of a foreign metal into the flame.

FIG. XXIV


SCALE READING.
60
50
40
30
20
10
0
2320
2288
2260
WAVELENGTH. Å
a.
b.
c.

Investigation of longer wavelengths did not show the expected presence of the 3261Å line. This was due to the lack in sensitivity of the simple apparatus used and also due to the high flame background obtained with air-acetylene flames. It is in fact possible to detect the 3261Å line in the more "clean" flame obtained from propane and air but it is still less than one tenth of the intensity obtained from the 2288Å line.

2. VARIATION OF ACETYLENE - GAS PRESSURE

With an air pressure controlled at 20 p.s.i. and exciting and analysing slit-widths set at 2.00 and 0.15 mm respectively, the acetylene-gas pressure was varied in order to obtain a range from lean to fuel-rich flames.

The fluorescence radiation from a 10^{-4}M solution of cadmium iodide was measured at each gas pressure. A graph of fluorescence intensity scale reading against gas manometer pressure was constructed and is shown in Fig. XXV. Little variation in signal was observed over the complete range. In subsequent experiments the gas pressure was controlled to obtain a translucent flame just below the level of luminosity.

FIG. XXV

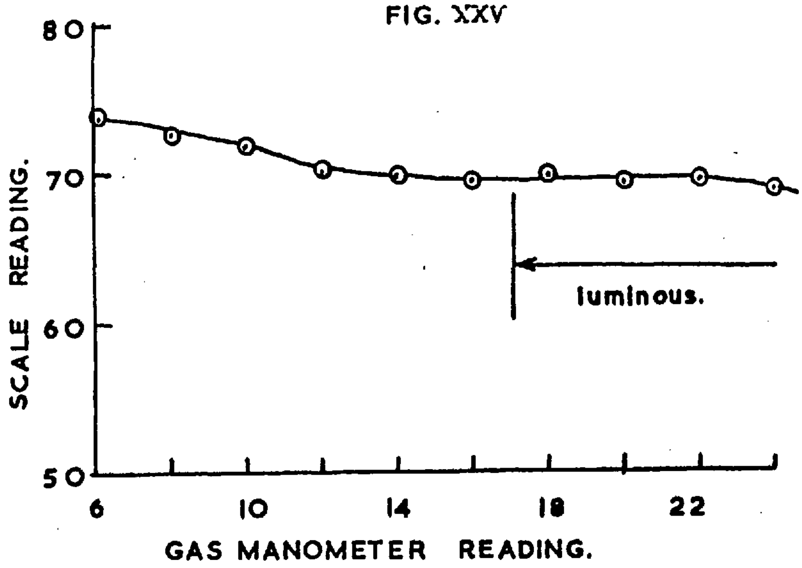
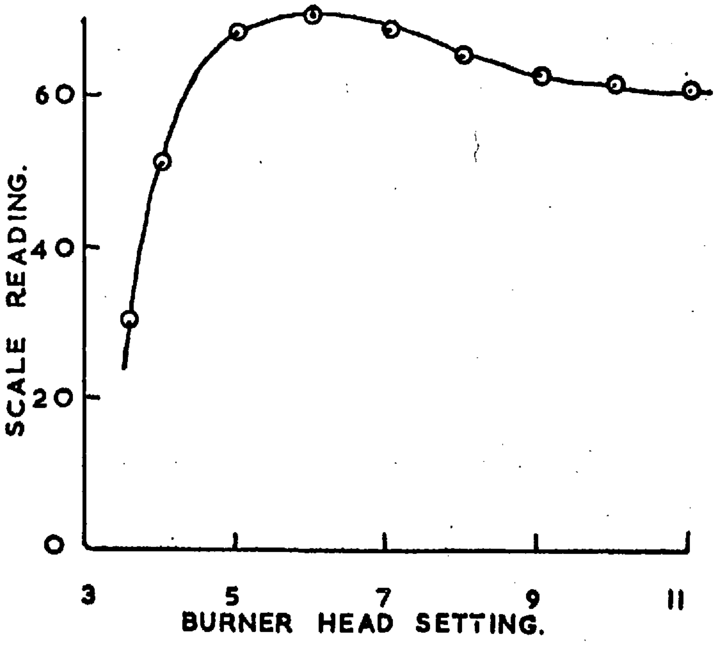


FIG. XXVI



3. LIGHT PATH

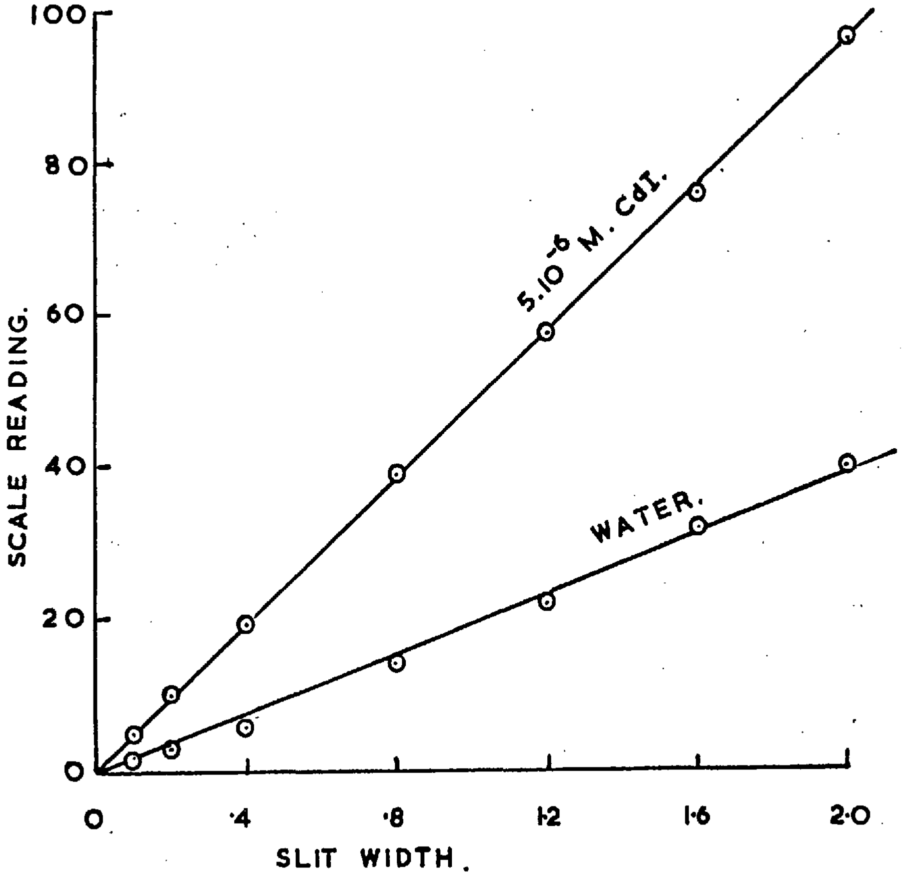
The optimum position of the light path was obtained by measuring the fluorescence radiation from a 10^{-4}M cadmium iodide solution and the scatter blank from distilled water, at different burner-head settings. The ratio of the fluorescence signal to the scatter signal plotted against the position of the burner-head is shown in Fig. XXVI. A maximum signal ratio was obtained with the inner cones of the flame situated just below the level of the monochromator entrance slit, but only a small decrease in response was observed as the burner-head was lowered.

4. ANALYSING SLIT-WIDTH

Variation of the analysing slit-width in the range up to 2.00 mm. produced a near linear increase in signal for a standard solution of 5.10^{-6}M cadmium iodide solution when the excitation slit-width was set at 2.00 mm. However, it will be seen from figure XXVII that it also produced a similar effect for the background signal from distilled water.

In subsequent work an analysing slit-width of 0.15 mm was chosen in order to obtain adequate sensitivity together with signal stability.

FIG. XXVII


100
80
60
40
20
0
SCALE READING.
0
·4
·8
1·2
1·6
2·0
SLIT WIDTH.
5.10⁻⁶ M. CdI.
WATER.

CALIBRATION CURVES

With the above optimised conditions a linear calibration curve was obtained over the range 10^{-5}M to 10^{-6}M cadmium iodide (1.0 to 0.1 ppm.). For more dilute solutions, 10^{-6} to 10^{-7}M cadmium iodide (0.1 to 0.01 ppm.), the analysing slit-width was opened out to the maximum setting of 2.00mm. A linear calibration curve was again obtained.

Calibration curves can be constructed over a much wider range of concentrations than those discussed above, but a sigmoid curve [115] [117] is then obtained. The curves described here were obtained over narrow ranges of the steepest part of the sigmoid curve.

STANDARD DEVIATION

The precision of the method was obtained at both the 10^{-5} and 10^{-6}M levels of concentration from the analyses of a set of eleven solutions at either concentration with the optimised conditions.

The results are shown in Table XV from which it will be seen that at the 10^{-5}M concentration there is a standard deviation of 1.0 per cent and at the 10^{-6}M concentration a deviation of 5.1 per cent.

TABLE XV

PRECISION OF METHOD

No. n.	Scale Reading	Deviance D	D^2.	Scale Reading	Deviance D	D^2
1	78.0	1.25	1.56	11.5	0	0
2	77.0	0.25	0.06	11.0	0.5	0.25
3	74.5	2.25	0.06	10.5	1.0	1.0
4	77.5	0.75	0.56	10.5	1.0	1.0
5	75.5	1.25	1.56	11.25	0.25	0.06
6	77.0	0.25	0.06	11.25	0.25	0.06
7	77.0	0.25	0.06	11.25	0.25	0.06
8	77.0	0.25	0.06	12.5	1.0	1.0
9	77.0	0.25	0.06	11.5	0	0
10	77.5	0.75	0.56	11.5		0
11	76.0	0.75	0.56	11.75	0.25	0.06
Total	844.0		5.16	125.25		3.49
Average	76.75			11.5		

Standard Deviation $= \sqrt{\frac{\leq D^2}{n - 1}}$

$\underline{10^{-5}M}$

Standard deviation $= \sqrt{\frac{5.16}{10}} = 0.75$

Per cent standard deviation = 1.0

$\underline{10^{-6}M}$

Standard deviation $= \sqrt{\frac{3.49}{10}} = 0.59$

Per cent standard deviation = 5.1

INTERFERENCES

The effects of 100-fold molar excesses of 41 cations and 18 anious over 10^{-5}M. Cd^{2+} were examined: viz. Ag, Al, As (III), Au(III), Ba, Be, Bi, Ca, Ce (IV), Co(II), Cr(III), Cu(II), Fe(III), Ga, Hg (II), In, K, Li, Mg, Mn (II), Mo (VI), Na, Nb, NH_4, Pb, Sb(III), Sc, Se(IV), Sn(IV), Sr, Te(IV), Th, Tl(I), Ti(IV), U(VI), V(V), W(VI), Y, Zn, Zr, acetate, B_4O_7, Br, CO_3 Cl, citrate, ClO_4, CN, F, I, NO_3, oxalate, PO_4, SiO_3, SO_3, SO_4, SCN and tartrate. Where hydrolysis of the interfering ion would occur, sufficient acid was added to maintain a clear solution. No single cation or anion caused variation of the response by more than ± 5 per cent.

The effects of five common reagents E.D.T.A., ascorbic acid, hydroxylammonium chloride, 1-10, phenanthroline and hydrogen peroxide were also investigated.

Of these only 1-10, phenanthroline interfered, but this interference was later shown to stem from precipitated Cd $(Phen)_2I_2$, and on addition of acid a true solution was obtained and no interference observed.

SOLVENT EFFECTS

10^{-5}M Cadmium iodide solutions were prepared in 10 per cent ($^v/_v$) concentrations of eight water-miscible solvents.

The solutions were sprayed into the flame under the usual conditions and the intensity of atomic-fluorescence obtained compared with the intensity from a 10^{-5}M aqueous solution.

A summary of the results are shown in Table XVI.

TABLE XVI

Solvent 10 per cent ($^{v}/_{v}$)	Scale Reading	10^{-5}M aqueous	Average increase per cent
Acetone	71.0 71.5	61.5	16.2
Acetic Acid	75.5 76.0	"	23.6
Methanol	74.0 68.5	"	16.2
Ethanol	73.5 71.0	"	17.9
iso-Propyl Alcolhol	79.0 80.5	60.0	33.3
Methyl Ethyl Ketone	82.5 82.5	"	37.5
Glycerol	61.5 62.5	"	3.3
Dioxan	79.0 81.0	"	33.3

The presence of only 10 per cent organic solvent caused little variation in the flame conditions; a constant air and acetylene gas pressure was, therefore, used throughout these measurements.

It will be seen from Table XVI that all the solvents investigated caused an increase in the signal from 10^{-5}M aqueous cadmium iodide. The outstanding feature here is the very slight increase caused by the viscous solvent, glycerol.

ATOMIC-FLUORESCENCE OF ORGANIC EXTRACTS

The use of solvent extraction with potential advantages of concentration and more favourable rates of vaporization was investigated. The extraction of cadmium iodide into *iso*-butyl methyl ketone was noted during the development of the spectrophotometric determination of lead. The extraction of cadmium from iodide solution has in fact been described[60] in Morrison and Freizer's textbook on solvent extraction, and their method was suitably adapted for these experiments.

To 20 ml of distilled water were added 0.5 ml of 10^{-3}M cadmium iodide solution, 5 g. of potassium iodide and 0.83 ml of concentrated sulphuric acid. The solution was then extracted with 20 ml of *iso*-butyl methyl ketone in a separating funnel. The lower aqueous phase was discarded and the organic phase diluted to 100 ml with pure *iso*-butyl methyl ketone. The solution was then sprayed directly into the flame under the usual conditions, except that the acetylene gas pressure was reduced so that the usual type of steady-state non-luminous flame was obtained.

The resulting ketone extract gave a scale reading about four times greater than that of an aqueous solution of equal concentration. Measurement in ketone solution, therefore, considerably increases the sensitivity of the determination of cadmium.

LIMIT OF DETECTION.

With the simple arrangement used and with optimised conditions the limit of detection for aqueous solutions of cadmium iodide was found to be at about 5.10^{-9}M. For *iso*-butyl methyl ketone extracts of cadmium iodide a detection limit of about 10^{-9}M was obtained. For both these detections a maximum analysing slit width of 2.00 mm. was used which, therefore, caused considerable fluctuations in the signal. Accurate evaluations were, therefore, impossible to obtain and values given above can only be regarded as approximations.

CONCLUSIONS

Obviously the limits of determination and detection depend on the sensitivity of the apparatus used and are capable of considerable improvement. In these experiments, for example, no attempt was made to focus the light from the discharge lamp onto the flame or to collect the fluorescence from the flame and focus this onto the monochromator entrance slit. Both these factors would yield a much lower limit of detection, and enhance the sensitivity of the method.

The use of a more intense source of radiation, such as electrodeless discharge tubes and of a more sensitive photomultiplier detector tube would considerably lower the limits of detection.

Yet, even with the experimental arrangement used in these investigations, considerable sensitivity is obtainable and A.F.S. shows promise to be a more sensitive technique than the corresponding method of absorption spectrophotometry. It is, however, impossible to draw an accurate comparison between the sensitivity and precision of each technique. At low dilutions the fluorescence technique follows a linear relationship between the analytical signal and the concentration of ion being determined, whereas atomic-absorption follows a logarithmic ratio between incident and transmitted light.

Comments on the respective merits of atomic-fluorescence and atomic-absorption spectrophotometry for the determination of a particular element, cadmium, will be given in the conclusion at the end of the following chapter which deals with the determination of cadmium by atomic-absorption.

CHAPTER V

THE DETERMINATION OF CADMIUM BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

SUMMARY

A method is described for the determination of cadmium by atomic-absorption spectrophotometry in an air-acetylene flame using the same instrument used for measurement of atomic-fluorescence.

The usual parameters of wavelength, acetylene-gas pressure, light path through the flame, lamp current and analysing slit-width are investigated. With these conditions optimised for maximum sensitivity a calibration curve over the range 5.10^{-6}M to 10^{-4}M, (0.5 to 11 p.p.m.), cadmium iodide is prepared.

The effects of the same 41 cations and 18 anions and of the same five common reagents investigated during the measurements of atomic-fluorescence are also examined here. The eight water-miscible solvents and iso-butyl methyl ketone extract are also investigated.

INTRODUCTION

Following the determination of cadmium by the measurement of atomic-fluorescence it was decided to investigate the complimentary technique of atomic-absorption using the same basic experimental arrangement in order to gain information about comparitive sensitivities.

Many references have been made to the sensitivity of detection of cadmium by atomic absorption spectrophotometry 96 100 102 119 120 but only a few papers have been published giving details of any analytical applications. 110 121.

EXPERIMENTAL

Measurements of atomic-absorption were made with the same Unicam SP.900A instrument, but the emission burner-head was replaced by a stainless steel absorption-head which gave a flame about 7 cm long and 0.3 cm wide when operated at 15 p.s.i. air pressure and sufficient gas pressure to give a non-luminous flame.

A cadmium hollow-cathode lamp provided the necessary radiation of the 2288 Å line and was mounted such that the emitted radiation passed directly through the flame and was focussed onto the analysing slit of the monochromator.

REAGENTS

The same 10^{-3}M stock solutions of cadmium iodide and sulphate were used as prepared for measurement of fluorescence. 10^{-4} to 10^{-9}M solutions were prepared by appropriate dilution immediately before measurement.

OPTIMISATION OF CONDITIONS FOR MAXIMUM SENSITIVITY

1. WAVELENGTH

The ultra violet region of the spectrum was scanned while the hollow-cathode lamp was operated at 15 mA. A very sharp peak was obtained at 2288 Å which was well separated from any other emitted lines.

2. ACETYLENE GAS PRESSURE

With a lamp current fixed at 10 mA, analysing slit - width set at 0.05 mm., the burner-head adjusted such that the inner cones were just below the level of the analysing slit and an air pressure of 20 p.s.i., the acetylene gas pressure was varied in order to obtain a range from lean to fuel rich flames.

The absorbance of a 10^{-4}M solution of cadmium iodide was measured at each gas manometer setting and the results are shown in Fig XXVIII.

It will be seen that there is very little variation in signal over the whole range of gas pressures. A value was chosen which gave a translucent flame just below the level of luminosity for further measurements.

3. LIGHT PATH

The optimum position of light path through the flame was obtained by measuring the absorbance of a 10^{-4}M cadmium iodide solution at different height settings of the burner head assembly.

From the graph of absorbance plotted against burner-head position, a maximum was observed when the inner-cones of the flame were situated just below the level of the monochomator entrance slit, (Fig. XXIX).

4. LAMP CURRENT

With the optimised conditions so far established, the current through the hollow-cathode lamp was varied from the minimum value of 4mA to about 11 mA. Above 11mA the lamp became unstable, due presumably to an over heating of the cathode.

FIG. XXVIII

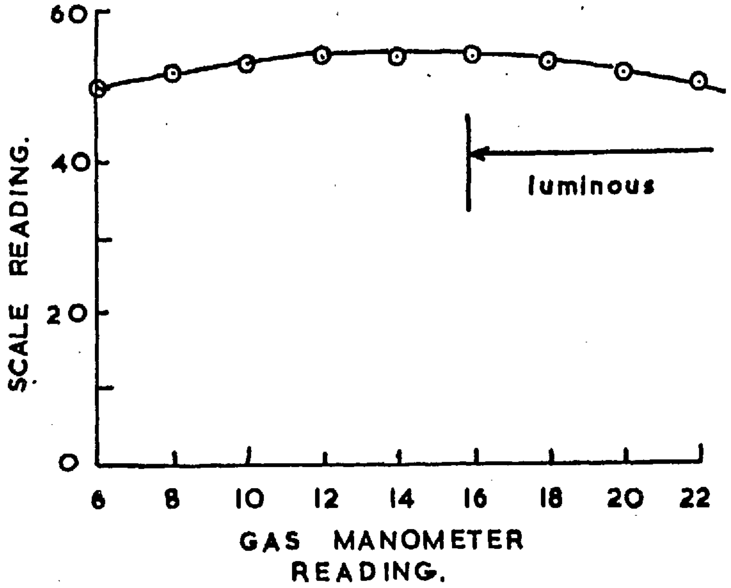
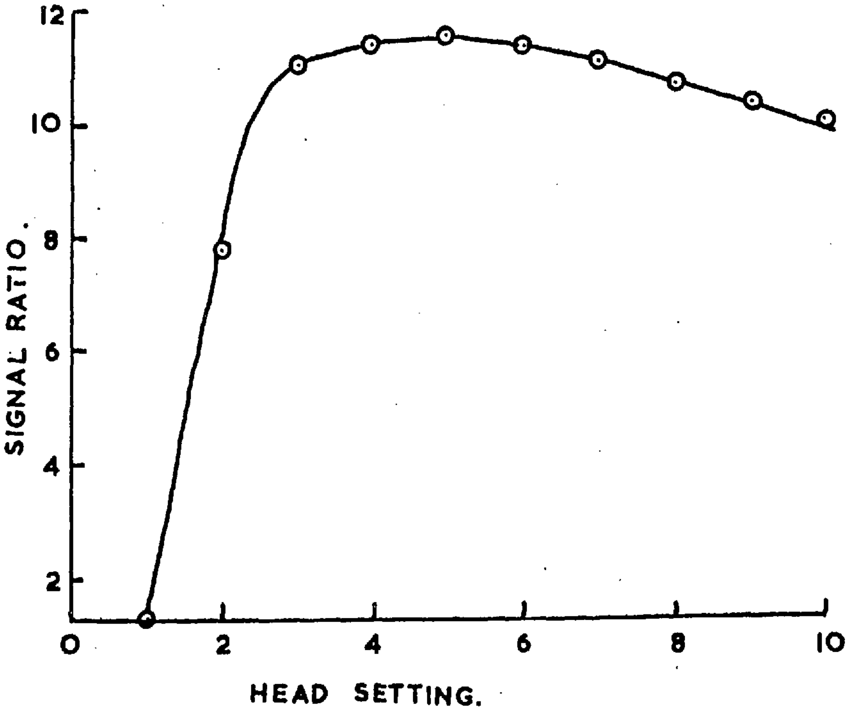


FIG.XXIX



A gradual decrease in sensitivity was observed as the lamp current was increased, as shown in Figure XXX. However, at the lower current values considerable fluctuations in response were observed. A value of 8 mA was therefore chosen to give the optimum response in conjunction with signal stability for subsequent measurements.

5. ANALYSING SLIT-WIDTH

The entrance slit to the monochromator was varied from 0.025 mm. to 2.00 mm. while the absorbance signal from a 10^{-4}M cadmium iodide solution was determined. As the slit-width was opened out to 0.10 mm. a very considerable increase in response was observed as shown in Figure XXXI. Above 0.10 mm. very little change in response was observed except that a more stable reading was obtained on the 0-10 mV recorder.

CALIBRATION CURVE

A calibration curve was prepared over the range 5.10^{-6}M to 10^{-4}M cadmium iodide, (0.5 to 11 ppm.), under the above optimised conditions. A non-linear curve was obtained over this wide region, but a near linear response is seen over the steepest part of the curve up to 5.10^{-5}M. (Figure XXXII.)

FIG. XXX

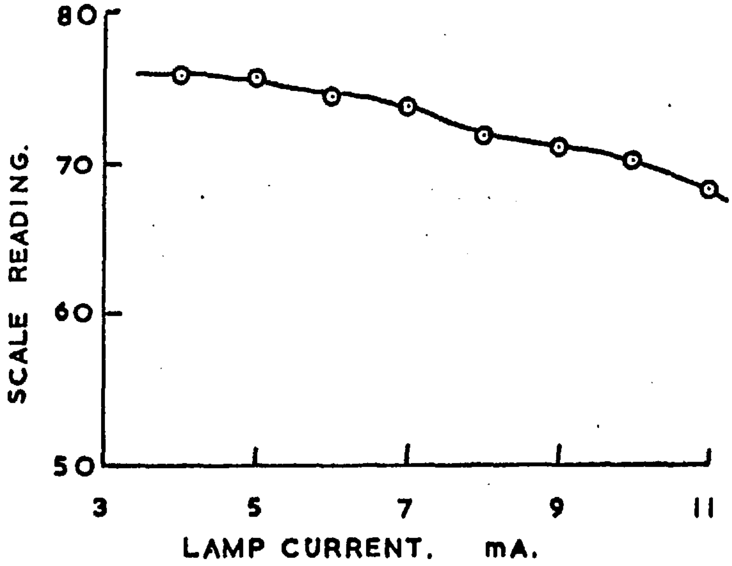


FIG. XXXI

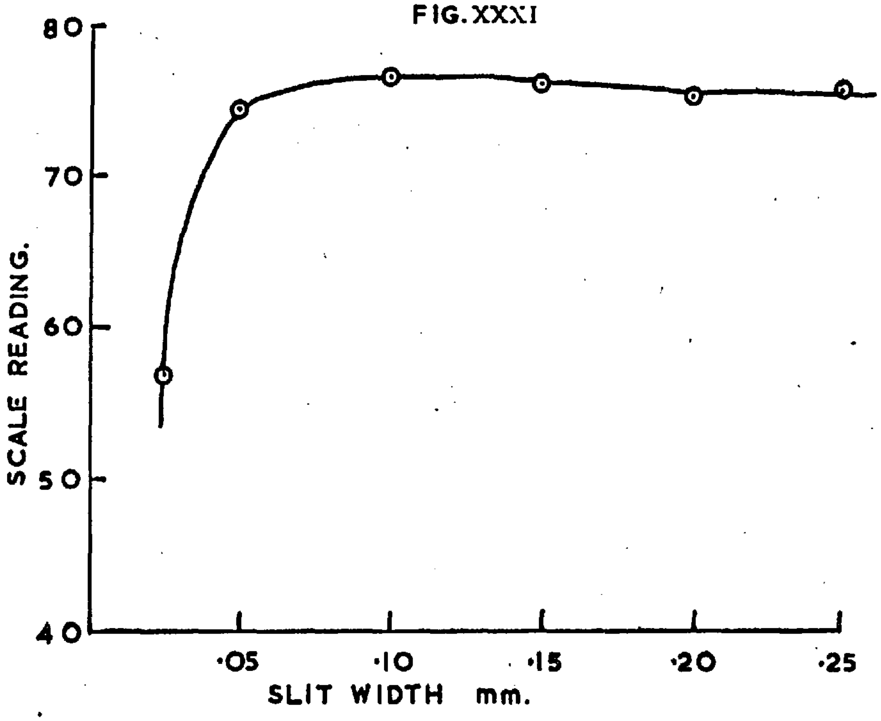
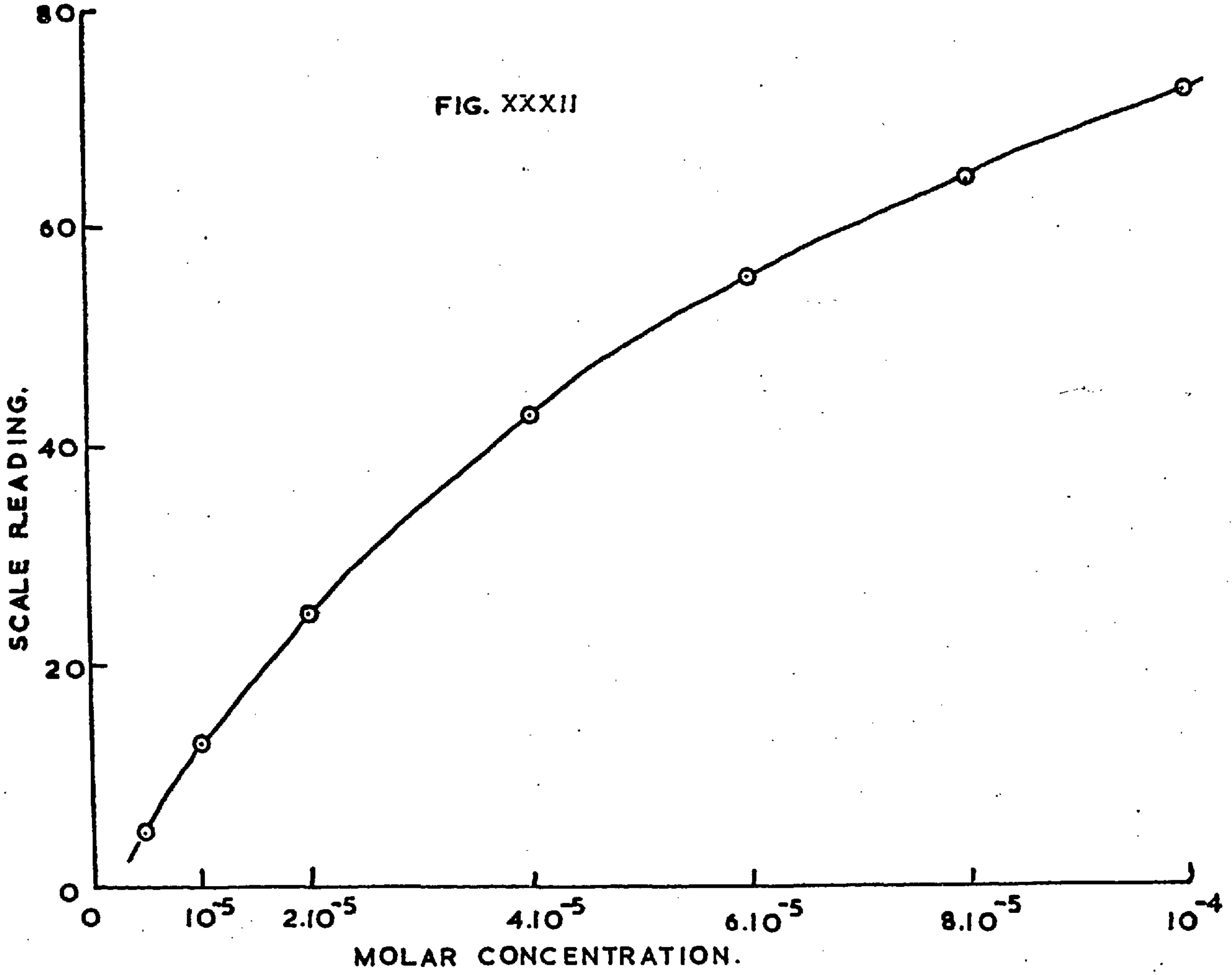


FIG. XXXII


80
60
40
20
0
SCALE READING.
0
10⁻⁵
2.10⁻⁵
4.10⁻⁵
6.10⁻⁵
8.10⁻⁵
10⁻⁴
MOLAR CONCENTRATION.

STANDARD DEVIATION

The precision of the method was obtained by measuring the absorbance of a set of eleven solutions each of concentration 5.10^{-5}M in cadmium under the above optimised conditions.

The results, from which a standard deviation of 1.3 per cent was obtained, are shown in Table XVII.

TABLE XVII

PRECISION OF METHOD

Sample No. n.	Scale Reading	Deviance D	D^2
1	41.5	1.0	1.0
2	42.25	0.25	0.06
3.	43.5	1.0	1.0
4	43.25	0.75	0.56
5	42.5	0.0	0
6	43.0	0.5	0.25
7	42.0	0.5	0.25
8	42.75	0.25	0.06
9	42.5	0.0	0.0
10	42.25	0.25	0.06
11	42.75	0.25	0.06
Total	468.25		3.3
Average	42.5		

Standard Deviation = $\sqrt{\frac{\sum D^2}{(n-1)}} = \sqrt{.33} = 0.57$

Per cent standardard deviation = $\frac{0.57}{42.5} \times 100 = 1.3$

INTERFERENCES

The effects of the same 41 cations and 18 anions investigated during the fluorescence measurements were examined for possible interference in the measurement of cadmium by atomic-absorption.

As expected no single cation or anion caused variation in response by more than ± 5 per cent.

The presence of the same five common reagents, E.D.T.A., ascorbic acid, hydroxyammonium chloride, 1,10 - phenanthroline and hydrogen peroxide was investigated and as with fluorescence measurements, no interference was observed provided that true solutions were maintained.

SOLVENT EFFECT

10% ($^v/_v$) aqueous solutions of the same eight water-miscible solvents containing a final concentration of 5.10^{-5}M cadmium iodide were sprayed into the flame and the absorbance of each solution was determined. All but glycerol increased the response, but the effects were much less marked than for atomic fluorescence. In this instance the effect of a viscous solvent, glycerol, was as expected[96 157]. A summary of the results are shown in Table XVIII.

TABLE XVIII

Solvent 10% . $(^{v}/_{v})$	Scale Reading	Aqueous Sol$^{\underline{n}}$.	Difference %	Scale Reading
Methyl Ethyl Ketone	67.25	78.75	14.5	66.0
iso-Propyl Alcohol.	67.25	"	14.5	67.0
Dioxan	62.5	"	6.4	61.75
Acetic Acid	63.5	"	8.1	64.5
Ethanol	64.5	"	9.8	63.5
Acetone	62.75	"	6.8	62.5
Methanol	62.0	"	5.6	62.5
Glycerol	55.0	"	-6.4	55.0

TABLE XVIII contd.

Aqueous Sol$^{\underline{n}}$.	Difference %	Average Diff.%
58.25	13.3	13.9
"	15.0	14.7
"	6.0	6.2
"	10.7	9.4
"	9.0	9.4
"	7.3	7.1
"	7.3	6.4
"	-5.6	-6.0

ATOMIC-ABSORPTION IN ORGANIC EXTRACTS

0.5 to 2.0 ml of a 10^{-3}M cadmium iodide solution were diluted to 20 ml with distilled water and 5.0 g of sodium iodide and 0.83 ml of concentrated sulphuric acid were added. The solutions were extracted with 20 ml of **iso**-butyl methyl ketone. The lower extracted phases were discarded and the remaining organic extracts were diluted to 100 ml with ketone.

The atomic-absorption from each solution was measured under the usual conditions except that the acetylene-gas pressure was reduced so as to obtain the steady state non-luminous flame.

Values approximately three and a half times greater than those for the corresponding aqueous solutions were obtained. The results were plotted on a graph and shown in Fig. XXXIII.

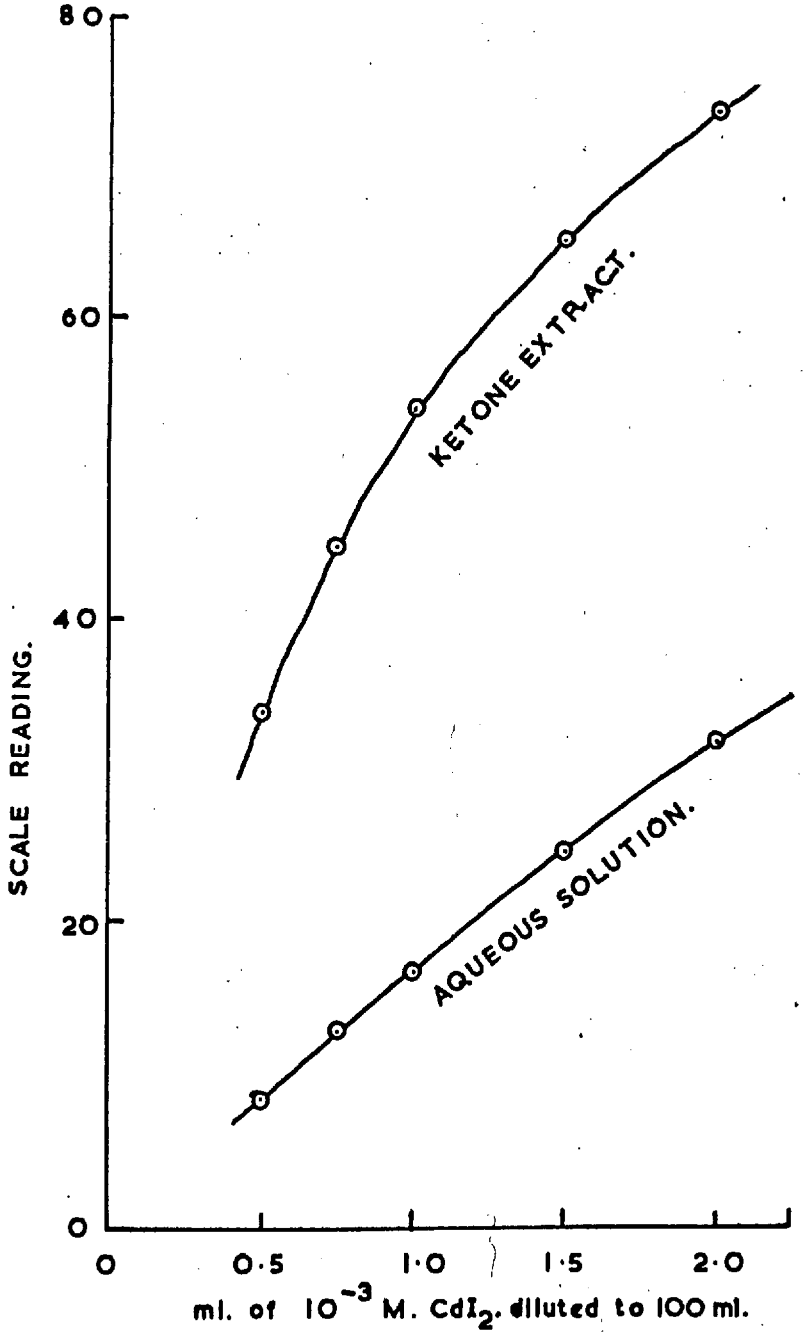
LIMIT OF DETECTION

The limits of detection for atomic-absorption measurements of cadmium in aqueous solution were found to be at about 2.5 10^{-6}M and, with the organic ketone extract, at about 10^{-6}M.

CONCLUSION AND DISCUSSION

As mentioned briefly in the conclusion to the last chapter, it is not possible to draw an accurate comparison

FIG. XXXIII


80
60
40
20
0
SCALE READING.
KETONE EXTRACT.
AQUEOUS SOLUTION.
0
0·5
1·0
1·5
2·0
ml. of 10^{-3} M. CdI_2. diluted to 100 ml.

between the sensitivity and precission of the atomic-fluorescence and atomic-absorption methods because of the different factors involved.

As shown in the general introduction, the atomic fluorescence technique follows a linear relationship between the analytical signal and the concentration of the ion being determined, i.e.

$$I_F = c.E_o.N_o.$$

where the symbols used are as before.

On the other hand, atomic-absorption, follows a law involving an exponential term which on intergration gives the quation;

$$A = \log \frac{Io}{I_v} = K_v.c.l.$$

where A is the absorbance signal, Io is the intensity of incident radiation, I_v is the transmitted intensity, K_v is an absorption coefficient, c is the concentration term and l the light path length.

In atomic-absorption we, therefore, see that for trace amounts, the ratio $^{Io}/_{I_v}$ tends to unity and hence the logarithmic term tends to zero. An increase in the intensity of the incident light will, therefore, be of no benefit. Similarly, increased amplifier gain will also yield no benefit in sensitivity. On the other hand, where fluorescence measurements are made, the fluorescence signal approaches zero linearly for decreasing atomic concentration. It can, therefore, be increased by use of a more intense source of excitation or by the use of a more sensitive detection devise. The fluorescence signal can also be increased, within the limits of electrol background noise and photomultiplier excitation resulting from thermal emissions, by increased amplifier gain.

With the simple arrangement used for measuring atomic-fluorescence it has been shown possible to decrease the determination limit by a factor of one order of magnitude down to the submicrogram range, i.e. 10^{-7}M, compared with the atomic-absorption determination limit of 10^{-6}M.

It has also been shown possible to decrease the limit of detection by three orders of magnitude down to the nanogram range, 10^{-9}M, by the measurement of atomic-fluorescence. This compares with a limit of detection for atomic-absorption of only 10^{-6}M

With the equal freedom from interelemental interference of the fluorescence and absorption techniques together with increased sensitivity, it therefore appears that the fluorescence technique could supercede its absorption counterpart.

Perhaps the most undesirable feature of both fluorescence and absorption-spectrophotometry has been the necessity for individual sharpline sources for each element. Multi-cathode lamps have recently been manufactured for absorption but usually include no more than two elements. Continuous sources have not been used for absorption measurements as extremely high quality monochromators would be required, however a continuous source could be used for atomic-fluorescence spectrophotometry and a much simpler monochromator can be used.

With a continuous excitation source, such as a high power xenon arc lamp, many elements may be determined in one solution by atomic-fluorescence spectrophotometry by simply scanning a portion of the spectrum.

CHAPTER VI

THE SPECTROPHOTOMETRIC DETERMINATION OF TIN IN STEEL

SUMMARY

The application of a spectrophotometric method to the determination of tin in steel samples is described.

After dissolving the sample in sulphuric acid tin (IV) is separated from the bulk of ferrous ion by extraction as the complex iodide into benzene from a perchloric acid - sodium iodide solution of high ionic strength.

The extracted stannic iodide complex is then stripped from the organic phase into dilute sulphuric acid and, after the addition of gelatin and an aqueous solution of pyrocatechol violet, the solution is adjusted to pH 2.2. After a short development time the absorbance of the solution is measured at 642 mμ against a reagent blank taken through the procedure.

The development and optimisation of conditions for maximum colour development will be desribed together with an investigation of alternative dispersing agents in place of the gelatin.

INTRODUCTION

The most widely used methods for the spectrophotometric determination of trace amounts of tin are those based upon reaction with dithiol, (4-methyl-1,2-dimercaptobenzene) [133 to 135] and phenylfluorone, (2,3,7-trihydroxy-9-phenyl-6-fluorone). [136 137]. Other methods, based on the reducing action of stannous tin, include the reduction of cacotheline [139] in acid solution to give a violet colour, and the reduction of heteropoly molybdic acids to give molybdenum blue [5].

All these methods suffer interference from foreign metal ions and, in consequence, require a careful preliminary separation of the tin.

The most widely used method of separation consists of volatilisation of stannic bromide by distillation from a hydrochloric-hydrobromic acid solution of the sample.

The volatilisation method is effective but requires rigid control of conditions and is very time-consuming.

In the present examination a search was made for a more rapid and reliable spectrophotometric method following a solvent extraction procedure for the isolation of tin from interfering metal ions.

The extraction of Sn (IV) as the iodide by a non-polar solvent, benzene, from aqueous solution has been described by Gilbert and Sandell [137]. The extraction procedure is more rapid and convenient than the distillation procedure, and it can be applied advantageously to the separation of microgram amounts of tin from steel samples.

A search of the literature showed that many colorimetric reagents for tin exist, but few possess high sensitivity.

A preliminary investigation of a large number of possible reagents, including a wide variety of tri-phenyl methane derivatives, showed that only three reagents warranted closer examination. These included Pyrogallol Red, Bromopyrogallol Red and Catechol violet which Malat has described [141] [142] as a possible spectrophotometric reagent for tin.

It was decided to investigate the use of these three reagents and to select one for the determination of tin following a benzene-iodide solvent extraction procedure.

EXPERIMENTAL

APPARATUS

Spectrophotometer	Beckman D.B with 1 cm. glass cuvettes.
pH. meter	E.I.L. Vibron. Model 39A

REAGENTS

Standard 10^{-3}M Tin (IV) solution:-

0.1187 g. of tin metal (AR.) was dissolved in 20 ml. of concentrated sulphuric acid and, after cooling, added to 250 ml. of ice-cold water. A further 60 ml of concentrated sulphuric acid were carefully added and the solution was then transferred to a 1 litre volumetric flask and diluted to the mark.

Standard 10^{-3}M. Catechol violet solution:-

0.286 g. Catechol violet (AR.) was dissolved in distilled water and diluted to 1 litre.

Gelatin Solution:-

A 1.0% aqueous solution of gelatin was prepared freshly each day.

Wash solution:-

228.5 g. of sodium perchlorate was dissolved in distilled water and 100 ml of 60% perchloric acid (AR.) added. The mixed solutions were then diluted to 500 ml.

Prior to the need of wash solution 0.75 g. of sodium iodide were added to each 10 ml of solution taken, and thoroughly mixed.

Dilute Sulphuric Acid.

1:4 aqueous solution of sulphuric acid was prepared as required.

Hydrogen peroxide solution:- 20 volume (AR)
Perchloric acid:- 60% aqueous (AR)
Benzene:- (AR)
Sodium Iodide:- (G.P.R)
Electrolytic Iron Powder:-

RECOMMENDED PROCEDURE

1. Preparation of Calibration Curve

Into a series of 100 ml beakers weigh 1.0 g. amounts of electrolytic iron powder and add from a pipette 0 to 5.0 ml aliquots of 10^{-3}M tin (IV) solution.

Dissolve the mixture in 25 ml of 1:4 sulphuric acid, warming to assist solution. Transfer the cooled solutions to 100 ml. volumetric flasks and dilute them to their marks with distilled water.

Pipette 10 ml. aliquots of these solutions into a series of 100 ml. separating funnels and add 7.1 ml of 60% perchloric acid and 7.5 g. of sodium iodide to each. Add a further 3 ml. of distilled water washing down any solid sodium iodide adhering to the necks of the funnels. The final solutions thereby obtained are _ca._ 2.5 M in perchloric acid and sodium iodide.

The stannic iodide produced is then extracted into 10 ml. amounts of benzene by shaking the funnels for one minute.

After discarding the lower aqueous phases, the remaining benzene phases are washed with 10 ml. of wash solution, and the washings are discarded.

To each separating funnel add 10 ml. of _ca._ 0.5 M sulphuric acid and shake the funnels for 30 sec. in order to back extract the tin into the aqueous phases. Run the aqueous extracts into a series of 100-ml beakers. To the remaining benzene phases add 10 ml. of distilled water and, after shaking the funnels for 30 secs., add the aqueous solutions to the 100-ml beakers.

To the combined aqueous solutions add 2.0 ml. amounts of 1% gelatin solution and 5.0 ml. of 10^{-3}M. Catechol violet solution. Dilute the solutions to approximately 50 ml. with water and adjust the acidity of each solution to pH 2.2 by the addition of dilute ammonia solution, using a pH meter.

Finally, transfer the solutions to a series of 100 ml. volumetric flasks and dilute them to their marks with distilled water.

Measure the absorbance of each solution after 10 minutes in 1-cm. cuvettes at 642 mμ . against the reagent blank, (containing no added Sn(IV) solution,) taken through the procedure.

A plot of absorbance against tin concentration is a straight line passing through the origin.

2. ANALYSIS OF STEEL SAMPLES

Dissolve a suitable weight of sample (usually 0.5 to 2.0 g), containing 50 to 500 μg. of tin, in 25 ml. of 1:4 sulphuric acid. The addition of a small quantity of hydrogen peroxide solution will assist solution and formation of Sn(IV) in the presence of large amounts of titanium. The small amount of ferric iron so produced does not affect later extractions.

Dilute the solutions to 100 ml. and continue as in the preparation of calibration curve.

RESULTS

A summary of the results obtained by the application of the recommended procedure to the analyses of a number of British Chemical Standard Certificated steels are shown in Table XIX.

TABLE XIX

ANALYSES OF BRITISH CHEMICAL STANDARD STEELS

Sample No.	Sample Weight	Tin Found %	Certificate Value %
BCS 273	1.0 g.	0.067	0.06_5
275	1.0 g.	0.040	0.04_0
277	2.0 g.	0.003	<0.005
320	1.0 g.	0.089	0.085
321	2.0 g.	0.014	0.014
323	1.0 g.	0.023	0.024
325	1.0 g.	0.046	0.046

The values reported in column three of tin found are the average of two or three results.

To gain a better idea of the accuracy of the method sample B.C.S. 325 was analysed several times and the results are shown in Table XX.

TABLE XX

REPLICATE ANALYSES OF B.C.S. 325

Sample No.	Tin Found %	Average %
BCS 325 1.0 g samples	0.042 0.042 0.045 0.046 0.046 0.047 0.049 0.049 0.050	0.046

It will be seen that at a concentration of ca. 0.046% tin one cannot argue the third decimal place to closer than ± 0.004%.

These results however are in good agreement with the certificated values which are the average of a number of inter-laboratory results. It will in fact be seen from the B.C.S. certificate that results for sample B.C.S. 325 range from 0.42 to 0.051%. These latter results were obtained by the standard titrimetric iodate method after reduction with aluminium. Some laboratories also used a preliminary separation of tin as the sulphide.

DEVELOPMENT OF PROCEDURE

From the literature survey untertaken the most promising spectrophotometric reagents for tin seemed to be based upon tri-aryl methane derivatives.

A preliminary investigation was made of a large number of tri-aryl methane derivatives including Methy Violet (C.I.42535), para-Rosanaline (C.I. 42500), Brilliant Green (C.I. 42040), and Malachite Green (C.I. 4200). The similar compounds Rhodamine B (C.I. 45170), Erythrosin (C.I. 45430), Bromopyrogallol Red, Pyrogallol Red and Catechol Violet were also investigated.

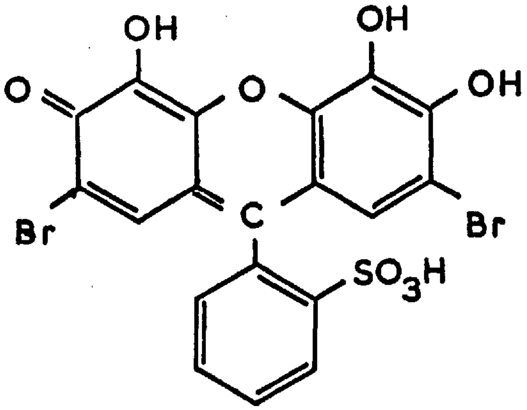
Of these reagents only the last three mentioned, viz. Bromopyrogallol Red, Pyrogallol Red and Catechol Violet, seemed to be suitable reagents.

Further preliminary investigations of these three reagents were therefore undertaken.

1. PRELIMINARY INVESTIGATIONS

1.1 BROMOPYROGALLOL RED
(B.P.R.)

Structure:-



REAGENTS

Standard 10^{-3}M B.P.R.

0.0558 g. of B.P.R. was dissolved in ethanol and diluted to 100 ml.

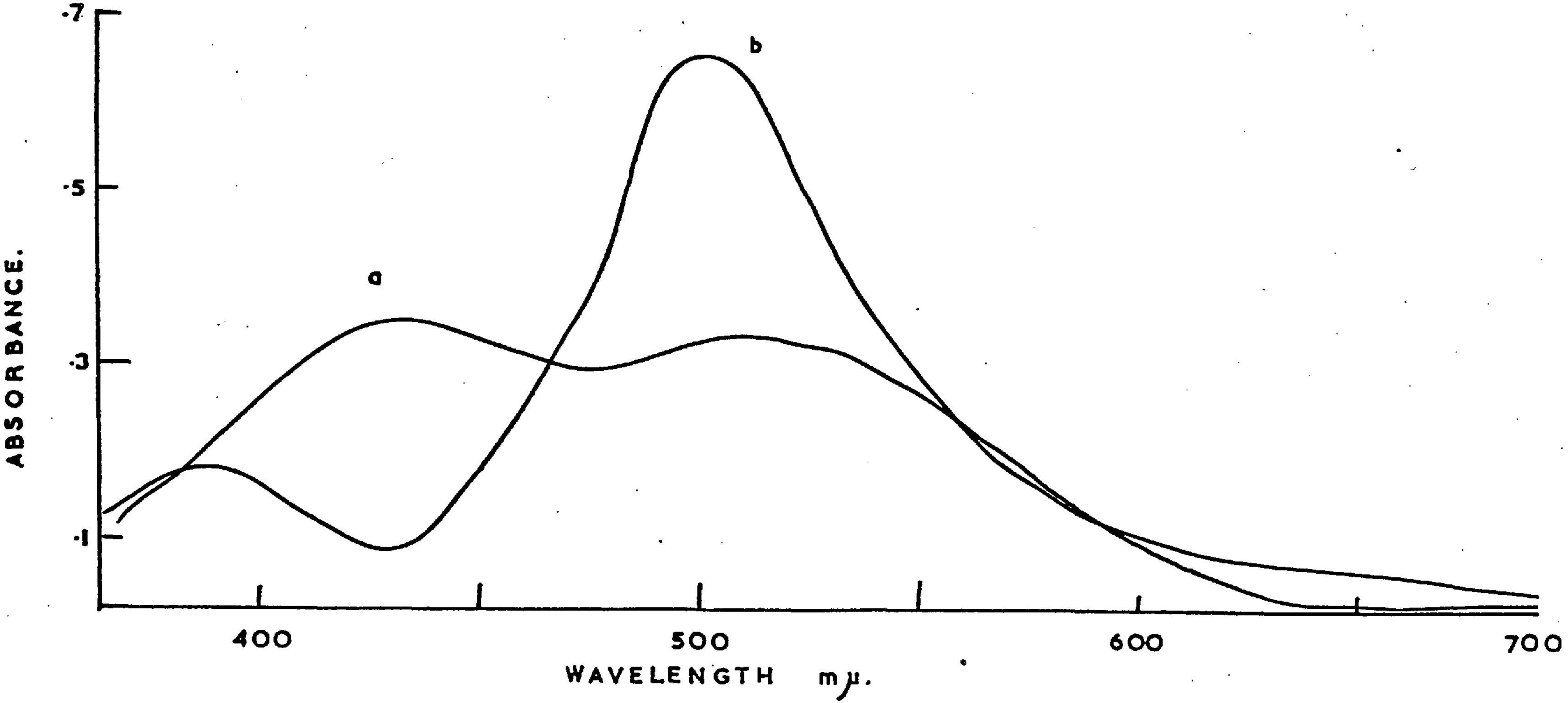
Standard 10^{-3}M Sn (IV).

Prepared as given under recommended procedure.

Preliminary Spectra

Figure XXXIV shows the absorption spectra for B.P.R. and its tin complex buffered at pH 1.6.

FIG. XXXIV.



Curve (a) was prepared by diluting 10 ml. 10^{-3}M B.P.R. to 100 ml with distilled water after adjustment to pH 1.6 with acetic acid. The absorbance was then measured in 0.5 cm cuvettes against a distilled water blank after 5 minutes.

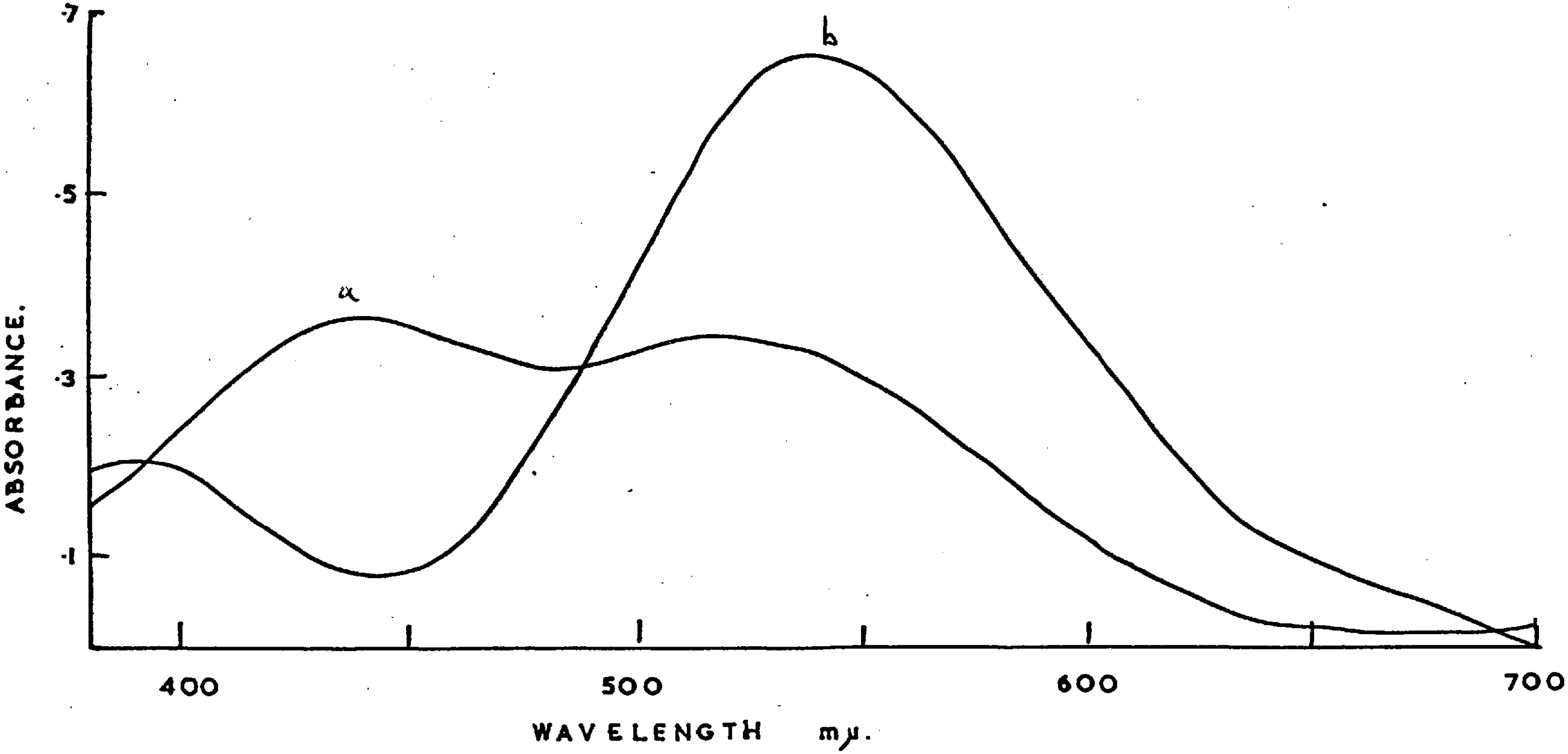
Curve (b) was prepared similarly but with the addition of 5 ml 10^{-3}M Sn(IV) solution.

It will be seen from these curves that the maximum absorption difference between the complex and reagent occurs at about 505 mμ. and gives an approximate molecular extinction coefficient of about 13,600.

Figure XXXV shows the similar absorption spectra as prepared for the first figure but with the addition of 2 ml of 1% gelatin to each solution. A shift in the complex absorption peak from 505 to 545 mμ was observed accompanied with a slight decrease in absorption giving a preliminary extinction coefficient of about 12,800.

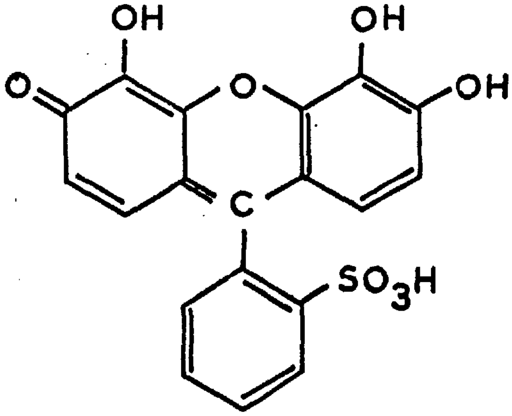
Similar experiments were carried out at pH 1.0 and pH 3.0 and similar spectra but lower values of molecular extinction coefficient were obtained.

FIG. XXXV.



1.2. PYROGALLOL RED
(P.R.)

Structure:-



REAGENTS

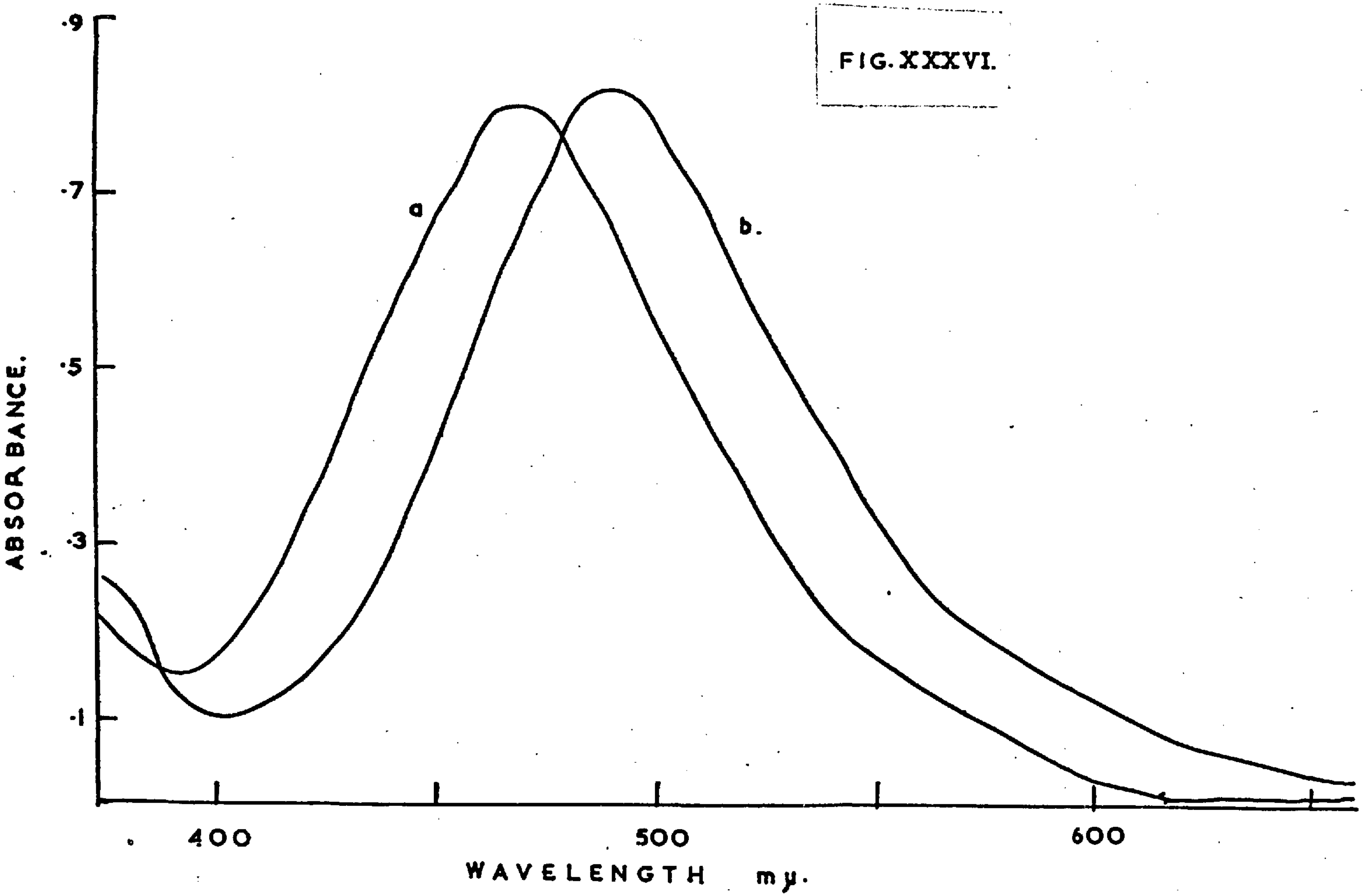
A 10^{-3}M solution of P.R. was prepared by dissolving 0.040 g. of P.R. in ethanol and dilution to 100 ml.

Preliminary Spectra

As with the bromo derivative preliminary absorption spectra were obtained for the reagent and its tin complex at pH 1.6 and the results shown in Figure XXXVI.

Curve (a) was prepared by diluting 10 ml of 10^{-3}M reagent to 100 ml and buffered at pH 1.6. The absorbance was then measured in 1 cm cuvettes against water blank after 5 minutes.

FIG. XXXVI.



Curve (b) was prepared in a similar manner but with the addition of 5 ml 10^{-3}M Sn(IV) solution.

Maximum absorption difference between the complex and reagent occurs at 510 mμ giving a preliminary molecular extinction coefficient of about 6,000.

The experiment was then repeated in the presence of 2 ml 1% gelatin as in the case with B.P.R. The absorption spectra are shown in figure XXXVII.

A shift in the complex peak was observed from 490 to 514 mμ and the maximum absorption difference between the complex and reagent shifted from 510 to 532 mμ . giving a molecular extinction coefficient of about 8,800, and increase of *ca.* 2,800 over the value obtained in the absence of gelatin.

Experiments conducted at pH 1.0 and 3.0 again showed little change in the form of spectra but again lower extinction coefficients were observed.

It was, therefore, seen that for both B.P.R. and P.R. optimum pH conditions were obtained at about pH 1.6 and that B.P.R. was about twice as sensitive as P.R. in the absence of gelatin and about one and a half times as sensitive in the presence of gelatin.

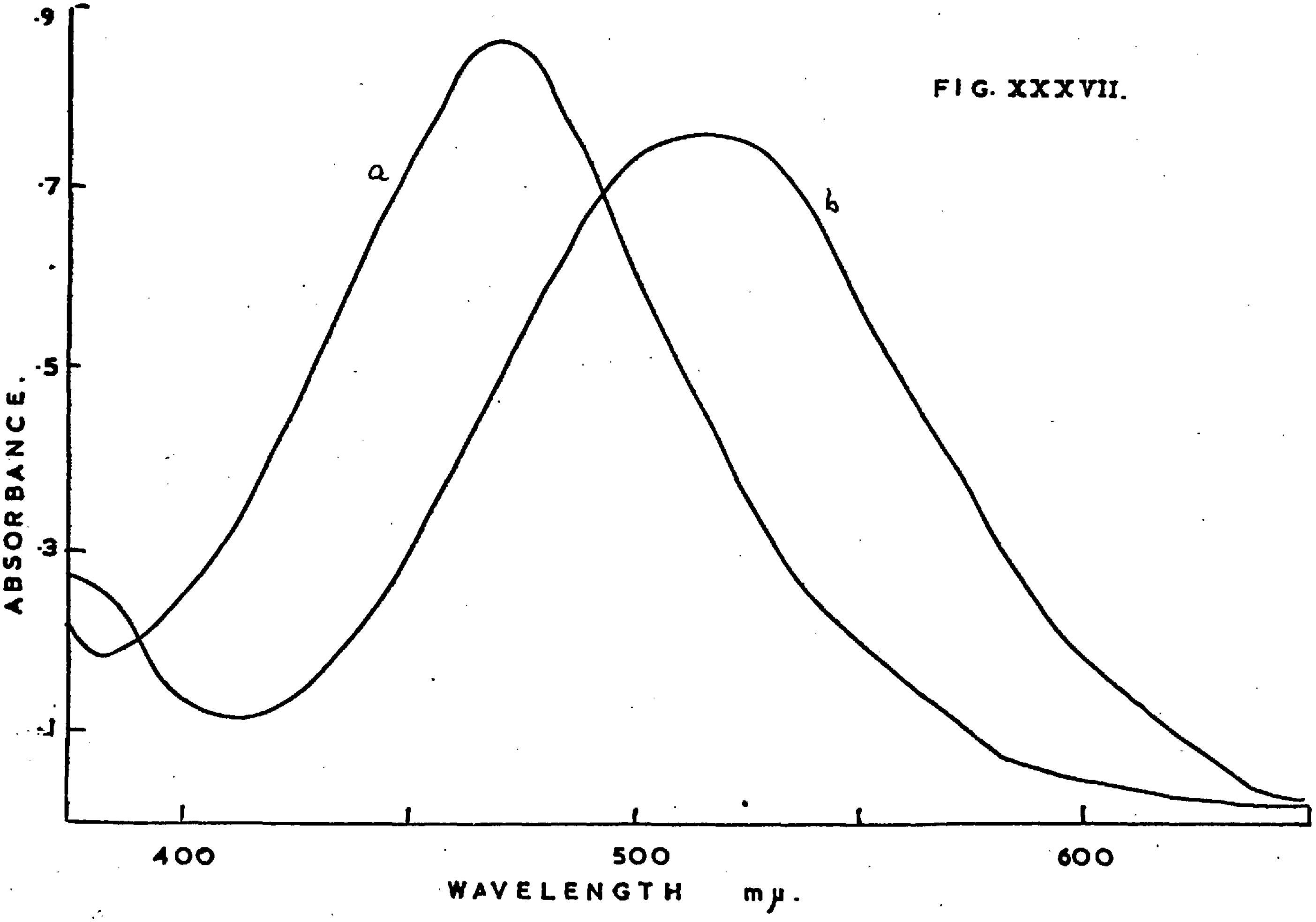
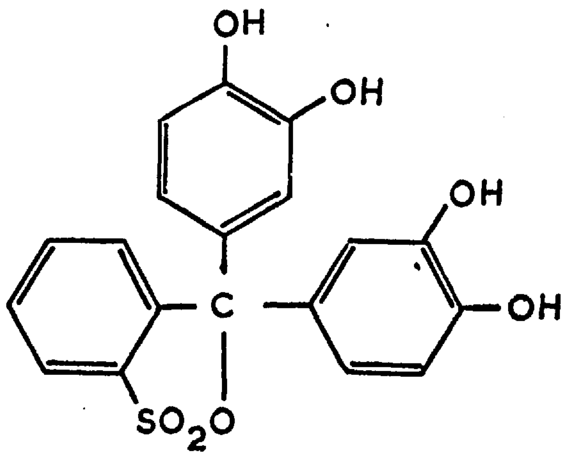


FIG. XXXVII.

1.3 CATECHOL VIOLET

Structure:-



REAGENT

A 10^{-3}M solution was prepared by dissolving 0.0286 g in distilled water and dilution to 100 ml.

Preliminary Spectra

Preliminary absorption spectra for catechol violet and its tin complex were obtained at pH 2.0. Figure XXXVIII shows the absorption spectra for catechol violet, (5 ml. 10^{-3}M diluted to 100 ml, curve a), and its tin complex (5 ml 10^{-3}M reagent + 0.5 ml 10^{-3}M Sn (IV), curve b), measured in 1-cm cuvettes versus distilled water after 5 minutes. Figure XXXIX shows

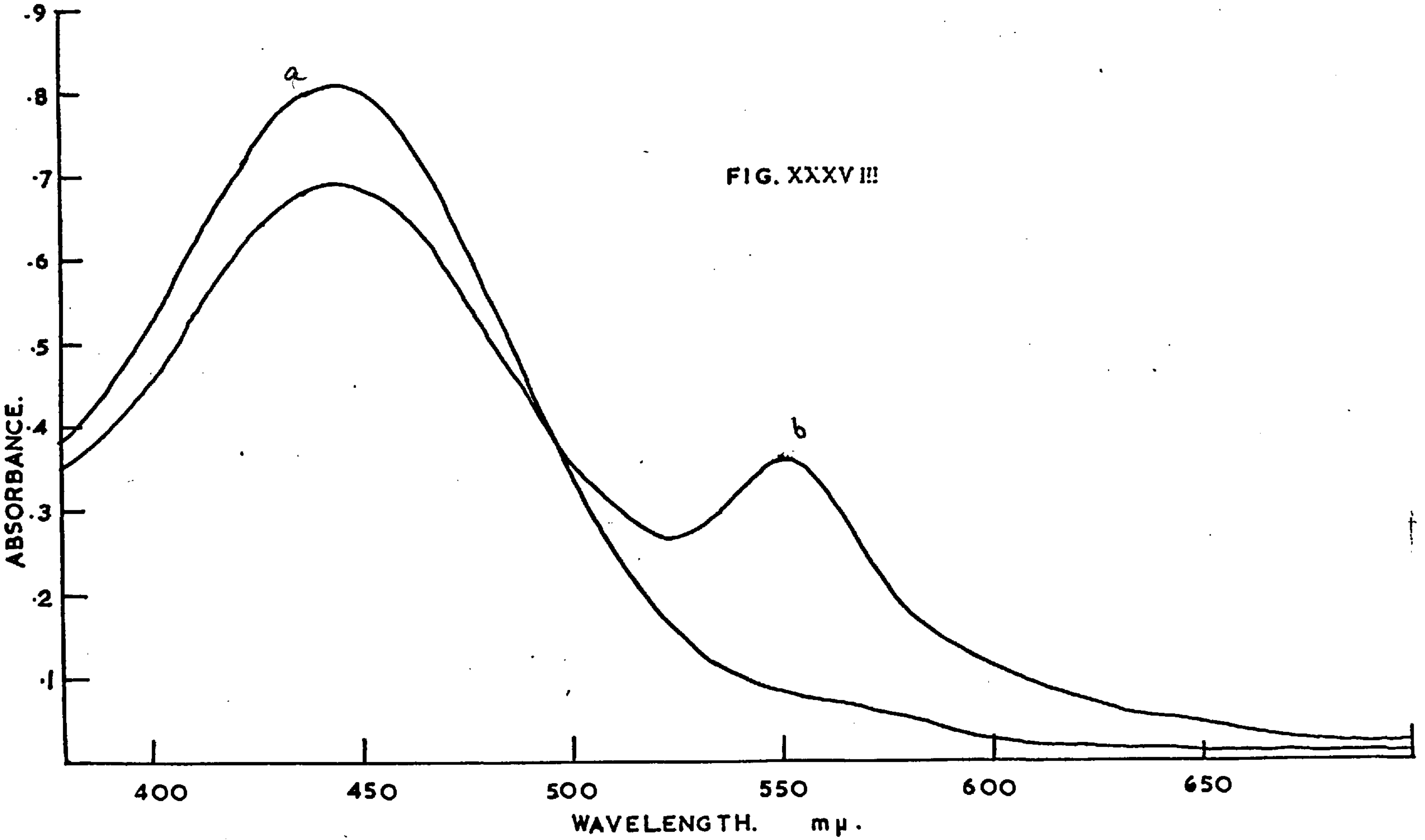


FIG. XXXVIII

a
b
ABSORBANCE.
·9
·8
·7
·6
·5
·4
·3
·2
·1
400
450
500
550
600
650
WAVELENGTH. mμ.

the absorption spectra of the same concentrations of catechol violet and its tin complex at pH 2.0 but in the presence of 0.02% gelatin.

It will be seen that in the presence of gelatin there is a shift in the Catechol violet-tin (IV) absorption peak from 550 to 642 mμ. It will also be seen that in the presence of gelatin there is a considerable increase in the absorption difference between the complex and reagent and at the complex absorption peak a molecular extinction coefficient of about 50,000 was obtained.

From the preliminary spectra and extinction coefficients Catechol violet was selected for future determination of the tin.

2. OPTIMISATION OF CONDITIONS FOR MAXIMUM COLOUR DEVELOPMENT OF THE CATECHOL VIOLET - TIN (IV) SYSTEM.

2.1 pH

The optimum pH for maximum colour development was obtained by preparing a series of solutions each containing 5 ml 10^{-3}M catechol violet, 1 ml 10^{-3}M Sn(IV) and 2 ml 1% gelatin solution buffered at varying pH values. The final pH of each solution was measured with a pH meter and the solutions diluted to 100 ml. The absorbance of each solution was measured in 1-cm cuvettes against a reagent blank buffered to the same pH.

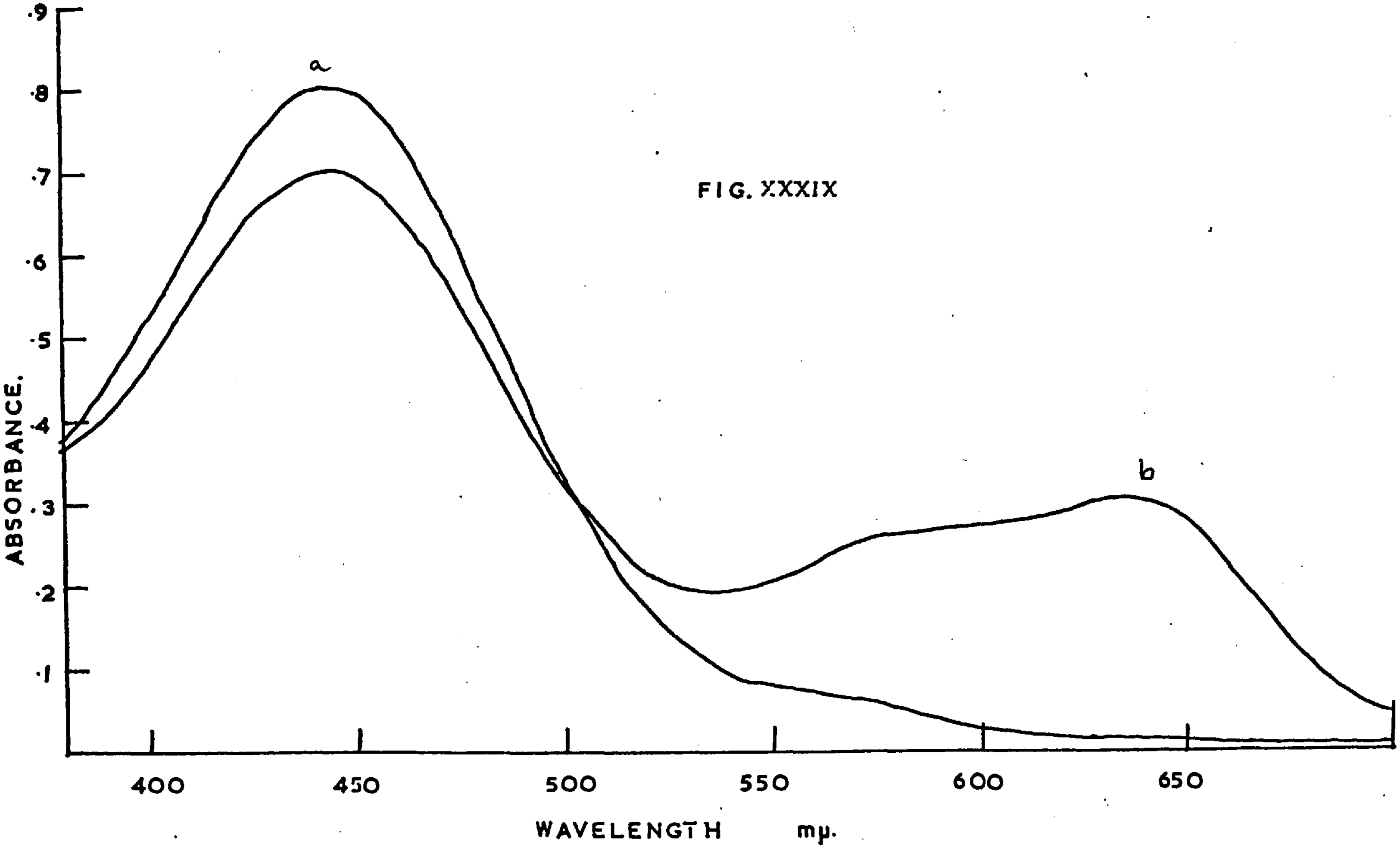


FIG. XXXIX

·9
·8
·7
·6
·5
·4
·3
·2
·1
ABSORBANCE.
a
b
400
450
500
550
600
650
WAVELENGTH mμ.

From the plot of absorbance against pH shown in figure XL a maximum was seen at pH 2.2.

2.2. REAGENT EXCESS

The absorbancies of a series of solutions containing 1 ml. 10^{-3}M Sn (IV) and a 1 to 32 fold molar excess of catechol violet in the presence of gelatin and buffered to pH 2.2 were measured against reagent blanks containing similar amounts of catechol violet.

Maximum absorbance was reached at *ca.* a 3 fold molar excess as seen in figure XLI above a 3 fold excess there is a gradual decrease in absorbance with increasing reagent concentration.

2.3. GELATIN CONCENTRATION

To a series of solutions containing 5 ml 10^{-3}M Catechol violet and 1 ml 10^{-3}M Sn (IV) solutions were added 0 to 5.0 ml 1% gelatin solution. After adjustment to pH 2.2 the solutions were diluted to 100 ml and the absorbance of each solution measured at 642 mμ against reagent blanks.

It will be seen from figure XLII that a maximum is reached at about 0.01% final gelatin concentration. The absorbance

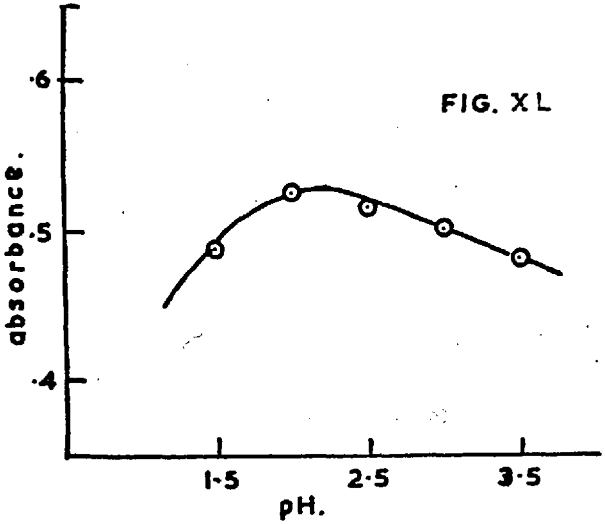


FIG. XL

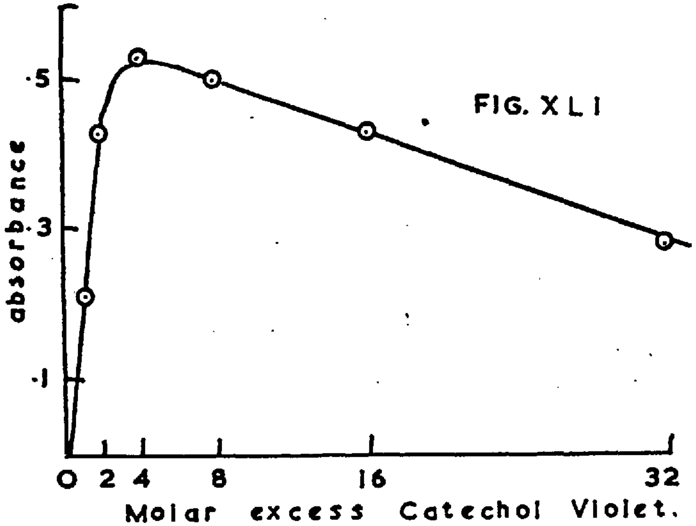


FIG. XLI

FIG. XLII

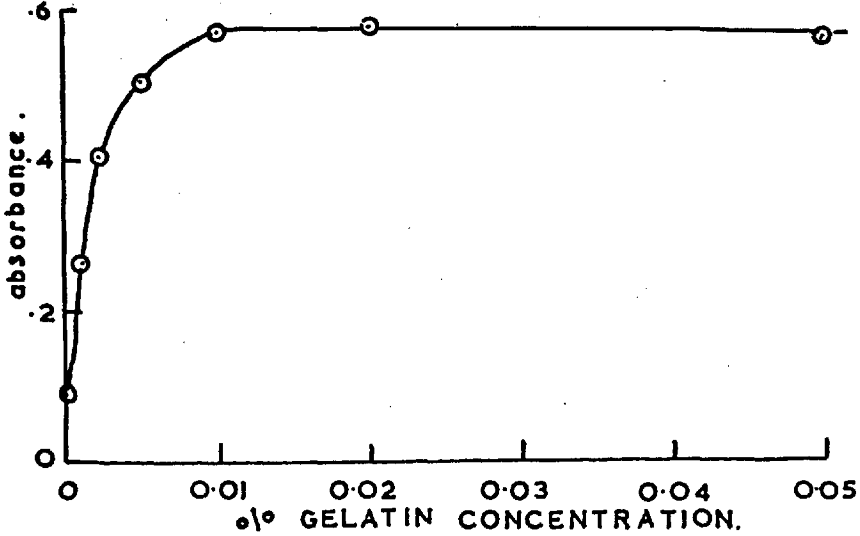
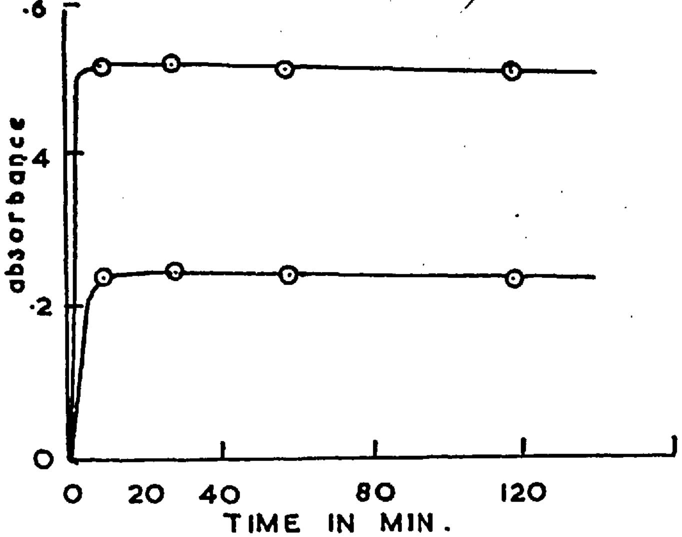


FIG. XLIII



remains constant to 0.02% gelatin but above this concentration there is a gradual decrease in absorbance.

2.4 DEVELOPMENT TIME

The maximum colour of the Catechol violet - tin (IV) complex was found to develop within one minute of mixing and to remain constant for about 2 hours.

Beyond 2 hours a gradual decrease is then observed with increasing time.

Large amounts of tin caused precipitation after several hours, but this may be due to inadequate addition of gelatin.

Figure XLIII shows the absorbance-time plots for both 1.0 and 0.5 ml of 10^{-3}M Sn (IV) solutions developed in the usual way.

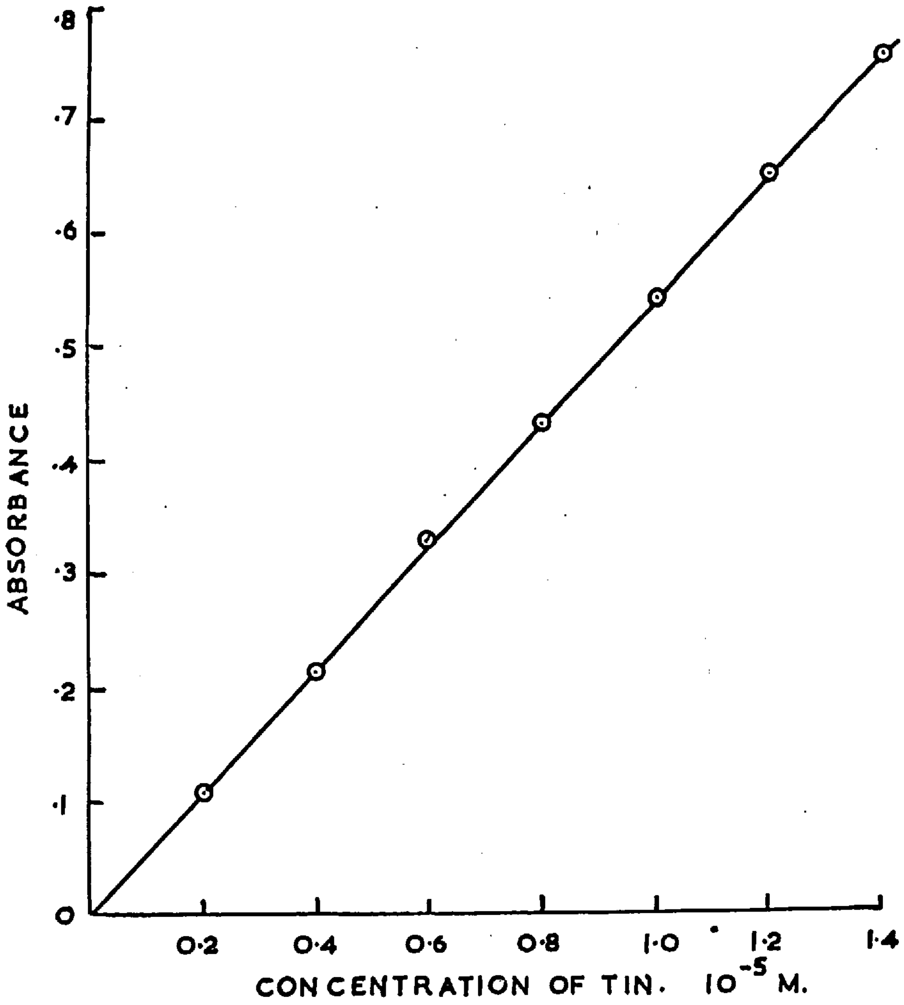
3. LAMBERT-BEER LAW CHECK

With the established optimum conditions a calibration curve was prepared in the usual manner.

Beer's law was obeyed between 0.2 10^{-5}M and 1.4 10^{-5}M final tin (IV) concentration, giving a molecular extinction coefficient of 55,000 at 642 mμ.

FIGURE XLIV

FIG. XLIV


ABSORBANCE
·8
·7
·6
·5
·4
·3
·2
·1
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
CONCENTRATION OF TIN. 10^{-5} M.

4. NATURE OF COMPLEX

A continuous variation plot measured at 642 $m\mu$ (figure XLV) exhibited clear indication of a 2:1 Catechol violet : tin(IV) complex. This was also verified at both higher and lower wavelengths, no other species being found.

Figure XLVI shows a mole-ratio plot for the same system, and again there is indication of a 2:1 catechol violet: tin (IV) complex.

The results obtained from a slope-ratio plot were not conclusive. However, the value of 2:1 does agree with Malat's[141] published results.

5. INTERFERENCES

Bearing in mind that a benzene-iodide extraction of tin (IV) was to be used for isolation of tin from steels, only a short list of possible iodide extractable interfering metal ions was investigated.

Two hundred-fold molar excesses of antimony (III), bismuth, gallium, germanium and mercury (II) interfered by the formation of precipitates, but no interference was observed from aluminium, arsenic (III), cadmium, iron (II), indium, lead, thallium (I) or zinc.

FIG.XLV

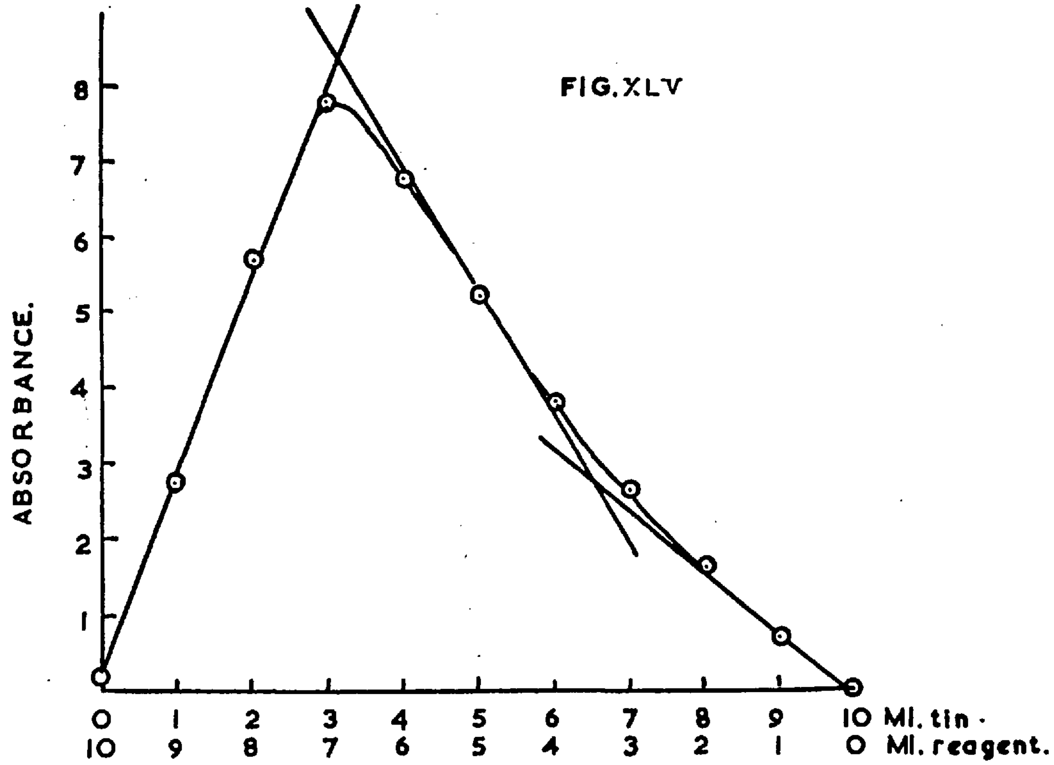
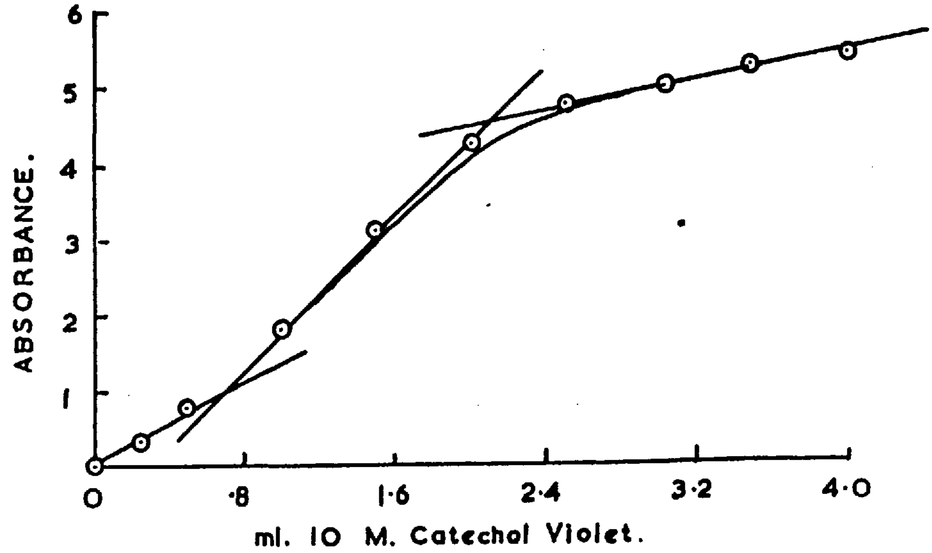


FIG. XLVI



6. SOLVENT EXTRACTION

According to Gilbert and Sandell [137], tin (IV) may be selectively and quantitatively extracted as the iodide into benzene.

Effective separation of tin requires conversion of most of thetin in the aqueous phase into undissociated SnI_4, which is favoured by high iodide and high hydrogen ion concentration. In addition a high electrolyte concentration increases the extractability of tin by its salting-out effect on the stannic iodide.

Because of the low complexing ability of the perchlorate ion acidification may beeffectedwith perchloric acid.

In a solution of 2.5 M perchloric acid and 2.5 M sodium iodide the extraction coefficient $\left((\mathrm{SnI_4})_{\mathrm{Benzene}} / \Sigma(\mathrm{Sn})_{\mathrm{H20}} \right) \simeq 2{,}100$ which should be sufficiently high for a satisfactory recovery of microgram amounts of tin with a single extraction.

The recovery of tin amounts to at least 99% under these conditions. For trace analysis a more complete extraction is unnecessary, however should a greater recovery be required a second extract could be made although interference from germanium and antimony may then be obtained.

Chloride interferes with the extraction procedure to the extent that extraction drops to ca. 95% in 0.1 M chloride solution. Chloride may be removed by fuming the solution with sulphuric acid, providing a concentration of 0.5 M sulphuric acid is not exceeded in the final solution.

Fluoride in very small amounts interferes seriously and must be removed by fuming with sulphuric acid.

The extraction of microgram amounts of tin from 20 ml aqueous solution 2.5 M in perchloric acid and sodium iodide into 10 ml of benzene was investigated and found to be satisfactory. The benzene extract was washed with 10 ml of aqueous solution of total molarity ca. 5M (i.e. ca. 1.5 M $HClO_4$, ca. 0.5M NaI and ca. 3.0 M $NaClO_4$). The tin was then back-extracted from the benzene phase into 10 ml. of 0.5 M sulphuric acid by shaking the mixture for 30 seconds. Finally the aqueous solution of isolated tin was developed colorimetrically with Catechol violet and gelatin in the usual way.

7. STANDARD DEVIATION

(Precision of Method)

The precision of the method was obtained from the multiple analyses of twelve samples each containing 1 g of electrolytic iron powder and 5 ml. 10^{-3}M tin (IV) by the recommended procedure.

The results are shown in Table XXI from which it will be seen that at the level of tin concentration investigated there is a standard deviation of 2.4%.

TABLE XXI

Precision of Method.

No. n	Absorbance X 1000	Deviance D	D^2
1	260	11	121
2	247	2	4
3	249	0	0
4	255	6	36
5	250	1	1
6	242	7	49
7	242	7	49
8	245	4	16
9	250	1	1
10	255	6	36
11	249	0	0
12	240	9	81
	Mean = 249	Total =394	

$$\text{Standard Deviation} = \sqrt{\frac{\Sigma D^2}{(n-1)}}$$

$$= \sqrt{\frac{394}{(12-1)}}$$

$$= \underline{6}$$

$$\%\ \text{Standard deviation} = \frac{6}{249} \times 100 = 2.4$$

INVESTIGATION OF POSSIBLE ALTERNATIVE DISPERSING AGENTS

Further investigations were carried out with regard to improved sensitivity resulting from possible alternative dispersing agents to gelatin.

Examinations showed that cetyl-trimethyl-ammonium bromide (cetavlon) gave an increased sensitivity to the Catechol violet - tin system.

Preliminary absorption spectra showed a further shift in the complex peak to 662 mμ, together with greatly increased absorption.

Figure XLVII shows the absorption spectra of catechol violet and its tin complex in the presence of cetavlon. Curve (a) was prepared by diluting a mixture of 1.0 ml. 10^{-3}M Sn (IV), 5 ml 10^{-3}M Catechol violet and 5 ml 1% cetavlon solutions to 100 ml after adjustment to pH 2.2. The absorbance was then measured in 1 cm cuvettes versus distilled water after 5 minutes. Curve (b) was prepared as above but with no addition of tin solution.

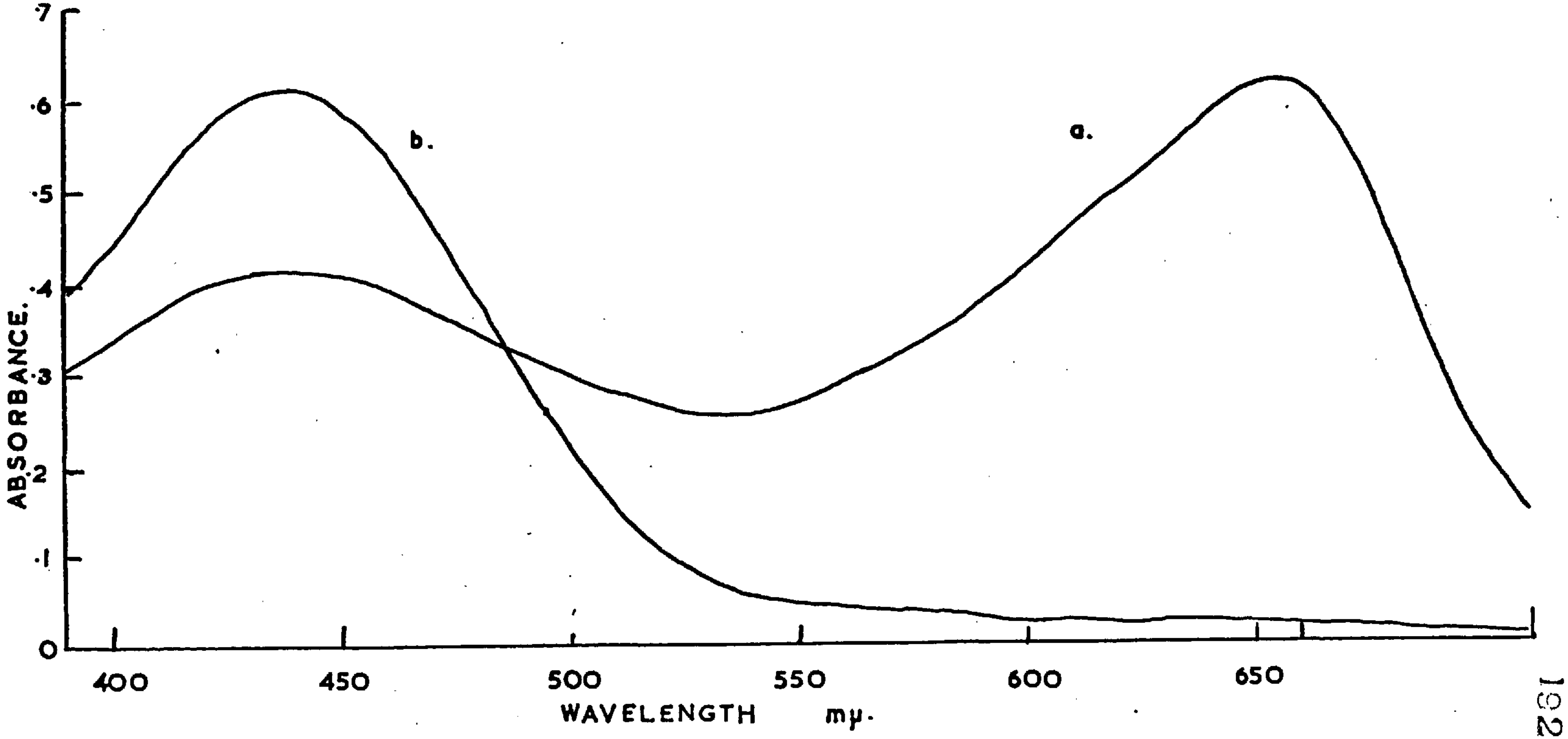
Optimum conditions for maximum colour development were re-established. pH, reagent excess and development time were all similar to the corresponding tin-catechol violet-gelatin system. The optimum amount of cetavlon concentration was found to be 0.002% in the final solution.

The ratio of ligand: metal in the complex was investigated by both the continuous variation method and mole-ratio method and was found to be the same as before, i.e. 2:1.

A calibration curve was prepared over the range from 10^{-6} to 10^{-5}M tin in the final solution. Lambert - Beer's law was obeyed and a very high extinction coefficient obtained, viz. $\varepsilon_{662m\mu} = 95,600$.

Attempts to combine this sensitive spectrophotometric technique with the benzene-iodide extraction procedure met with failure. Small amounts of iodide/iodine present in the

FIG. XLVII


·7
·6
·5
·4
·3
·2
·1
0
ABSORBANCE.
b.
a.
400
450
500
550
600
650
WAVELENGTH mμ.

aqueous back extracted tin solution caused precipitation of the cetavlon thereby giving erroneous results.

However, it has been shown that in the absence of iodide this technique is by far the most sensitive spectrophotometric determination of tin.

CONCLUSIONS

The phenomenon of a bathochromic shift in the absorption spectrum of the Catechol violet - tin (IV) complex, caused by short range electrostatic forces on the surface of the micelle double layers of cationic micelle forming detergents, (e.g. gelatin), provides a sensitive means of determining traces of tin.

The spectral characteristics, optimisation of conditions for maximum colour development and complex nature of the tin (IV) - Catechol violet - gelatin system were established and found to be in close agreement with Malat's results.

Combination of the Catechol violet finish with a preliminary benzene-iodide extraction procedure provided a rapid and simple means for the determination of tin in steel. A single determination may be carried out within 1½ hours.

CHAPTER VII

THE DETERMINATION OF TIN BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY

SUMMARY

An investigation is carried out into the determination of tin by atomic-absorption spectrophotometry.

The most suitable line for absorption mreasurements is seen to be at 2863Å.

The sensitivity of the determination of tin in an air-acetylene flame is very poor as a result of the formation of stable oxides. For example in aqueous solutions containing 10^{-2}M tin absorbance values of only 0.01 to 0.02 are obtained. The values are improved by the use of solvent extraction into organic solvents which are then sprayed directly into the flame.

Even with solvent - extraction techniques insufficient sensitivity is obtainable in air-acelytene flames for application to the determination of trace amounts of tin.

An investigation is therefore carried out into the use of a more reducing flame obtainable from the combustion of nitrous oxide and acetylene.

INTRODUCTION

As yet there are no published procedures for the analytical application of atomic-absorption spectrophotometry for the determination of tin. There are, however, a number of references to the sensitivity limits for tin by this technique[96, 101, 102, 119, 158]. None of these, however, is very promising. The low sensitivities obtained result from the formation of stable tin oxides in the flame which bring about a reduction in the number of free ground-state atoms. With only a very small proportion of the tin existing as ground-state atoms, little absorption can occur.

The degree of dissociation of the stable tin oxides in the flame can be increased by using fuel-rich flames.

It was, therefore, decided to investigate the possible use of fuel-rich air-acetylene flames for the measurement of tin by atomic-absorption spectrophotometry in conjunction with solvent extraction into organic solvents which could be sprayed directly into the flame.

EXPERIMENTAL

APPARATUS

A unicam SP.900A atomic-absorption/flame-emission spectrophotometer, equipped with a 0-10 mV. Honeywell-Brown recorder, was used.

Two tin hollow-cathode lamps were used in these studies, one obtained from Hilger and Watts Limited, London, and latterly one obtained from Unicam Instruments Limited, Cambridge.

REAGENTS

A 10^{-2}M tin (II) solution was prepared by dissolving 1.187 g. of tin metal (AnalaR) in hydrochloric acid and diluting to 1 litre.

A 10^{-3}M tin (IV) solution was prepared by dissolving 0.1187 g. of tin metal in 20 ml of concentrated sulphuric acid. and, after cooling, adding to 250 ml of ice-cold water. A further 60 ml of concentrated sulphuric acid was added and the solution diluted to 1 litre.

PRELIMINARY SPECTRUM

Part of the ultraviolet region of the spectrum was scanned while the hollow-cathode lamp (Hilger and Watts), was operated at 10 mA and an analysing slit-width of 0.025 mm. was used. Principle emission peaks were obtained at 3034Å, 3009Å, 2863Å, 2841Å, and 2706Å.

The 2863 Å line, corresponding to the $5s^2\,5p^2\;{}^3P_2 - 5s^2\,5p'\,6s'\;{}^3P^o_2$ transition, was found, in common with others[96, 101, 102, 158], to be the most suitable for absorption measurements.

RESULTS

With the hollow-cathode lamp operating at the manufacturers recommended current and with a very fuel-rich flame (obtained with an air-pressure of 15 p.s.i. and maximum acetylene pressure), the absorbance of an aqueous solution containing 10^{-2}M tin was determined.

Very low absorbances, of the order of 0.01 to 0.02, were obtained.

It was therefore decided to use solvent extraction techniques and to spray the organic extract directly into the flame. This would have the added advantage from the higher input ratio into the flame with the experimental arrangement used.

Initial extractions were made as the undissociated stannic iodide into iso-butyl methyl ketone from controlled acid solutions. The ketone solution was aspirated under the same air pressure of 15 p.s.i. and with a very luminous flame.

Approximately 3 times the aqueous values were obtained provided measurements were made low down toward the base of the flame, e.g. a 4.10^{-3}M solution in iso-butyl methyl ketone gave an absorbance of about 0.03. When measurements were made at the top of the flame no signal at all was observed.

The extraction of tin cupferrate has been described by Morrison and Freiser [60] and by Stary [159]. It was decided to utilise this separation procedure for the concentration of tin into an organic solvent and to aspirate this directly into the flame.

25 ml of a 10^{-2}M tin (II) solution was made 1.1N in hydrochloric acid, and 0.25 g. of the ammonium salt of N - nitrosophenylhydroxylamine, (cupferron), was added. The solution was then extracted with 25 ml of iso-butyl methyl ketone and the extract aspirated into the flame at 15 p.s.i. Absorbances ranging from 0.125 to 0.187 were obtained depending on the ratio of fuel to air. Maximum absorbance was obtained

in the most fuel-rich flame, giving about a ten fold increase over the aqueous solution of similar concentration. The use of an alternative organic solvent, ethyl acetate, was also investigated. Similar amounts of tin (II) were extracted as its cupferrate from 1.1N hydrochloric acid into 25 ml of ethyl acetate and the organic extract sprayed into the flame under the same conditions as used before. Only one fifth of the corresponding ketone extract value was obtained.

The extraction and spectrophotometric determination of tin with 8 - hydroxyquinoline has recently been described by Eberle and Lerner [160], who extracted small quantities of tin (IV) into chloroform at pH 0.85 containing a controlled amount of chloride ion. The recommended extraction procedure was investigated and closely followed with the exception that the chloroform was replaced by iso-butyl methyl ketone as the combustion of chloroform produces obnoxious gases.

To a series of separating funnels were added 0 to 40 ml. aliquots of a 10^{-3}M tin (IV) solution, each solution having been adjusted to pH 0.85 with dilute ammonia or sulphuric acid solutions. All solutions were made to about the same volume of 45 ml. with pH 0.85 aqueous solution. To each funnel was added 20 ml of a 4% aqueous solution of 8 - hydroxyquinoline and 5 ml of a 20% aqueous solution of ammonium chloride, each solution having been adjusted to pH 0.85 with dilute sulphuric acid. The solutions were then extracted into 20 ml aliquots of *iso*-butyl methyl ketone and the solutions sprayed into the flame with an air pressure of 15 p.s.i. and maximum acetylene pressure.

The absorbances plotted against the final tin concentration gave a straight line (Fig. XLVIII), which shows an increase of about 40-50 fold over aqueous solutions of similar concentrations.

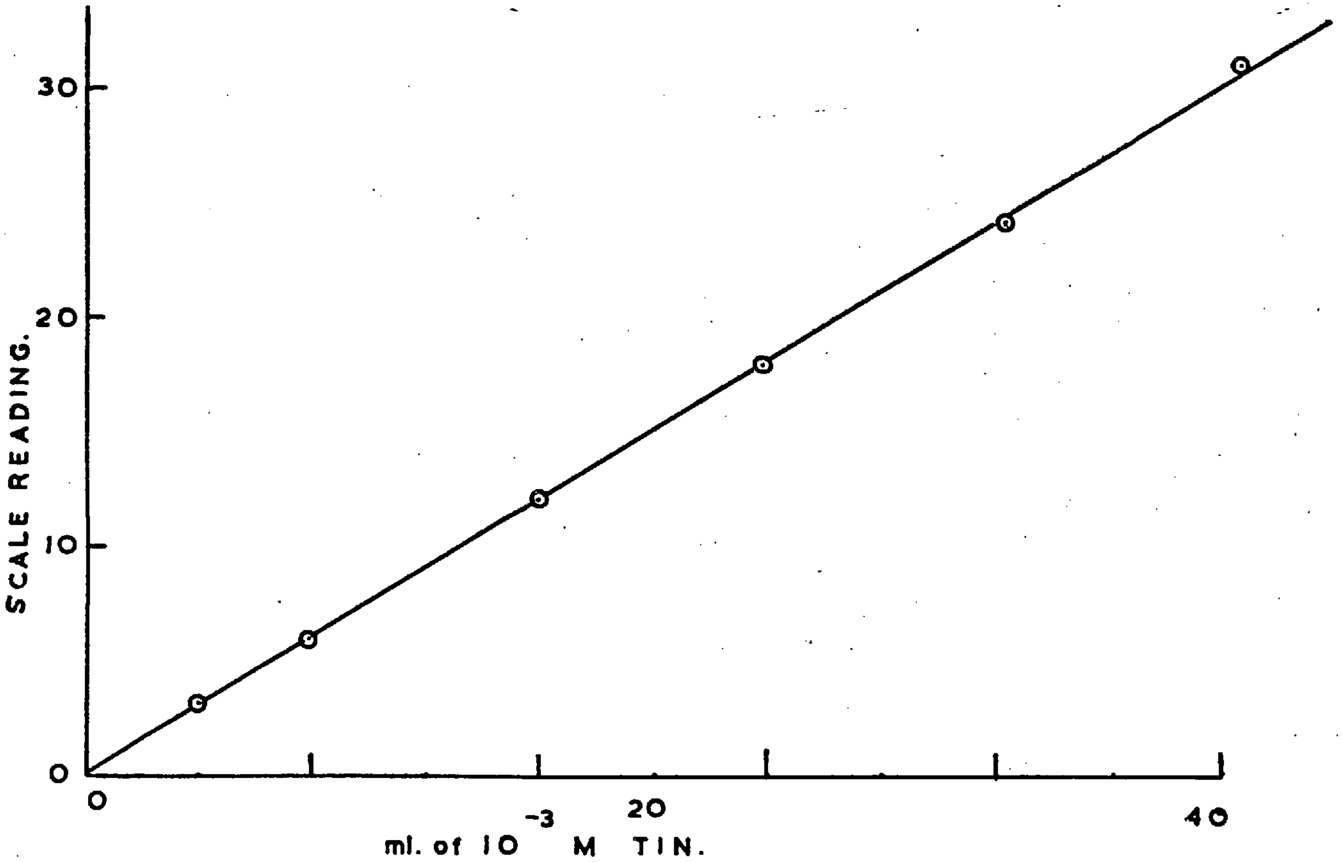
The sensitivity of the results obtained above are still far too low for application to trace determinations. It was, therefore, decided to reject the use of air-acetylene flames and investigate the use of a more reducing flame obtained from nitrous oxide and acetylene.

NITROUS OXIDE - ACETYLENE FLAMES

APPARATUS

The existing stainless-steel absorption head supplied by Unicam Instruments was replaced by a brass head of similar external dimensions. In place of the 7 cm line of 1 m.m. holes, as in the steel head, a slot about 5 cm. long and 0.015" wide

FIG. XLVIII.



was used. The acetylene gas jet at the base of the burner head assembly was also replaced with a brass jet of larger bore.

The nitrous oxide supply was obtained from a cylinder and its flow was regulated by use of a rotameter. The air supply was also controlled via a rotameter and allowed the flame to be first ignited on air-acetylene. A T - junction into the air supply enabled the nitrous oxide to be fed into the flame while a corresponding flow of air was decreased. By using two rotameters a smooth changeover from air to nitrous oxide was obtained. This considerably economised the useage of nitrous oxide and also provided a safe means of igniting the flame.

Replacement of the Hilger and Watts hollow-cathode lamp with the Unicam lamp considerably eased the pre-focussing of the emitted radiation onto the monochromator entrance-slit.

RESULTS

Using the 2863 Å line and with the nitrous oxide and acetylene gas controlled at 16 p.s.i. and 11 cm. manometer pressure respectively an aqueous 10^{-2}M solution was aspirated into the flame. A considerable increase in sensitivity over the conventional air-acetylene flame was observed, viz. 0.45 cf. 0.02 absorbance values for 10^{-2}M solutions.

However, considerable background fluctuations were obtained which prevented the determination of accurate absorbance values.

The fluctuations were thought to result from flame emissions. An investigation of longer and shorter wavelengths for absorption was, therefore, undertaken but the fluctuations were still obtained together with decreases in sensitivity.

It, therefore, became apparent that the use of atomic-absorption spectrophotometry in acetylene flames would have no benefit over existing spectrophotometric procedures.

SUGGESTIONS FOR FUTURE WORK

During the development of the spectrophotometric method for the determination of aluminium in steels, (Chapter I), an interesting reaction between aluminium and 8 - hydroxyquinaldine was observed. Such a reaction tended to contradict reports in the literature [43 161], where 8 - hydroxyquinaldine was used as a reagent for the removal of interferences prior to the determination of aluminium with 8 - hydroxyquinoline. Although not directly concerned with the initial project preliminary investigations into the nature of the aluminium - 8 - hydroxyquinaldine complex were undertaken. A commercial sample of 8 - hydroxyquinaldine, (B.D.H, Poole, England) was recrystallised twice from aqueous ethanol. The dried product melted at 73 °C (*cf.* reported value [153] of 74 °C).

Although aluminium does not form a coloured complex with 8 - hydroxyquinaldine, as indicated in Chapter I, it does form an extractable fluorescence species with excitation and emission peak values at 370 and 480 mμ respectively.

Preliminary measurements of the fluorescence intensity at various pH values showed a maximum at pH 8.5. An attempt was, therefore, made to construct a continuous variation plot at this pH. Extraction was made into chloroform and the fluorescence intensity was measured at 370/480 mμ. A value ca. 20:1, reagent: aluminium was obtained. This indicated that only part of the total aluminium present was reacting with the 8 - hydroxyquinaldine. Mole-ratio plots also gave similar values of 20:1.

Measurement of the fluorescence intensity in a completely non-aqueous medium indicated at 1:1 complex which agreed with the value given by Ohnesorge and Burlingame [162] for ethanolic solutions of aluminium and 8 - hydroxyquinaldine at an apparent pH of 8.

Further investigations into the aluminium - 8 - hydroxyquinaldine system should be carried out to determine the exact nature of the complex in both aqueous and non-aqueous media.

During the development of the spectrophotometric determination of tin a very sensitive reaction between tin (IV) and catechol violet in the presence of cationic detergent, cetavlon, was observed. Further work should be carried out to combine this sensitive determination with separation techniques for the isolation of tin from interferences. It may be possible to utilise the selective Benzene-iodide extraction procedure given in Chapter VI providing all traces of iodide-iodine are removed or complexed prior to the addition of cetavlon.

The reaction between catechol violet and other metals in the presence of cetavlon should be investigated with regard to improved sensitivities. For example preliminary experiments with germanium-catechol violet-cetavlon showed a blue complex, $\mathcal{E}_{max} = 665 \text{ m}\mu$, giving a molecular extinction coefficient of <u>ca</u>. 70,000. Other metals which should be investigated include antimony, bismuth, gallium, selenium and tellurium.

In atomic-absorption and atomic-fluorescence spectrophotometry there are still many avenues to explore. For example in the measurement of atomic-absorption of metals which form refractory oxides in air-acetylene or air-propane flames the use of a more unconventional flame may be beneficial. As shown in Chapter VII increased sensitivity is obtainable by using nitrous oxide-acetylene flames for the determination of tin. This may well be true of other refractory oxide forming metals. The use of hydrogen flames with hydrocarbon additives may prove to be even better for the determination of tin and other metals and should be investigated.

There are many other unconventional flames which could be examined with regard to application for both atomic-absorption and fluorescence spectrophotometry and include the reversed use of air-acetylene (i.e. aspirate with acetylene), cyanogen, nitrogen-oxygen-acetylene, carbon subnitride, tetracyanoethylenes and fluorine-hydrogen flames.

There are many and various new means of improving, reproducing and extending the versatility of emission sources for both atomic-absorption and atomic-fluorescence spectrophotometry. Probably the most useful advances will be made with the use of continuous sources, plasma jets and electrodeless discharge tubes. In addition there are many other electrically and thermally excited sources which could also be examined; e.g. the arc or spark in spray or flame discharges, Tesla discharge, induction-coupled high frequency discharge and the possible use of the thermite flame and of focussed lasers.

REFERENCES

1. The Society for Analytical Chemistry, "Official, Standardised and Recommended Methods for Analysis" W. Heffer and Sons Ltd., Cambridge, 1963.

2. The American Society for Testing Materials, "1960 Book of A.S.T.M. Methods for Chemical Analysis of Metals". E30 - 56, New York, 1960.

3. The United Steel Cos. Ltd., "Standard Methods of Analysis of Iron, Steel and Associated Materials", Percy Land, Humphries and Co. Ltd., London, 1961.

4. Westwood, W. and Mayer, A., "Chemical Analysis of Cast Iron and Foundary Materials", 2nd Edition, George Allan and Unwin, London, 1960.

5. Sandell, E.B., "Colorimetric Determination of Traces of Metals", 3rd Edition, Interscience, New York, 1959.

6. Holler, A.C. and Yeager, J.P., *Ind. Eng. Chem., Analyt. Ed.*, 1942, *14*, 719.

7. Codell, M. and Norwitz, G., *Analyt. Chem.*, 1953, *25*, 1437.

8. Banerjee, D.K., *ibid*, 1957, *29*, 55.

9. Taylor-Austin, E., *Analyst.*, 1938, *63*, 566.

10. Wells, J.E., and Hunter, D.P., *ibid*, 1948, *73*, 671.

11. Stafford, N. and Wyatt, P.F., *ibid*, 1947, *72*, 52.

12. Vogel, A.I., "Textbook of Quantitative Inorganic Analysis", 2nd Edition, Longmans, London, 1951.

13. Box, F.W., *Analyst.*, 1946, *71*, 317.

14. Willard, H.H. and Tang, N.K., *Ind. Eng. Chem., Analyt. Ed.*, 1937, *9*, 357.

15. Groot, C., Peekema, R.M. and Troutner, V.H., *Analyt. Chem.*, 1956, *28*, 1571.

16. Rooney, R.C., *Analyst.*, 1958, *83*, 546.

17. Snyder, L.J., *Ind. Eng. Chem. Analyt. Ed.*, 1945, *17*, 37.

18. Hale, M.M., *ibid,* 1946, *18*, 568.

19. Bushey, A.H., *Analyt. Chem.*, 1948, *20*, 169.

20. Beck, M. and Szabo, Z.G., Analyt. Chim. Acta, 1952, 6, 316.

21. Elliot, C. and Robinson, J.W., ibid, 1955, 13, 309.

22. Strafford, N. and Wyatt, P.F., Analyst., 1943, 68, 319.

23. Horton, A.D. and Thompson, P.F., Analyt. Chem., 1956, 28, 1326.

24. Hill, U.T., ibid, 1956, 28, 1419.

25. Millner, T., Z. anal. Chem., 1938, 113, 83.

26. Millner, T. and Kumas, F. ibid, 1938, 113, 102.

27. Richter, F., ibid, 1944, 126, 438.

28. Idem, ibid, 1944, 127, 113.

29. Parker, C.A. and Goddard, A.P., Analyt. Chim. Acta, 1950, 4, 517.

30. Knudson, H.W., Meloche, V.W. and Juday, C., Ind. Eng. Chem., Analyt. Ed., 1940, 12, 715.

31. Jean, M., Analyt. Chim. Acta, 1954, 10, 526.

32. White, C.E. and Lowe, C.S., Ind. Eng. Chem., Analyt. Ed., 1940, 12, 229.

33. Davydov, A.L. and Devekki, V.S., Zavod. Lab., 1940, 10, 134, Chem. Abstr., 1941, 35, 5056.

34. Weissler, A. and White, C.E., Ind. Eng. Chem., Analyt. Ed., 1946, 18, 530.

35. Kirkbright, G.F., West, T.S. and Woodward, C., Analyt. Chem., 1965, 37, 137.

36. Goon, E., Retley, J.E., McMullen, W.H. and Wiberley, S.E., ibid, 1953, 25, 608.

37. Dagnall, R.M., West, T.S. and Smith, R., Chem. and Ind., 1965, 1499.

38. Dagnall, R.M., West, T.S. and Smith, R., Talanta. in press.

39. Scholes, P.H. and Smith, D.V., Analyst., 1958, 83, 615.

40. Pollack, F.F. and Pelowe, E.F., Metallurgia, 1950, 41, 281.

41. Wibberly, S.E. and Bassett, L.G., Analyt. Chem., 1949, 21, 609.

42. Kassner, J.L., and Ozier, M.A., ibid, 1951, 23, 1453.

43. Hynek, R.J. and Wrangell, L.J., ibid, 1956, 28, 1520.

44. Claassen, A., Bastings, L. and Visser, J., Analyt. Chim. Acta, 1954, 10, 373.

45. Elving, P.J. and Zook, W.C., Analyt. Chem., 1953, 25, 502.

46. B.I.S.R.A. Methods of analysis Committee, J. Iron and Steel Inst., 1959, 193, 350.

47. Rosanquist, I.J., *Amer. J. Sci.*, 1942, *240*, 359.

48. Treadwell, F.P. and Hall, W.J., "Analytical Chemistry" 9th Edition, Wiley, New York, 1942.

49. Weiser, H.B., *J. Phys. Chem.*, 1916, *20*, 659.

50. Brown, D.J., Moss, J.A. and Williams, J.B., *Ind. Eng. Chem., Analyt. Ed.*, 1931, *3*, 134.

51. Mahr, C. and Ohle, H., *Z. anorg. Allgem Chem.*, 1937, *234*, 224.

52. Berg, R. and Fahrenkamp, E.S., *Z. analyt. Chem.*, 1938, *112*, 161.

53. Spaca, G. and Kuras, M., *ibid*, 1936, *104*, 88.

54. Ligett, W.B. and Biefeld, L.P., *Ind. Eng. Chem. Analyt. Ed.*, 1941, *13*, 813.

55. Maynes, A.D. and McBryde, W.A.E., *Analyt. Chem.*, 1957, *27*, 1259.

56. Muller, H., *Z. analyt. Chem.*, 1938, *113*, 164.

57. Hart, H.V., *Analyst*, 1951, *76*, 693.

58. Cage, J.C., *ibid*, 1955, *80*, 789.

59. Kolthoff, I.M. and Elving, P.J., "Treatise on Analytical Chemistry", Part II, Vol. 6, Interscience, New York, 1964.

60. Morrison, G.H. and Freiser H., "Solvent Extraction in Analytical Chemistry", J. Wiley and Sons, New York, 1962.

61. Bamback, K. and Cholak, J., Ind. Eng. Chem. Analyt. Ed., 1941, 13, 504.

62. Ulmland, F. and Kirchner, K., Z. Analyt. Chem., 1954, 143, 259.

63. Lingane, J.J. and Jones, S.L., Analyt. Chem., 1951, 23, 1798.

64. Kutzenlnigs, A., Z. analyt. Chem., 1949, 127, 382.

65. Fricke, R. and Sammet, R., ibid, 1943, 126, 13.

66. Evans, B.S., Analyst, 1939, 64, 2.

67. Kolthoff, I.M. and Lingane, J.J., "Polarography" 2nd Edition, Vol. II, Interscience, New York, 1952.

68. Weber, O.A. and Vouk, V. B., Analyst, 1960, 85, 40.

69. Irving, H. and Butler, E., ibid, 1953, 78, 571.

70. Irving, H., Cooke, S.J.H., Woodger, S.C. and Williams, R.J.P., J. Chem. Soc., 1949, 1847.

71. Cooper, S.S., and Sullivan, M.L., Analyt. Chem., 1951, 23, 613.

72. Snyder, L.J., ibid, 1947, 19, 684.

73. Silverman, L., *ibid*, 1947, *19*, 698.

74. Holness, O., *Analyst.*, 1944, *69*, 145.

75. Trillat, M.A., *Compt. Rend.*, 1903, *136*, 1205.

76. Tertoolen, J.F.W., Detmar, D.A. and Buijzee, C., *Z. analyt. Chem.*, 1959, *167*, 401.

77. Cazeneuve, M.P., *Compt. Rend.*, 1900, *130*, 1479.

78. Vasserman, E.S. and Suprousvitsch, I.B., *Ukrain. Khlm. Zhur.*, 1934, *9*, 330, *Chem. Abstr.*, 1936, 2517.

79. Pollard, F.H. Hanson, P. and Geary, W.J., *Analyt. Chim. Acta*, 1959, *20*, 26.

80. Geary, W.J, Nickless, G. and Pollard, F.H., *ibid*, 1962, *27*, 71.

81. Idem, *ibid*, 1962, *26*, 575.

82. Kristiansen, K. and Langmyhr, F.E., *Acta. Chem. Scand.*, 1959, *13*, 1473.

83. Bush, G.H., *Analyst*, 1954, *79*, 697.

84. Rosanquist, I.T., *Amer. J. Sci.*, 1942, *240*, 356.

85. Dean, J.A., "Flame Photometry", McGraw Hill, New York, 1960.

86. Flickinger, L.C., Polley, E.W. and Galletta, F.A., *Analyt. Chem.*, 1957, *27*, 1778.

87. Fischer, H., *Angew. Chem.*, 1929, *42*, 1025.

88. Bricker, L.G., and Procter, K.L., *Ind. Eng. Chem.*, *Analyt. Ed.*, 1945, *17*, 511.

89. "Spectrochemical Data", I.U.P.A.C. Commission on Spectrochemical and Other Optical Procedures for Analysis, Butterworths, London, 1963.

90. Hain, G. and Barnes, W.C.E., *Ind. Eng. Chem. Analyt. Ed.*, 1942, *14*, 867.

91. Rooney, R.C., *Analyst*, 1958, *83*, 83.

92. Milner, G.C.W. and Townsend, J., *Analyt. Chim. Acta*, 1951,5, 584.

93. Young, R.S. and Leibowitz, A., *Analyst*, 1946, *71*, 477.

94. Tertoolen, J.F.W., Detmar, D.A. and Buijze, C., *Z. analyt. Chem.*, 1959, *167*, 401.

95. Jones, W.G. and Walsh, A., *Spectrochim. Acta*, 1960, *16*, 249.

96. Ellwell, W. T. and Gidley, J.A.F., "Atomic Absorption Spectrophotometry", Pergamon, Oxford, 1961.

97. Menzies, A.C., *Analyt. Chem.*, 1960, *32*, 898.

98. Hermann, R., *Optik*, 1961, *18*, 422.

99. Walsh, A., *Spectrochim. Acta*, 1955, *7*, 108.

100. Russell, W.T. Shelton, J.P. and Walsh, A., ibid, 1955, 8, 317.

101. Gilbert, P.T., Analyt. Chem., 1962, 34, 210R.

102. Idem, 6th Conference, "Analytical Chemistry in Nuclear Reactor Technology, Gatlingburg, Tenn., 1962.

103. Scribner, B.F. and Margoshes, M. Analyt. Chem., 1964, 36, 329R.

104. Elwell, W.T. and Gidley, J.A.F., Analyt. Chim. Acta, 1961, 24, 71.

105. Gidley, J.A.F., "Colloq. Spectroscopicum Internationale", Vol. III, Lyons, 1961.

106. Stumpf, K.E., ibid, Vol. III, 1961.

107. Dagnall, R.M. and West, T.S., Talanta, 1963, 11, 1553.

108. Robinson, J.W., Analyt. Chim. Acta, 1961, 24, 451.

109. Willis, J.B., Nature, 1961, 191, 381.

110. Idem, Analyt. Chem., 1962, 34, 614.

111. Mitchell, A.C.G. and Zemansky, M.W., "Resonance Radiation and Excited Atoms", University Press, Cambridge, 1961.

112. Nichols, E.L. and Howes, H.L., Phys. Rev. 1924, 23, 472.

113. Robinson, J.W., Analyt. Chim. Acta, 1961, 24, 254.

114. Winefordner, J.D. and Vickers, T.J., Analyt. Chem., 1964, 36, 161.

115. Winefordner, J.D. and Staab, R.A., ibid, 1964, 36, 165.

116. Idem, ibid, 1964, 36, 1369.

117. Mansfield, J.M. Winefordner, J.D. and Veillon, C, ibid, 1965, 37, 1051.

118. Willis, J.B., Australian, J. Sci. Res., 1951, A4, 172.

119. Hilger and Watts Ltd., Catalogue No. CH407, 1959.

120. Willis, J.B., Spectrochim. Acta, 1961, 17, 710.

121. Polnektov, N.S. and Vitkun , R.A., Zhur. Analyt. Chem., 1962, 17, 935.

122. Kolthoff, I.M. and Elving, P.J., "Treatise on Analytical Chemistry", Part II, Vol. 3, Interscience, New York, 1961.

123. Holness, H. and Schoeller, W.R., Analyst, 1946, 71, 70.

124. Idem, ibid, 1946, 71, 217.

125. Leutwin, F., Z. analyt. Chem., 1940, 120, 233.

126. Baker, I., Miller, M. and Gibbs, R.S., Ind. Eng. Chem., Analyt. Ed., 1944, 16, 269.

127. Hoffman, J.I. and Lundell, G.E.F., J. Res. Natl. Bur. Stds., 1939, 22, 465.

128. Mogermann, W.D., ibid, 1944, 33, 301.

129. Farnsworth, M. and Pekola, J., Analyt. Chem., 1954, 26, 735.

130. Jantsch, G., Hummer-Kroupa, A. and Gansinger, I., Z. Analyt. Chem., 1948, 128, 451.

131. Ohishi, H, and Sandell, E.B., Analyt. Chim. Acta, 1956, 14, 153.

132. Fairchild, J.G., Ind. Eng. Chem. Analyt. Chem., 1943, 15, 625.

133 Law, N.H., Analyst, 1942, 67, 283.

134. Clarke, R.E.D., ibid, 1936, 61, 242.

135. Idem, ibid, 1937, 62, 661.

136. Luke, C.L., Analyt. Chem., 1956, 28, 1276.

137. Gilbert, D.D. and Sandell, E.B. Mikrochem. J. 1960, 4, 491.

138. Buchanan, G.S. and Schryver, S.B., Analyst, 1909, 34, 121.

139. Newell, I.L. Ficklen, J.B. and Maxfield, L.S., Ind., Eng. Chem. Analyt. Ed., 1935, 7, 26.

140. Danilova, V.N., Zavod Lab., 1963, 29, 407, Chem. Abstr., 1964, 1249.

141. Malát M, Z. analyt. Chem., 1962, 187, 404.

142. Malát M, and Suk, vV., Chemist Analyst, 1956, 45, 30.

143. Dagnall, R.M., West, T.S. and Young, P., Analyst, 1965, 90, 13.

144. Herrero-Lancina, M., M.Sc. Thesis, Birmingham Univ., 1963.

145. Gentry, C.H.R. and Sherrington, L.G., Analyst, 1946, 71, 432.

146. Stary, J., Analyt. Chim. Acta, 1963, 28, 132.

147. Fasola, G.B., Malvano, R. and Massaglia, A., ibid, 1963, 29, 569.

148. Dagnall, R.M., West, T.S. and Young, P., Talanta, 1965, 12, 583.

149. Idem, ibid, 1965, 12, 589.

150. Yoe, J.H. and Jones, A.L., Ind. Eng. Chem., Analyt. Ed., 1944, 16, 111.

151. Harvey, A.E. and Manning, D.L., J. Amer. Chem. Soc., 1950. 72, 4488.

152. West, P.W. and Carlton, J.K., Analyt. Chim. Acta, 1952, 6, 406.

153. Vogel, A.I.,"A Text-Book of Practical Organic Chemistry", Longmans, Green and Co., London, 1948.

154. Dagnall, R.M. West, T.S. and Young P., Analyt. Chem., 1966, 38, 358.

155. Dagnall, R.M. and West, T.S., Talanta , 1963, 11, 1257.

156. C. Candler, "Atomic Spectra", Hilger and Watts Ltd., London, 1964.

157. Belcher. R., Dagnall, R.M. and West, T.S., Talanta, 1964, 11, 1257.

158. Gatehouse, B.M. and Willis, J.B. Spectrochim. Acta, 1961, 17, 710.

159. Stary, J. "The Solvent Extraction of Metal Chelates", Pergamon, Oxford, 1964.

160. Eberle, A.R. and Lerner, M.W., Analyt. Chem., 1962, 34, 627.

161. Merrit, L.L. and Walker, J.K., Ind. Eng. Chem., Anal. Ed. 1944, 16, 387.

162. Ohnesorge, W.E. and Burlingame, A.L., Analyt. Chem., 1962, 34, 1086.

PUBLICATIONS

1. The Determination of Aluminium in Plain Carbon Steels,

   Analyst, 1965, 90, 13.

2. Determination of Lead with 4-(2-pyridylazo)-resorcinol, Part I.
   (Spectrophotometry and Solvent Extraction).

   Talanta, 1965, 12, 583.

3. Determination of Lead with 4-(2-pyridylazo)-resorcinol, Part II.
   (Application to Steel, Brass and Bronze).

   Talanta, 1965, 12, 589.

4. Determination of Trace amounts of Lead in Steels, Brass and Bronze Alloys by Atomic-Absorption Spectrometry.

   Analytical Chemistry, 1966, 38, 358

5. The Determination of Cadmium by Atomic-Fluorescence and Atomic-Absorption Spectrophotometry.

   Talanta, in press.