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FLAME SPECTROSCOPIC STUDIES OF BISMUTH, LANTHANUM, LEAD AND SILVER WITH PARTICULAR REFERENCE TO THEIR DETERMINATION IN STEELS

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SUMMARY

This thesis discusses the atomic spectroscopy of bismuth, lanthanum, lead and silver and describes the determination of trace amounts of the four metals in steel after the preliminary solvent extraction of the metals. A study of the interference effects of the matrix elements upon both the extraction and determination of each metal is included.

The thesis also describes an investigation into lock-in amplification systems in both atomic absorption and fluorescence spectrometry and discusses their effect upon the detection limits for bismuth, lead and silver, as well as the advantages of spectrometers incorporating lock-in amplifiers in the analysis of steel.

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POSTGRADUATE STUDIES

The following courses of study were attended in the Department of Chemistry and Biology at Sheffield Polytechnic:-

1. Physical Metallurgy, Dr. D. W. Clegg
2. Introduction to Fortran IV, Mr. N. Willis
3. Electronics, Dr. N. C. Hilyard

CONTENTS

CHAPTER ONE

GENERAL INTRODUCTION

The variety of uses of steel is continually increasing. This has necessitated the development of new steels whilst the increase in quality of existing ones must, at least, keep pace with, and if possible surpass the demand. Trace elements are beginning to play a large part in these new alloys as the mechanical properties of the steel depend to a large extent on its actual composition.

The determination of four metals which occur in trace amounts in steel is the subject of this thesis. Three of these metals; lead, silver and bismuth are residual elements present in the basic materials of steelmaking. The fourth metal, lanthanum, is a constituent of the rare-earth mixture, known as Mischmetal, which is used as a deoxidant and desulphurant of steel. While trace amounts of rare-earth elements improve the ductility and impact strength of heat treated carbon steels (1, 2) the presence of the other metals can have serious effects on the workability of stainless steels. The effect of lead (3) and bismuth (4, 5) being typical.

1.1. General Methods of Analysis

The concentration of lanthanum in carbon steels and of lead, silver and bismuth in stainless steels is less than 100μg.g.$^{-1}$ Consequently the usual classical procedures of volumetric and gravimetric analysis are of little use in methods where very small amounts of the metals are involved. The gravimetric procedures include the organic precipitants dimethylglyoxime and oxalic acid for bismuth (6) and lanthanum (7), whilst silver and lead are determinable as chloride (8) and sulphide (9) respectively. Volumetric procedures include the famous Volhard process for silver (10) where silver is titrated with potassium thiocyanate. Volumetric procedures for lead and bismith are few due mainly to the insolubility of their salts. Complexometric titrations for these elements are more numerous. Ethylenediaminotetraacetic acid has been used for the titration of all four metals, directly in the case of lead, bismuth and lanthanum (14) and indirectly with nickel in the case of silver (15).

All four metals can be determined by solution spectrophotometry. General procedures include the determination of bismuth by formation of the yellow iodobismuthite ion (16), and an extension of the sulphide procedure (9) for lead where absorption of the colloidal suspension of trace amounts of lead sulphide is measured. Silver is determined with p-dimethylaminobenzalrhodanine (17) whilst alizarin red 'S' has been used (18) to determine lanthanum and other rare earth elements. Solvent extraction has long since been regarded as an excellent procedure for increasing both the sensitivity and selectivity of solution spectrophotometry, its wide use in the analytical chemistry of these four metals being typical. Bismuth (19) and lead (20, 21) have both been complexed, extracted and determined as dithizonates, whilst reagents for silver include nile-blue (22) and diethyldithiocarbamate (23). Tributyl phosphate (24) and n-hexanol (25) have been used in nitrate separations of rare-earth elements.

Physical methods for the determination of metals have long since replaced wet chemical methods in the rapid analysis of both major and minor constituents of steel. Direct reading emission spectrometry (26, 27) and X-ray fluorescence (28,

29) encompass the bulk of routine steel analysis today. This does not mean, however, that chemical methods are obsolete as accurate methods of analysis of standard steels are needed to compile the many calibration graphs needed for each type of steel analysed. These physical methods often suffer from serious inter-element interference problems and involve lengthy sample preparation procedures. Until recently these problems have precluded the use of direct reading emission spectrometry and X-ray fluorescence as tools for the determination of trace elements in steel. X-ray fluorescence has now, however, been used to determine trace amounts of silver and lead in carbon steels (30).

During the first half of the last decade polarographic techniques became popular in steelworks laboratories because of the high sensitivity of the technique, particularly when used in conjunction with masking agents. The application of polarography to the analysis of steel is limited due to extensive interference problems. However, two of the four metals discussed in this thesis, lead and bismuth, have been determined in steel by polarography (3). Today, many of these instruments are lying idle due to the introduction of atomic absorption spectrometry, a technique which has proved to be both highly versatile and sensitive.

This thesis shows how atomic absorption and the associated flame techniques of atomic emission and/fluorescence spectrometry have been utilised in the determination of trace amounts of lead, lanthanum, silver and bismuth in steel.

1.2. Flame Spectroscopy

1.2.1. A History

The technique of flame spectroscopy has been used in analysis for a considerable length of time. Indeed, since the latter half of the 19th century interest has been shown in this branch of science but it was not until the nineteen thirties that flame emission photometry became practical. Since then the applications and instrumental development of the technique has fl~~ou~~uorished, particularly in the immediate post war years, being heralded by the appearance of a wealth of papers and books dealing with all aspects of the technique.

The roles in analytical chemistry of the three techniques of ~~atomic~~ flame emission, atomic absorption and fluorescence has changed over the last fifteen years. Until 1955 analysis involving the flame had been solely by ~~atomic~~ flame emission but in this year Walsh (31) outlined the practical applications of atomic absorption spectrophotometry. Since this date the number of elements which can be determined by atomic absorption has grown until now the detection limits are available for most of the elements in the periodic table. With the onset of atomic absorption the analytical applications of ~~atomic~~ flame emission have declined, due mainly to the belief that atomic absorption suffers less from interference problems and also due to the tremendous interest shown in the technique generally.

The latter half of the last decade has seen considerable interest in atomic fluorescence spectroscopy, in both applications to individual metals (e.g. 32,33) and in instrumentation (e.g. 34,35). A study of atomic fluorescence is included in this thesis. Comparisons of the detection limits, interferences and instrumentation of the three techniques have been discussed in the literature (36). At the present time the development of atomic fluorescence has not reached a stage where it has any significant advantages over atomic absorption with industry consequently preferring atomic absorption to fluorescence.

1.2.2. The Techniques

The basis of flame spectroscopy is the detection and measurement of the radiation absorbed or emitted at discrete wavelengths by atoms in a flame. A solution of the metal is sprayed into the flame as a fine mist suspended in the oxidant gas. The flame causes the solvent to evaporate and the metal to be dissociated, mainly into ground state atoms.

A ground state atom is capable of receiving energy, either as a photon, in the case of atomic absorption and fluorescence, or as thermal energy in flame ~~atomic~~ emission. This energy excites the atom from its ground state to an excited state by promotion of electrons. There are a number of excited states, each state requiring more energy than the former for the electronic transition. In atomic absorption and fluorescence this excitation energy is provided by a light source, the spectrum of which is generated by the same metal as that being determined. In atomic absorption this beam of light is passed through the flame and into the monochromator and detection system. The difference in light intensity which occurs when the metal solution is sprayed into the flame is measured in terms of absorbance. The absorbance is proportional to the concentration of ground state atoms present in the flame and hence the concentration of the metal in solution. This is so, since, at the temperature of the flame used in flame spectroscopy (< 3000°C), the number of atoms in excited states is negligible compared with the number in the ground state (31). The number of atoms in the flame, therefore, is virtually equal to the number of atoms in the ground state. It follows, therefore, that only transitions involving the ground state are utilised in atomic absorption. The wavelengths of such transitions are termed 'resonance lines'.

In atomic fluorescence the beam of light from the source is focused onto the flame, usually at 90^{o} to the optical axis from the flame to the monochromator slit. Transitions from the ground states to excited states are again effected. The reduction in light intensity from the flame is not measured, instead light is emitted by the atoms in the flame in terms of fluorescence. Fluorescence occurs when the electron drops back to the ground state configuration of the atom. If this transition occurs directly from an excited state to the ground state then the wavelength of fluorescence is termed 'resonance fluorescence'. Other main types of fluorescence include 'direct line' and 'stepwise line fluorescence'. Direct line fluorescence results when an atom is raised to an excited electronic state above the ground state and then undergoes a radiational transition to a lower excited state (which is not the ground state). Stepwise line fluorescence occurs when the atom is excited to a high electronic state, then undergoes radiation-less deactivation to a lower excited state before finally undergoing fluorescence to another lower excited state or to the ground state.

The fluorescence intensity is proportional to the ground state atom concentration in the flame and hence the concentration of the element in solution. In addition it is directly proportional to the intensity of the source as this determines how many atoms reach excited states.

Flame ~~Atomic~~ emission spectra are again generated by electron movements within the atom~~.~~ or molecule. In atomic emission only the lowest excited states are involved and are thus generally confined to the longer wavelengths of the visible/ultra-violet spectrum. The emission intensity is once again proportional to the concentration of the metal in solution. Flame ~~Atomic~~ emission spectra are prone to spectral interferences from other metals whose ~~atomic~~ emission spectra occur at wavelengths which are very near that of the metal being determined. Spectral interferences are virtually non-existent in atomic absorption or fluorescence.

1.3. The Application of Atomic Spectroscopy to the Analysis of Steel

Of the three flame techniques the steel industry has paid most attention to atomic absorption as it is this technique which has been able to cater most effectively for its needs. The application of atomic absorption to the determination of both minor and trace elements in steel is well documented (e.g. 37-39).

Scholes (40) has reviewed the analysis of a number of metals in steel, including lead, by atomic absorption. He has shown that most metals which occur in amounts above 0.1% are, in general, readily determinable by the technique. However the difficulty in achieving adequate sensitivity has rendered the technique unsatisfactory for trace element analysis much below 0.1% without a prior concentration stage being incorporated into the procedure.

1.3.1. Concentration Techniques

In trace metal analysis there is often a need to separate the element of interest from the matrix either to improve the sensitivity, eliminate interference from the matrix or to prevent blockage of capillary and burner. This is accomplished by either removal of the matrix or by the extraction of the element of interest from the matrix. In steel analysis the former usually involves the removal of iron. A rapid and excellent way is by the extraction of iron (111) as its tetrachloride into di-isopropyl ether (41). A variety of techniques are used to extract the particular element from the matrix, two of the most common ones being solvent extraction and ion-exchange. Headridge and Smith (38) have determined trace amounts of antimony in steels by extraction of its iodide complex into isobutylmethylketone whilst Sellers (42) has determined lead in steel after a preliminary ion-exchange separation. The extraction procedure is also an excellent concentration procedure because, often, a many fold reduction in solvent volume is inherent with the procedure. The use of an organic solvent in atomic absorption gives rise to a better sensitivity in most cases, due to an increase in the atomisation rate when an organic solvent is sprayed (43, 44). The solvent must be carefully chosen as not only must it extract the metal complex but it must also give stable burning conditions in the flame. Common organic solvents include isobutylmethylketone and ethyl propionate.

Over the last few years the use of solvent extraction techniques in atomic absorption has flourished particularly now that it is possible to selectively extract one element from another. Selectivity is accomplished by a combination of complexing agent and the careful control of pH. Organic and inorganic reagents are both utilised in solvent extraction although the use of inorganic reagents is not as widespread as the former. Morrison and Freiser (45) have discussed many such reagents for the solvent extraction of most metals, many of which are readily adaptable for use in atomic absorption.

The existing methods for the determination of lead, lanthanum, silver and bismuth in amounts less than $100\mu g.g^{-1}$ in steel are unsatisfactory with regard to precision, sensitivity and speed of analysis. This thesis describes procedures for the determination of trace amounts of these metals in steels by atomic spectroscopy which are better suited to meet the demands of the metallurgical industry today.

The last chapter describes lock-in amplification systems in both atomic absorption and fluorescence spectrometry and discusses their effect upon the detection limits for bismuth, lead and silver in each of the techniques. The possible advantages of spectrometers incorporating lock-in amplification when applied to the analysis of steel is also outlined.

CHAPTER TWO

EXPERIMENTAL

2.1. Apparatus

2.1.1. Flame Spectrophotometry

The flame spectroscopic studies in this thesis were performed using two different instruments; the Unicam SP 90 Spectrophotometer and the Jarrell Ash 82-529 Maximum Versatility Flame Spectrometer.

The former instrument was used in the atomic absorption studies of lead and bismuth and also for the determination of lanthanum by ~~atomic~~ flame emission. The ancillary equipment, e.g. air compressor, nitrous oxide controller, chart recorder and burners; slot for atomic absorption and 'Meker' type for emission; were also supplied by Unicam.

The Jarrell-Ash Spectrometer, used in the atomic absorption study of silver and the atomic fluorescence investigations detailed in Chapters 6 and 7, was used in conjunction with a Tri-Flame nebulizer and burner for atomic absorption and a Hetco burner for the atomic fluorescence study of bismuth. For the atomic fluorescence investigation discussed in Chapter 7 the flame was supported on a Beckman - R.I.I.C. 'Meker' burner and flame separation attachment whilst Unicam supplied the solution nebulization equipment.

The hollow cathode lamps were manufactured by Unicam (lead) and Westinghouse Ltd. (silver and bismuth).

Air Products Ltd. supplied the acetylene, argon, hydrogen, nitrous oxide and propane gases used by the various flames.

2.1.1.1. Electrodeless Discharge Lamps.

The very high spectral intensity associated with electrodeless discharge lamps (EDLs) was used to advantage in the atomic fluorescence investigation detailed in Chapters 6 and 7.

The lead and bismuth EDLs were supplied by E.M.I. Ltd. whilst the silver EDL was prepared in the laboratory in a method similar to that described by Zacha et al (46).

EDLs consist of sealed quartz tubes containing a small quantity of the metal or metal compound whose spectrum is desired and a rare gas at low pressure. The characteristic discharge of the metal is generated when the lamp is placed in a microwave field of sufficient energy, in this case 2450 MHz. The microwave field was generated inside a type 214L cavity coupled to a Microtron 200, Mk.II microwave generator and modulator. The generator and ancillary equipment were obtained from Electromedical Supplies Ltd.

2.1.2. Solution Spectrophotometry

Solution spectrophotometric measurements were obtained on Unicam SP 500 and SP 800 Spectrophotometers equipped with 1 cm. and 2 cm. silica cells whilst a Pye Model 292 pH Meter was used for the measurement of hydrogen ion concentrations.

2.1.3. Mercury Cathode Electrolysis

A Baird and Tatlock Electrochemical Analyser was used for the mercury cathode electrolysis separation described in the study of lanthanum. Electrolysis consisted of a water cooled glass cell containing 50 ml. of mercury (cathode) and a sulphuric acid based electrolyte. The anode was a platinum wire, wound into a flat spiral, immersed in the electrolyte and resting 1 cm. above the mercury. Electrical connection to the cathode was by an insulated platinum wire passing through the electrolyte into the mercury. A tap was provided for emptying the electrolyte and mercury. In the equipment used in this study the mercury was continuously stirred by a glass stirrer operated by a motor above the cell.

2.2. Reagents

The reagents used in these studies were all of 'Analytical-Reagent' grade. Concentrated hydrochloric, nitric, perchloric and sulphuric acids, concentrated ammonia solution, liquified sulphur dioxide and the organic reagents; isobutylmethylketone, carbon tetrachloride, ethanol, ethylmethylketone, ethyl propionate, methanol i-propanol and n-propanol were all supplied by British Drug Houses Ltd.

2.2.1. Preparation of Reagent Solutions

Solutions of the reagents and metals were stored in stoppered polythene bottles and distilled water was used throughout the experiments involving these aqueous solutions. The preparation of the solutions of these reagents and metals is shown in Tables 2.1 and 2.2 respectively.

TABLE 2.1

Preparation of Reagent Solutions

Solution	Weight (g.)	Solvent	Final Volume (ml.)	Note
1M Ammonium Acetate	77	Water	1000	
APDC	0.41	Water	100	a
1%(w/v) Ascorbic Acid	1	Water	100	b
0.004%(w/v) Dithizone	0.004	ETP	100	c
EDTA (disodium salt)	7	Water	70	
50%(v/v) Hydrochloric Acid	500 ml.	Water	1000	
8M Hydrochloric Acid	356 ml.	Water	500	
6%(w/v) Hydroxyammonium chloride	30	Water	500	
50%(v/v) Nitric Acid	500 ml.	Water	1000	
40%(v/v) Perchloric Acid	40 ml.	Water	100	
0.025M Potassium Dichromate	3.675	Water	500	
Saturated Potassium Iodide	150	Water	100	d
43%(w/v) Potassium Iodide	43	Water	100	
20%(w/v) Sodium Acetate	20	Water	100	
0.5M Sodium Citrate	147	Water	1000	
30%(w/v) Sodium Citrate	300	Water	1000	
0.1M Sodium Hydroxide	0.4	Water	100	
5M Sodium Nitrate	42.5	Water	100	
0.1M TTA	11.1	1BMK	500	e

Notes

a The solution of ammonium 1-pyrrolidinedithiocarbamate (APDC) was filtered through a Whatman 541 filter paper before dilution with water. A fresh solution was prepared weekly.

b A fresh solution of this reagent was prepared daily.

c ETP = ethyl propionate.

d This reagent was prepared by treating 150 g. of potassium iodide with 100 ml. of water, filtering the excess of the reagent before use.

e The solution of 2-thenoyltrifluoroacetone (TTA) in isobutylmethylketone (lBMK) was filtered through a Whatman 541 filter paper before dilution with lBMK.

TABLE 2.2

Preparation of Metal Solutions

Solution	Metal or Metal Compound Used	Weight (g.)	Solvent[a]	Final Volume (ml.)	Note
Al(1mg.ml^{-1})	Al foil	0.1	20ml. 50%(v/v)HCl	100	
Bi(100μg.ml^{-1})	Bi granules	0.10	25ml. water, 40ml. conc. HNO_3	1000	
0.5M $CrCl_3$	$CrCl_3.6H_2O$	33.3	Water	250	
Cr (111) (50 mg.ml^{-1})	Cr Powder	12.5	100 ml. conc. HCl	250	b
Cr (VI) (5 mg.ml^{-1})	$K_2Cr_2O_7$	1.41	Water	100	
Cu(10mg.ml^{-1})	Cu foil	1.0	Minimum volume of 50%(v/v)HNO_3	100	c
0.5M $FeCl_3$	$FeCl_3.6H_2O$	33.8	Water	250	
Fe (111) (0.1 g.ml^{-1})	Fe Powder	10	50 ml. conc. HCl	100	d
Fe (11) (0.1 g.ml^{-1})	Fe Powder	10	Minimum volume of conc. HCl	100	
La(100μg.ml^{-1})	La_2O_3	0.117	20%(v/v) HNO_3	1000	b
Pb(100μg.ml^{-1})	$Pb(NO_3)_2$	0.1599	Water	1000	
1M $MnCl_2$	$MnCl_2.4H_2O$	49.5	Water	250	
Mn (11) (1 mg.ml^{-1})	Mn Powder	0.1	20 ml. 50%(v/v) HCl	100	
1M $NiCl_2$	$NiCl_2.6H_2O$	59.4	Water	250	
Ni(0.05g.ml^{-1})	Ni foil	12.5	100 ml. 50%(v/v) HNO_3	250	b
Ag(100μg.ml^{-1})	$AgNO_3$	0.0158	Water	100	

Notes

a In each case the solvent shown was that used to dissolve the metal or metal compound. Distilled water was used to dilute the solution to the volume shown.

b The solvent was evaporated until precipitation occurred, 50 ml. of distilled water were added and the solution cooled before diluting to the volume shown.

c After dissolution of the copper 10 ml. of conc. HCl were added and the solution was treated as described in Note b.

d After dissolution of the iron conc. HNO_3 was added dropwise until oxidation of the iron was complete. The solution was treated as described in Note b.

e.g. The 1M ammonium acetate (Table 2.1) was prepared by dissolving 77 g. of the reagent in water. The solution was then diluted to 1 litre with distilled water using a graduated flask.

e.g. The $100 \mu g.ml^{-1}$ solution of bismuth (Table 2.2) was prepared by dissolving 0.10 g. of bismuth in 20 ml. of water and 40 ml. of concentrated nitric acid before dilution to 1 litre with distilled water, using a graduated flask.

2.2.2. Miscellaneous Solutions

The masking agent used in the study of bismuth was prepared by dissolving 50 g. of disodium EDTA and 294 g. of sodium citrate in 267 ml. of concentrated ammonia solution. The solution was then diluted to 1 litre with water.

The salicyclic acid, di-n-butylamine reagent (SABA) described in Chapter 5 was prepared by dissolving 1.6 g. of the acid and 15 ml. of di-n-butylamine in 1BMK. The solution was then diluted to 500 ml. with 1BMK.

2.3. Measurement of Signal Intensity

A general procedure for the measurement of signal intensity was adopted to account for any variation in signal strength due to alteration of the flame conditions. The procedure for spraying the solutions into the flame is shown below:-

(a) Spray solvent;
(b) spray the solution of highest metal concentration;
(c) spray solvent;
(d) spray the solution of lowest metal concentration;
(e) spray solvent;

(f) spray the solution of highest metal concentration;

(g) spray solvent;

(h) spray the solution of next lowest metal concentration;

(i) spray solvent;

(j) spray the solution of highest metal concentration;

and so on.

Using this procedure the signal intensity measured, i.e. absorbance, emission or fluorescence, was referred to one standard measurement, i.e. the highest metal concentration, using the relationship:-

$$\text{Corrected signal intensity, } Y = \frac{2\,Y_1\,X_0}{X_1 + X_2}$$

where:-

Y_1 = the signal intensity of the test solution,

X_0 = the signal intensity of the standard solution, i.e. the solution of highest metal concentration - solution (b),

X_1, X_2 = the intensity of the signals of the solution of the highest metal concentration measured immediately before and after that of the test solution.

2.4. Sensitivity and Detection Limits

The usual way of representing sensitivity in atomic absorption and emission is defined as 'that concentration of analyte which produces a signal equal to the 1% absorption or emission signal'. This method of calculating the sensitivity was used in the atomic absorption determination of lead, silver and bismuth and in the study of lanthanum by atomic emission.

An alternative representation of sensitivity data may be made in terms of the 'detection limit'. The detection limit defined as 'that concentration of analyte which produces a signal of equal intensity to the average peak to peak (p/p) noise' is most often used in atomic fluorescence and is usually quoted in conjunction with the signal to noise ratio (S : N). In the definition above the S : N ratio is unity and it is this definition which is applied to the atomic fluorescence investigations discussed in this thesis.

CHAPTER THREE

LEAD

3.1. Introduction

The presence of lead in steels is found within two distinct ranges. In the higher range (0.2 to 0.5%) lead is added to free cutting steels to increase their machinability without affecting their physical properties.

Many analytical procedures for the determination of lead in this range are available including a British Standard method (47) based on the work of a British Iron and Steel Research Association (BISRA) committee (9) which recommends the precipitation of lead as sulphide followed by its conversion to lead molybdate for subsequent weighing. An alternative to this procedure is also described (48) whereby lead is determined colorimetrically as its dithizonate. Atomic absorption has been used for the direct determination of lead in this range.

Elwell and Gidley (50), in one of their earliest papers, described the determination of lead in steels after acid dissolution quoting an analysis time which was a great improvement on the two British Standard procedures (47,48).

Up to 0.05% of lead is found in stainless steels and has been shown to cause hot rupture of the steel during rolling and forging. In 1963 BISRA initiated a study group to develop a method for the determination of trace amounts of lead in steels including the use of atomic absorption. However, the lack of sensitivity and the interference problems associated with the direct determination of lead at this level prompted the group to select a solution spectrophotometric procedure. The problems involved in using atomic absorption were later reiterated by Scholes (40) in his review of the progress made towards the determination of lead and other metals in steel by atomic absorption.

In the procedure adopted by the group (51) the iron, after dissolution of the steel in hydrochloric and nitric acids, was extracted into pentyl acetate. Bismuth and lead were coextracted as diethyldithiocarbamate into chloroform before the lead was back extracted into the aqueous phase for its colorimetric determination with dithizone. This method, covering the range 0.0005 to 0.05% of lead in steel, was adopted as the British Standard procedure (49).

This method although extensively used in steelworks laboratories is time consuming; a batch of eight samples requires about eight hours analysis time. The method also involves the use of cyanide; a potential hazard in the hands of unskilled laboratory assistants. In routine analysis the precision is ± 0.00025% of lead in the sample. Since the procedure was invoked the degree of precision required has increased. There is now a need to establish the fourth decimal place. The work described in this chapter shows how atomic absorption coupled with solvent extraction can be utilised to determine trace amounts of lead in stainless steels.

Three resonance lines have been used in the atomic absorption studies of lead, namely 217.0, 283.3 and 405.8 nm. The highest wavelength is of little use at the low concentrations of lead involved. Sensitivities have been quoted for aqueous solutions in a variety of flames (Table 3.1).

TABLE 3.1

Sensitivity Data

Wavelength (nm.)	Sensitivity $(\mu g.ml.^{-1})$ 1% absorption	Flame	Reference	Note
Aqueous solution				
283.3	2^a	air-C_2H_2	50	a = calculated from figures in text
	2^a	air-C_3H_8	54	
	0.67	O_2-H_2	52	
	0.87	O_2-H_2	53	
	0.81	O_2-C_2H_2	53	
217.0	0.013	O_2-H_2	52	Reversed flame T-piece
	0.45	O_2-H_2	52	
	0.41	O_2-H_2	53	
	0.37	O_2-C_2H_2	53	
405.8	150	O_2-H_2	52,53	
	329	O_2-C_2H_2	53	
Organic solution				
217.0	0.08	O_2-C_2H_2	53	Without adapter
	0.1	O_2-H_2	53	
	b	O_2-C_2H_2	53	With adapter
	0.007	O_2-H_2	53	

b = Not practic

Some workers (52,53) have used T-piece adapters to improve the sensitivities although flame absorption and noise also increased somewhat. The best sensitivity for the determination of lead in aqueous solution has been obtained by Chakrabarti et al (52) who quoted a figure of $0.013 \mu g.ml^{-1}$ for a 1% absorption using a oxy-hydrogen flame, a T-piece adapter and the 217.0 nm. resonance line.

The effect of water miscible organic solvents, such as acetone and methanol, upon the determination in aqueous based solution seems to have a mixed effect. In the oxy-hydrogen flame of Chakrabarti and coworkers (52) very little enhancement of signal was noted. Dagnall and West (54) however reported enhancement, particularly for propan-2-ol in the air-propane flame. Enhancement of the signal by organic solvents was attributed to an increase in nebulizer uptake rate.

All workers (50,52-54) indicated that the atomic absorption of lead was relatively interference free even with a 1000-fold molar excess of the interferent. Dagnall and West (54) did note interference from 1000-fold molar excesses of aluminium (111), beryllium (11), thorium (1V) and zirconium (1V) which they attributed to the inability of the relatively cool air-propane flame to decompose the refractory type oxides formed by these elements. Anionic interferences were also reported from anions which formed precipitates with lead. Chakrabarti et al (52) added EDTA to retain the lead in solution. They also reported interference from high salt concentrations.

Many workers have studied the determination of lead in organic solvents by atomic absorption. Robinson (55) has determined lead in iso-octane using an oxy-hydrogen flame and found no interference from a 9:1 excess of many elements including chromium and copper. Dagnall and West (54) studied the determination of lead in gasoline products. They also extracted lead with 8-hydroxyquinoline into both chloroform and isobutylmethylketone (IBMK), finding the combustion of IBMK more suitable than chloroform. They used a 1% solution of the reagent to extract the lead from an aqueous phase of pH 7-11 noting a three-fold increase in sensitivity, relative to aqueous solution. The same authors also extracted lead as its diethyldithiocarbamate complex quoting a three-fold increase in sensitivity over the 8-hydroxyquinoline extraction. West and Carlton (56) investigated the extraction of complex metal iodides into a variety of solvents. Of the metals studied; bismuth, mercury, iron, lead, copper, palladium, cadmium, rhodium, gold and ruthenium; some were at least only partially extracted. Lead, however, was found to be 97% extracted into methylisopropylketone (MIPK) from a phase which was 5% in hydrochloric acid and contained 3.75 ml. of saturated potassium iodide. An investigation of the interferents upon the extraction of lead revealed that the metals cadmium and ruthenium posed the major problem. Chakrabarti et al (52) applied the iodide extraction to determine lead concentrations of less than $0.1 \mu g.ml^{-1}$ in water samples using the 217.0 nm. line and a burner fitted with a T-piece adapter supporting the oxy-hydrogen flame. Dagnall, West and Young (57) substituted IBMK for the MIPK used in the original work to determine lead in steels and brass/bronze alloys. In their steel analysis iron was removed prior to the iodide extraction using iso-amylacetate. They used an air-acetylene flame and the 283.3 nm. resonance line for their determinations and noted a five to six fold increase in sensitivity over the aqueous determinations. Lead was extracted from aqueous solutions containing 1000-fold molar excesses of many elements found in steel and copper alloys. No interference was encountered from fifteen metals including copper (11), molybdenum (Vl), tin (lV), iron (111) and chromium (111). This method enabled lead in excess of 0.003% to be determined in steels with a precision of ± 0.0005% lead. Chakrabarti (53) has studied the determination of lead in MIPK after the iodide extraction in both oxy-hydrogen and oxy-acetylene flames concluding that the 217.0 nm. line gives the best sensitivity but suffers from greater background noise. The high background radiation from the T-piece when using the oxy-acetylene flame at 217.0 nm. rendered the determination in MIPK inpractical at this wavelength. The sensitivities quoted (Table 3.1) were considerably better than those obtained in aqueous solutions.

The work described in this chapter shows how the extraction of potassium tetraiodoplumbate into IBMK has been developed to provide a procedure whereby lead can be determined in stainless steels in the range 0.0001 to 0.05% (1 to 500μg.g^{-1}).

The method which is similar to that described by Dagnall et al (57) is reliable, applicable to a wide range of steels and is less time consuming than the British Standard Procedure (49). Unlike Dagnall et al, who found the extraction to be interference free for many metals present in steels, interference was encountered from metals, such as copper and iron, which react with iodide ions to liberate iodine into the organic phase.

This chapter discusses these problems associated with iron and copper in particular and shows how they were overcome.

3.2. Preliminary Investigation

The work described in this section enabled the optimum conditions to be found for the determination of lead in aqueous solution at 217.0 and 283.3 nm. in each of three flames:- air-propane, air-acetylene and nitrous oxide-acetylene.

A solution containing 30μg.ml^{-1} of lead was aspirated into the appropriate flame whilst the burner height, slit width, lamp current and fuel flow rate were varied in turn. The optimum conditions (Table 3.2) associated with each parameter were established from the maximum absorbance coupled with minimum noise. The use of the nitrous oxide-acetylene flame was discontinued as a very noisy signal was obtained when solutions containing less than 50μg.ml^{-1} of lead were sprayed.

TABLE 3.2

Optimum Instrumental Parameters

Parameter		Air-Propane		Air-Acetylene		
		Aqueous Solution		Aqueous Solution		1BMK
		283.3 nm.	217.0 nm.	283.3 nm.	217.0 nm.	217.0r
Slit	mm.	0.03	0.10	0.04	0.10	0.10
Burner Height	mm.	12	14	10	4	4
Lamp current	mA.	6	6	6	6	6
Fuel pressure	p.s.i.	10	10	10	10	10
Fuel flow rate	l.min^{-1}	0.40	0.40	1	1	0.60
Air pressure	p.s.i.	30	30	30	30	30
Air flow rate	l.min^{-1}	5	5	5	5	5
Sensitivity (μg.ml^{-1}/ 1% absorption		0.58	0.28	0.97	0.43	0.14

Table 3.2 also shows the sensitivities for lead attained under the conditions shown. The air-propane flame at 217.0 nm. showed the better sensitivity for lead in aqueous solution and so this flame and wavelength were selected for further investigation.

The effect of various water miscible alcohols upon the absorbance of 10μg.ml^{-1} of lead was examined (Table 3.3). The degree of enhancement of signal produced was of similar order to that quoted in a previous study (54).

TABLE 3.3

Water Miscible Alcohols

% Alcohol	Absorbance of 10μg.ml^{-1} Pb at 217.0 nm. Air-Propane Flame			
	Ethanol	Methanol	Propan-1-ol	Propan-2-ol
0	0.185	0.185	0.185	0.185
10	0.214	0.188	0.281	0.265
20	0.199	0.207	0.295	0.262
30	0.193	0.213	0.285	0.235
40	0.202	0.217	0.279	0.241
50	0.212	0.251	0.269	0.235
60	0.215	0.271	0.279	0.217

The absorbance of lead was measured under the conditions shown in Table 3.2.

In order to cover the desired concentration range (1 to 100μg.g^{-1} of lead in steels) a solution of 2 g. of steel per 20 ml. would be required, and the solution would contain up to 15 mg.ml^{-1} and 25 mg.ml^{-1} of nickel and chromium on this basis (equivalent to concentrations of 150 mg.g^{-1} and 250 mg.g^{-1}

in stainless steel). The effect of these two metals in these concentrations upon the absorbance of 5μg.ml^{-1} of lead was investigated (Table 3.4) and found to be particularly serious.

TABLE 3.4

The Interference of Nickel and Chromium

Concentration of Metals (μg.ml^{-1}) Pb	Ni	Cr	Absorbance Air-Propane, 217.0 nm.
5	-	-	0.079
-	15000	-	0.020
-	-	25000	0.035
5	15000	-	0.120
5	-	15000	0.129

The absorbance of lead was measured under the conditions shown in Table 3.2.

In addition to the serious interference of nickel and chromium the sensitivity was barely adequate for the determination of lead in aqueous solution and hence it was considered necessary to isolate lead from the matrix. The solvent extraction of lead was considered to offer the best method of isolating lead as an increase in sensitivity is usually inherent with the determination of metals in organic solutions (54,57). The use of one such system for lead is discussed in the following sections.

3.3. The Extraction of Lead into Isobutylmethylketone

Various solvent extraction systems for lead have already been discussed in section 3.1. However other systems which have not been applied to atomic absorption have been used to determine trace amounts of lead in steels, notably the British Standard procedure (49) and that of Bricker and Proctor (58) which are based on dithizone. In each of these methods a dithizone solution in chloroform is used but, because of the noxious gases generated in the flame, chloroform is not a suitable solvent for use in atomic absorption. Dithizone has been shown to be unstable in the widely used solvent, lBMK, making extractions unreliable (59). Dagnall, West and Young (59,60) have used 4-(2-Pyridylazo)-Resorcinol (PAR) to extract lead from steels. This system, however, lacked specificity, too many extractions of interferents were required before the extraction with PAR. Of the systems discussed the iodide extraction (56) was chosen as being most favourable in that it was fairly selective. lBMK was chosen as solvent because of its suitability in the flame, its relative insolubility in water (40) and its excellent solvating properties for the iodo complex.

3.3.1. Optimisation of Extraction Parameters

The extraction procedure of West and Carlton (56) was investigated to determine the optimum conditions for both the initial extraction and the determination by atomic absorption.

4 ml. of lead solution ($50\mu g.ml^{-1}$) were pipetted into a 125 ml. separatory funnel adding 4 ml. of saturated potassium iodide solution and 1.25 ml. of concentrated hydrochloric acid before dilution to 25 ml. with water. 20 ml. of lBMK were added and the funnel was shaken for 2 minutes. The phases were allowed to separate and the lower aqueous phase run to waste before collecting the organic phase for spraying into the air-propane flame under the conditions described in Table 3.2.

Unfortunately the organic solvent produced an unstable, very luminous flame. The propane flow was reduced in an attempt to regain normal condition but the flame 'lifted-off' before this point was reached. A similar effect was observed in the air-acetylene flame but a reduction in the acetylene flow to 600 ml.min^{-1} regained the normal flame conditions. The acetylene flame under these conditions was much more stable than the propane flame and was subsequently used throughout the remaining work on lead. As with the aqueous solution the instrumental parameters of burner height, slit width and lamp current were varied in turn to establish the best conditions for the determination of lead in lBMK solutions (Table 3.2).

In a series of experiments the method of extraction of the lead complex into lBMK as described by Dagnall et al (72) was evaluated with regard to optimum concentrations of potassium iodide and hydrochloric acid and with regard to extraction time. To cover the required concentration range for an extraction into 20 ml. of IBMK an aqueous volume of about 25 ml. is required if the procedure of the authors is followed. As it was not feasible to concentrate 2 g. of steel into 25 ml. of solution the effect of increasing the aqueous volume was investigated whilst both the hydrochloric acid concentration of 5% and the organic phase of 20 ml. of lBMK were kept constant. On examination of the absorbance of the lBMK extracts from aqueous solutions whose total volume ranged from 25 to 200 ml. the aqueous volume which gave the most efficient extraction was 150 ml.

The extraction conditions for 0 to 200μg. of lead which were used in subsequent experiments is summarised in Table 3.5. The method changed very little from that described by the previous authors, although in this study better extraction was achieved using 4 ml. of saturated potassium iodide instead of 2.5 ml. and a shaking time of 1 minute rather than 30 seconds.

TABLE 3.5

The Extraction of Lead into lBMK

Aqueous Phase

Total volume	150 ml.
Concentration of lead	0 - 200μg.
Concentration of acid	15 ml. of 50%(v/v) hydrochloric acid
Concentration of potassium iodide	10 ml. of 43%(w/v)

Organic Phase	20.0 ml. of lBMK
Time of Shaking	1 minute

The organic extracts were dried over anhydrous sodium sulphate and stored in stoppered polythene bottles.

The use of the drying agent was found to aid in the breakdown of an emulsion which was carried through the funnel with the lBMK and to remove suspended water droplets from the organic phase. After drying much less flame noise was evident when the solutions were sprayed. 10 ml. of 43%(w/v) potassium iodide was the equivalent of 4 ml. of the saturated salt.

The efficiency of the extraction was determined by extracting three solutions of 100μg. of lead with four successiv 20.0 ml. aliquots of lBMK each. The lead absorbance of each extract was measured and the percentage extraction and absolute sensitivity determined. The average absorbances of the three solutions for each of the successive extractions with IBMK were 0.132, 0.028, 0 and 0. Assuming linearity of the absorbance vs. concentration plot over 0 to 100μg. of lead the percentage of lead extracted in one shaking was given by

$$\% \text{ Extraction} = \frac{100 \times 0.132}{(0.132 + 0.028)} = 82.3$$

This figure was somewhat lower than that obtained by previous workers (53,56) but was found to be reproducible throughout the remaining work. The absolute sensitivity, i.e. where the organic phase contained 4.12μg.ml^{-1} of lead instead of 5μg.ml^{-1}, was 0.14μg.ml^{-1} for a 1% absorption. A calibration curve of 0 - 200μg. lead extracted into 20.0 ml. IBMK under the conditions described in Table 3.5 was found to be linear from 0 to 160μg. lead (Figure 3.1).

3.4. Interference by Iron, Chromium and Nickel

Assuming a 2 g. sample weight, a steel containing 0.01% lead gives an aqueous solution containing 200μg. of lead. Similarly 55, 25 and 20% of iron, chromium and nickel gives an aqueous solution containing 1.1, 0.5 and 0.4 g. of each metal respectively. It has been shown that this amount of chromium and nickel interferes in the aqueous determination (section 3.2). Neither chromium nor nickel have been reported by previous workers to co-extract with lead and hence should not interfere in the organic determination. Iron (111), however, has been found to co-extract (57). The influence of these metals was ascertained by adding increasing amounts of iron (111), iron (11), chromium (111) and nickel to both the 'blank' solutions and the leaded solutions before the extraction.

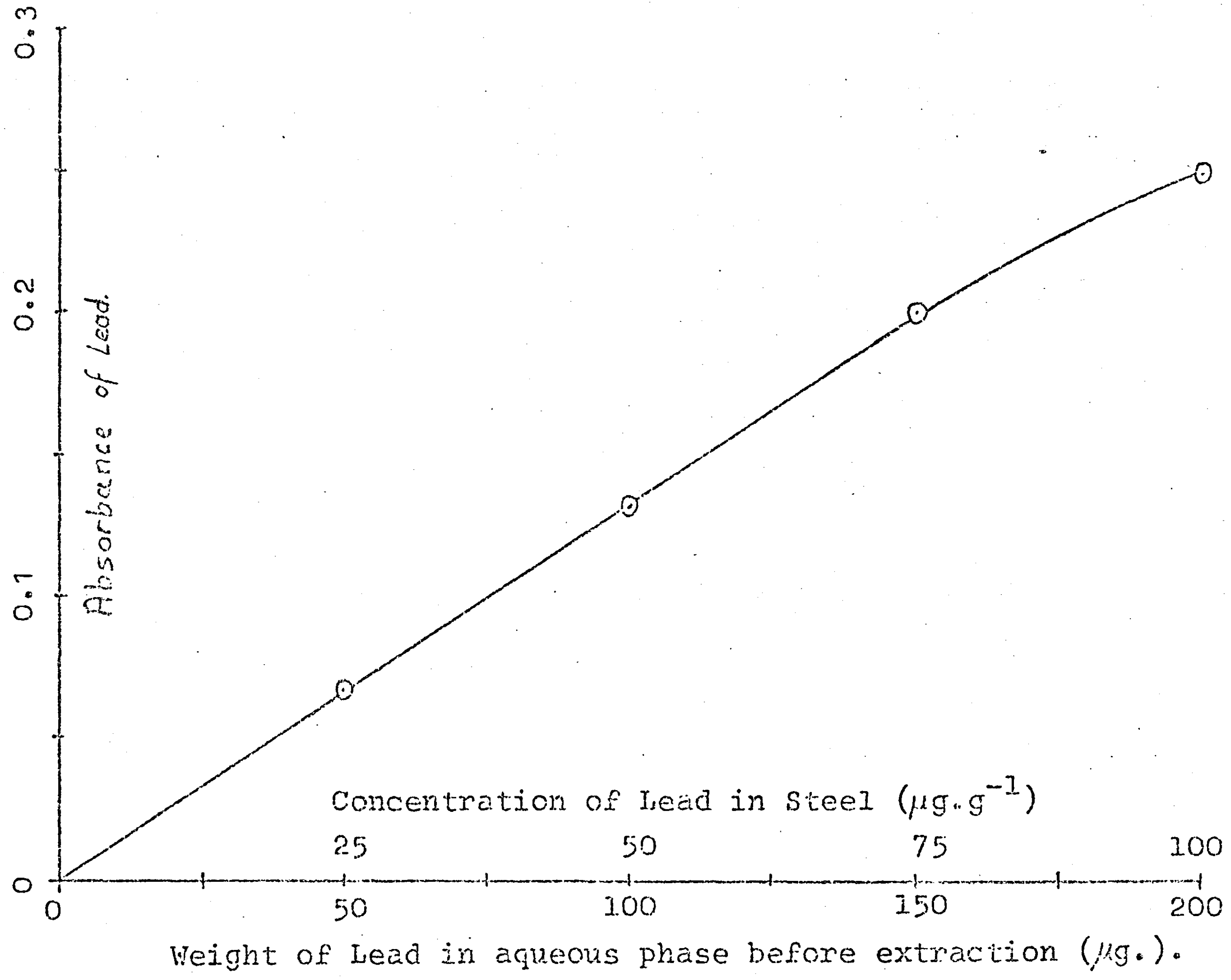

Figure 3.1

Calibration Curve

The absorbance of Pb was measured under the conditions shown in Table 3.2.

3.4.1. Experimental Procedure

0 to 60 ml. aliquots of iron (111) and iron (11) solutions (0.02 g.ml^{-1}), 10 to 50 ml. of chromium (111) solution (0.01 g.ml^{-1}) and 10 to 40 ml. aliquots of nickel solution (0.01 g.ml^{-1}) were treated with iodide and 1BMK as described in Table 3.5 both in the presence and absence of 10.0 ml. of lead solution (20μg.ml^{-1}).

The variation in the absorbance of the 1BMK extracts with increasing concentration of the three metals is shown in Figure 3.2 for iron and in Table 3.6 for chromium and nickel.

TABLE 3.6

The Interference of Nickel and Chromium on the Determination of Lead in 1BMK

Weight of metal in aqueous solution (g.)		Absorbance from	
Ni	Cr (111)	Blank	200μg. Pb
-	-	0	0.255
0.1	-	0.001	0.252
0.2	-	0.001	0.255
0.3	-	0	0.252
0.4	-	0	0.252
-	0.1	0.001	0.252
-	0.2	0.002	0.249
-	0.3	0.001	0.249
-	0.4	0.002	0.249
-	0.5	0.002	0.250

The absorbance was measured under the conditions shown in Table 3.2.

3.4.2. Interpretation of Results

Minimal interference from chromium and nickel was experienced on spraying both the 'blank' solutions and the leaded solutions of IBMK. The maximum suppression of signal of 3% occurred in the presence of chromium.

A dark red colouration of the aqueous phase was noted when the potassium iodide was added to the solutions containing iron (111). This colour was partly transferred to the IBMK phase on shaking and was due to the formation of iodine according to the reaction:-

$$2\ Fe^{3+} + 2\ I^{-} \longrightarrow I_2 + 2\ Fe^{2+}$$

The formation of iodine was no doubt responsible for the low absorbance readings of lead after the extractions in the presence of iron (111). When lead was extracted from solutions containing up to 0.4 g. of iron (11) the absorbances showed little deviation from that of the pure lead solution (Figure 3.2). Slight colouration of the lBMK was noted after the extraction in the presence of 0.3 g. of iron (11). The colour increased in intensity after extractions involving higher concentrations of iron (11). This reflected the difficulty in maintaining a reduced iron solution. Clearly the way of preventing interference from iron was by either extraction of the iron from the matrix or by reduction to iron (11). In practice it was found to be very difficult to keep iron reduced in a complex matrix such as steel. Hydroxylamine, hydrazine and ascorbic acid were tried but the absorbance of the lead solutions in IBMK were suppressed. EDTA was used to complex the iron but this inhibited the extraction of lead, the stability constant of Pb^{2+} - EDTA being greater than that of PbI_4^{2-}.

3.4.3. The Removal of Iron

The extraction of iron as its tetrachloride into an organic solvent has been reported (41,61). Dodson, Forney and Swift (41) have described an extraction, which is 99.9% efficient, into diisopropyl ether from an aqueous phase 7.75 to 8.0 molar in hydrochloric acid. This extraction was investigated and a procedure was adopted which allowed maximum extraction of iron (111) from the aqueous solution of the steel.

In the investigation a 50 ml. aliquot of iron (111) solution (0.04 $g.ml^{-1}$) was evaporated to dryness and carefully baked for five minutes to expel nitrogen gases. The residue was dissolved in 25 ml. of 8M hydrochloric acid, boiling being kept to a minimum to prevent loss of the acid. The solution was transferred to a 125 ml. separatory funnel, adding 50 ml. of diisopropyl ether before shaking for one minute. The phases were allowed to separate and 2 ml. of the lower, aqueous phase were placed in a test tube, the remainder of the aqueous phase being transferred to a second funnel. 43%(w/v) potassium iodide was added to the test tube yielding an intense iodine colour.

The solution in the second funnel was subjected to three further extractions with the ether. Each time a 2 ml. portion of the aqueous phase was treated with the iodide solution. The red iodine colour decreased in intensity over the three further tests. After the fourth extraction the colour was only just visible.

A preliminary iron separation would require four extractions with ether to prevent a reaction with iodide. As this would have rendered any procedure too lengthy an alternative to these extractions was sought. It was thought that the amount of iron remaining after one extraction with ether would not interfere with the extraction of lead.

The iron from three 50 ml. aliquots of iron (111) solution (0.04 $g.ml^{-1}$) was extracted into diisopropyl ether as outlined above. The aqueous phase was run into a 400 ml. conical flask and any remaining aqueous solution in the funnel was rinsed into the flask with 8M hydrochloric acid. The iron (111) was reduced to iron (11) using stannous chloride (11), 5 ml. each of concentrated sulphuric and orthophosphoric acids added and the iron content of the solutions was determined by titration with 0.025M potassium dichromate using barium diphenylaminesulphonate as indicator. The average titre was 12.06 ml. of 0.025M potassium dichromate.

The iron content was calculated from the following equation:-

$$6\ Fe^{2+} + Cr_2O_7^{\ 2-} + 14\ H^+ \longrightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$$

$$1\ \text{Mole}\ K_2Cr_2O_7 \equiv 6\ \text{Moles Fe}$$

i.e. $12.06\ \text{ml.}\ 0.025M\ K_2Cr_2O_7 = 12.06 \times 0.0083775\ \text{g. Fe}$

$= 0.101\ \text{g. Fe}$

The amount of iron extracted by the ether was:-

$$\frac{(2 - 0.101)}{2} \times 100\ \% = 94.95\%$$

The amount of iron remaining after one ether extraction has been shown to interfere with the extraction of lead if present as iron (111) (Figure 3.2). However, if iron is reduced to iron (11) before the extraction of lead then interference was not expected as 0.1 g. of iron (11) falls on the plateau in Figure 3.2.

The reduction of 0.1 g. of iron was accomplished using hydroxyammonium chloride. After the extraction of iron from a 50 ml. aliquot of iron (111) solution (0.04 $g.ml^{-1}$) the lower aqueous phase was returned to the beaker and evaporated to dryness to remove the last traces of ether. The salts were redissolved by simmering with 25 ml. of water. 15 ml. of 50%(v/v) hydrochloric acid and 10 ml. of 6%(w/v) hydroxyammonium chloride were added and the solution was heated to boiling point and allowed to simmer. After about three minutes the solution had lost its yellow tinge and appeared colourless. The solution was cooled and subjected to the iodide extraction (Table 3.5), but on separation of the phases, the upper IBMK phase had a red tinge. This procedure was repeated adding a further 10 ml. of 6%(w/v) hydroxyammonium chloride before the dilution to 150 ml. On examination of the IBMK phase this time, no colouration was observed.

Dodson et al (41) in their investigation did not include lead in their study of the behaviour of other elements in the iron extraction system. The non-extraction of lead was ascertained by the preparation of the aqueous solutions detailed in Table 3.7. 10 ml. of concentrated hydrochloric acid were added to solutions 1 to 7 in beakers and each was evaporated to dryness and baked for five minutes. The residues were redissolved in 25 ml. of 8M hydrochloric acid before transferring to 125 ml. separatory funnels. Any remaining solution was rinsed into the respective funnels using a little 8M hydrochloric acid. 50 ml. of diisopropyl ether were added and the funnels were shaken for one minute. After separation of the phases the lower aqueous phases were run back into the beakers washing the organic layers three times each with 2 ml. portions of the 8M acid. The washings were added to the beakers and the solutions were evaporated to dryness, cooled and the salts redissolved in 25 ml. of water. 15 ml. of 50%(v/v) hydrochloric acid and 10 ml. of 6%(w/v) hydroxyammonium chloride were added and the solutions were simmered for five minutes. A further 10 ml. of 6%(w/v) hydroxyammonium chloride were added to the solutions after cooling. The solutions were transferred to 250 ml. separatory funnels and the lead was extracted into IBMK (Table 3.5).

TABLE 3.7

Analysis of Aqueous Solutions after Removal of Iron

Solution Number	Composition	Absorbance
1	10 ml. Pb solution (20μg.ml.$^{-1}$)	0.254
2	As solution 1	0.253
3	10 ml. Pb solution (20μg.ml.$^{-1}$) and 50 ml. Fe (111) solution (0.04 g.ml.$^{-1}$)	0.254
4	As solution 3	0.255
5	50 ml. Fe (111) solution (0.04 g.ml.$^{-1}$)	0.001
6	As solution 5	0
7	Reagent blank	0
8	10 ml. Pb solution (20μg.ml.$^{-1}$) (Pb extraction only)	0.256

The absorbance of the 1BMK extracts were measured under the conditions shown in Table 3.2.

The absorbance (Table 3.7) of the solutions when sprayed into the flame indicated close agreement (within 1%) with the standard extraction of lead (solution number 8) which led to the conclusion that virtually no lead was extracted by the ether and that all interference by iron upon the lead extraction into IBMK had been eliminated.

3.5. Interference from Minor Elements

Steels contain many other elements present in minor amounts both as alloying constituents and as impurity elements in steelmaking materials. The interference effects of the more common minor elements were investigated. The aqueous phase of the extraction medium contained each element in turn in amounts corresponding to the maximum concentration likely to be found in steel and were obtained by dissolving the appropriate metal or metal oxide in a suitable solvent, i.e. concentrated nitric or hydrochloric acid. The solutions of sulphur and phosphorus were prepared by dissolving either potassium sulphate or tri-potassium phosphate in water.

The organic phase of 20.0 ml. of lBMK was sprayed into the flame after the extraction of lead. Interference was considered to have occurred if the amount of lead recovered (Table 3.8) differed by more than ± 4% from its value in the absence of any interferent. This value was chosen as a satisfactory criterion for the determination of lead in this region. Of the elements investigated copper, molybdenum and vanadium caused suppression of the lead signal and, in each case the red iodine colour was seen in the IBMK phase after the extraction. The aqueous solutions of lead plus interferent were treated with 20 ml. of 6%(w/v) hydroxyammonium chloride in a similar way to that described for the reduction of iron. This treatment reduced the molybdenum, titanium and vanadium to lower oxidation states. When the lead was extracted into lBMK and sprayed into the flame interference had been eliminated from all elements but copper. The problem of copper was the subject of a further investigation.

TABLE 3.8

The Interference of Minor Elements

% Element[a]	Before Reduction O.S.[b]	Before Reduction Absorbance[c]	Before Reduction µg.Pb	After Reduction O.S.[b]	After Reduction Absorbance[c]	After Reduction µg.Pb
100µg.Pb	-	0.132	100[d]	-	0.132	100[d]
100µg.Pb and additions of:-						
10% Mn	2	0.132	100	2	0.132	100
10% Al	3	0.126	96	3	0.131	98
5% Cu	2	0.021	15	2	0.026	20
5% Mo	6	0.102	76	5	0.131	98
2% Co	2	0.132	100	2	0.132	100
2% V	6	0.027	20	4	0.126	96
2% Nb	5	0.135	102	5	0.132	100
1% Ti	4	0.130	97	2	0.135	102
0.5% S	6	0.131	98	6	0.131	98
0.5% P	5	0.135	102	5	0.132	100

[a] 100% was equivalent to 2 g. of the element.

[b] O.S. = Oxidation state of the element.

[c] The absorbance of each IBMK extract was measured under the conditions shown in Table 3.2.

[d] The 100µg. solution of Pb was used as calibrant for the other solutions.

3.6. Interference from Copper and Iodine

The severe suppression of the lead absorbance noted for copper (11) was thought to be due to iodine liberated in a reaction similar to that with iron (111), namely:-

$$2\ Cu^{2+} + 4\ I^{-} \longrightarrow 2\ CuI + I_2$$

EDTA was unsuccessfully tried as complexing agent for copper (11). Apart from the suppression of signal from EDTA observed before (section 3.4.2), iodine was again released into the 1BMK.

3.6.1. The Effect of Increasing Copper Concentration

The magnitude of the interference of copper was investigated by extracting 100μg. of lead into IBMK in the presence of 0 to 50 ml. aliquots of copper solution (10 mg.ml^{-1}) in a method similar to that described for iron in section 3.4.1. The variation in absorbance of the lead with the amount of copper present in the aqueous phase and with the equivalent iodine concentration is shown in Figure 3.3. The equivalent iodine concentration was calculated from the reaction above, i.e.

$$2\text{ moles Cu} \equiv 1\text{ mole } I_2$$

$$\therefore\ 0\text{–}0.05\text{ g. Cu} \equiv 0\text{ to }0.10\text{ g. } I_2$$

After the extraction no trace of the red iodine colour was seen in the aqueous phase. Thus this amount of iodine was co-extracted with lead into the 1BMK. A grey-white precipitate, formed in the interface between the two phases after the extraction with copper present in amounts of 0.012 g. and above, was found to be cuprous iodide with 0.012 g. marking the maximum solubility in 1BMK of the extractable copper complex. If this was the case then both copper and iodine were present when the lead absorbance was measured indicating that the interference was, possibly, a combined effect from both copper and iodine. Figure 3.3 revealed that the suppressive effect reached a maximum at copper concentrations of 0.012 g. and above. In view of the diverse nature of the interference encountered the influence of both copper and iodine was investigated further.

3.6.2. The Extraction of the Copper-Iodide Complex into IBMK

The amount of copper extracted into 1BMK was ascertained by treating 4.0 ml. of copper solution (10 mg.ml.$^{-1}$) with potassium iodide and 1BMK as described in Table 3.5, retaining both the aqueous and organic phases. The lower aqueous phase was transferred to a 400 ml. beaker whilst the 1BMK, which contained some cuprous iodide precipitate, was filtered through a Whatman 541 filter paper. The filter paper was placed into the 400 ml. beaker containing the aqueous solution along with 5 ml. of concentrated sulphuric acid and the solution was evaporated until the filter paper started to char. Concentrated nitric acid was added to decompose the paper, additions being made until the solution evolved the white sulphur trioxide fumes without charring and all iodine had been evolved from the decomposed potassium iodide. After cooling, the residue was dissolved in 25 ml. of water, cooled and diluted to 1 litre with water. This procedure was repeated with 8, 12, 20 and 30 ml. aliquots of the copper solution (10 mg.ml.$^{-1}$).

The amount of copper retained in the residue solutions was determined by extraction of its diethyldithiocarbamate complex into carbon tetrachloride (12), the copper absorption of the organic extracts being measured on the Unicam SP 500 Spectrophotometer. 0 to 10 ml. aliquots of copper solution (10μg.ml^{-1}) were used in calibration of the procedure.

The percentage of copper extracted into IBMK was calculated from the copper content of the residue solutions (Table 3.9), the results indicating that up to 70% of the copper is extracted by 20 ml. of IBMK under the same conditions as the lead extraction. Saturation point of the solubility of the copper complex in lBMK occurs when 8.2 mg. of copper have been extracted. All amounts of copper have been shown to suppress the lead absorption (Figure 3.3); either as copper interference, as iodine interference or a combination of both; the minimum absorbance being obtained when the copper content of the aqueous phase is greater than 0.012 g. As 0.012 g. of copper is the concentration which gives saturation of the lBMK phase by cuprous iodide then this explains the plateau in Figure 3.3. This reasoning does not take into account the effect of liberated iodine on both the extraction of lead or its determination.

TABLE 3.9

The Extraction of the Copper-Iodide Complex

Weight of Copper in Aqueous Phase before extraction (mg.)	Weight of Copper in Aqueous Phase after extraction (mg.)	Weight of Copper transferred to IBMK Phase (mg.)	% Copper Extracted into IBMK
4	1.17	2.83	70.8
8	2.22	5.78	72.3
12	3.88	8.12	67.7
20	11.80	8.20	40.6
30	21.80	8.20	27.4

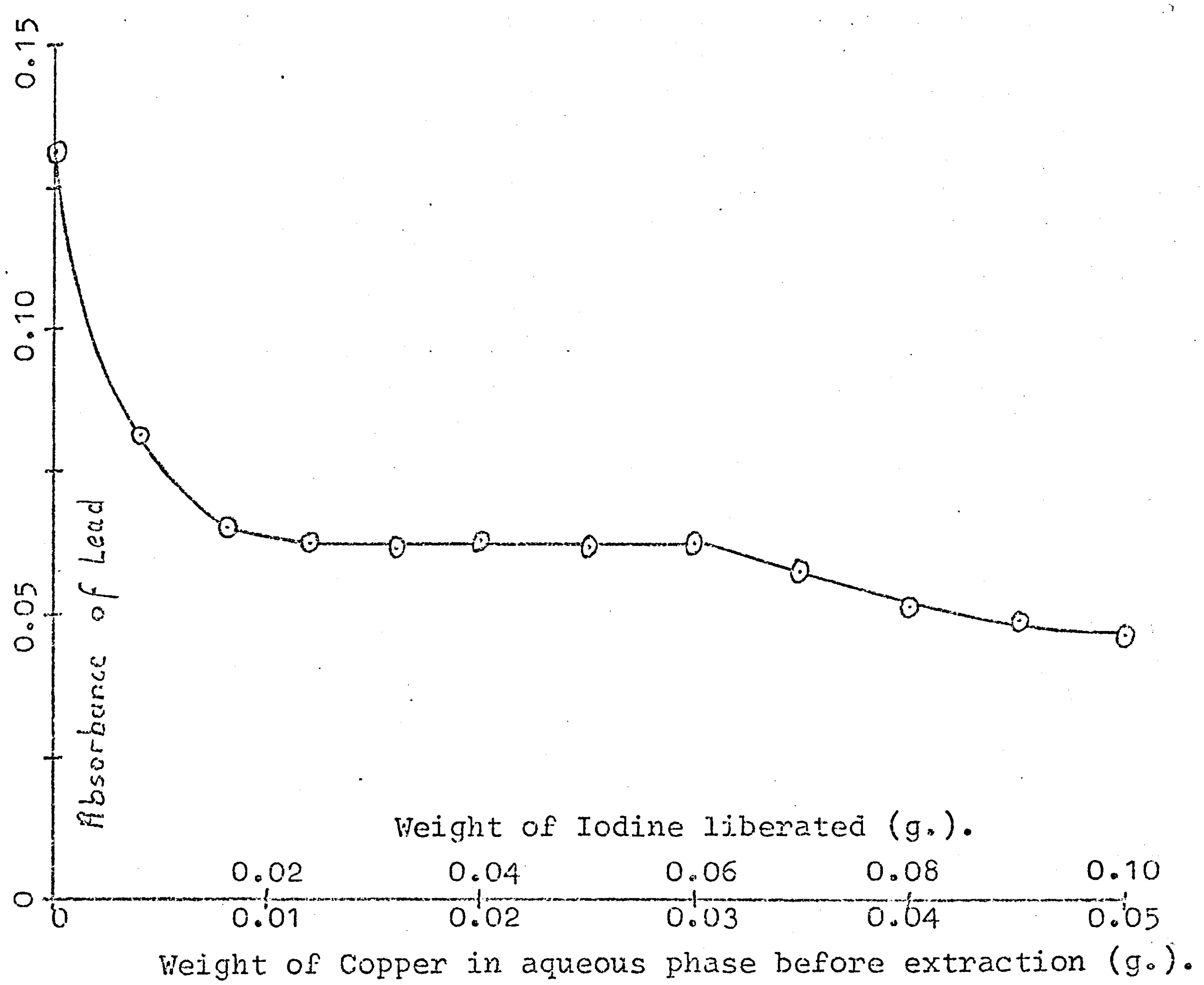

Figure 3.3

The Interference of Copper

The absorbance of Pb was measured under the conditions shown in Table 3.2.

3.6.3. The Liberation of Iodine

The effect of iodine on both the extraction of lead into lBMK and upon the atomic absorption determination of lead was investigated by adding up to 0.06 g. iodine to both the aqueous and organic phases before extraction and to the lBMK after the extraction of lead.

3.6.3.1. The Extraction of Lead and Iodine into IBMK

The solubility of iodine in water is limited. An aqueous iodine solution was prepared by dissolving 0.5 g. of iodine in 84 ml. of 43%(w/v) potassium iodide, diluting to 100 ml. with water. 0 to 12 ml. aliquots of this solution were pipetted into a series of 250 ml. separatory funnels containing 100μg. of lead. The iodide concentration was adjusted to the correct amount by addition of 43%(w/v) potassium iodide and the lead was extracted into IBMK as described in Table 3.5. The variation in the absorbance of the IBMK extracts with iodine concentration is shown in Figure 3.4.

A 10.0 ml. aliquot of the iodine solution was diluted to 100 ml. with water and a visible absorption spectrum was recorded on the Unicam SP 800 Spectrophotometer between 300 and 700 nm. using 1 cm. silica cells, the spectrum showing one peak at 350 nm. Aliquots of each of the aqueous phases after extraction were placed in 2 cm. silica cells and the absorption at 350 nm. of each solution was noted using the Unicam SP 500 Spectrophotometer. No absorbance was found for any of the solutions indicating that all iodine had been transferred to the IBMK.

3.6.3.2. The Extraction of Lead into an IBMK Solution of Iodine

In a second experiment 100μg. of lead were extracted into IBMK containing 0 to 0.06 g. of iodine. The iodine solution was prepared by dissolving 0.5 g. of iodine in 100 ml. of IBMK. The lead from a 5.0 ml. aliquot of lead solution (20μg.ml^{-1}) was extracted into the organic phase as detailed in Table 3.5. The organic phase consisted of 0 to 12 ml. (x) of iodine solution and (20 - x) ml. of IBMK. The variation in the absorbance of the IBMK extracts with iodine concentration is shown in Figure 3.4.

3.6.3.3. The Addition of Iodine to lBMK Extracts containing Lead

The lead from eight 5.0 ml. aliquots of lead solution (20μg.ml^{-1}) was extracted into lBMK as described in Table 3.5. The phases were given time to completely separate before transference of each dried lBMK phase to one polythene container. After mixing the combined extracts, 20.0 ml. aliquots were pipetted into 25 ml. graduated flasks, adding 0 to 3.0 ml. of iodine solution (prepared by dissolving 0.5 g. of iodine in lBMK and diluting to 25 ml. with lBMK) before diluting to the mark with lBMK. After mixing, the solutions were sprayed into the flame and the absorbance noted (Figure 3.4).

3.6.3.4. Discussion

Referring to Figure 3.4 the absorbance of plot A, where the lead extract is diluted with iodine solution before measurement, deviates very little from the absorbance in the absence of iodine, indicating that iodine has very little effect upon the determination of lead by atomic absorption.

The two remaining plots where lead is extracted

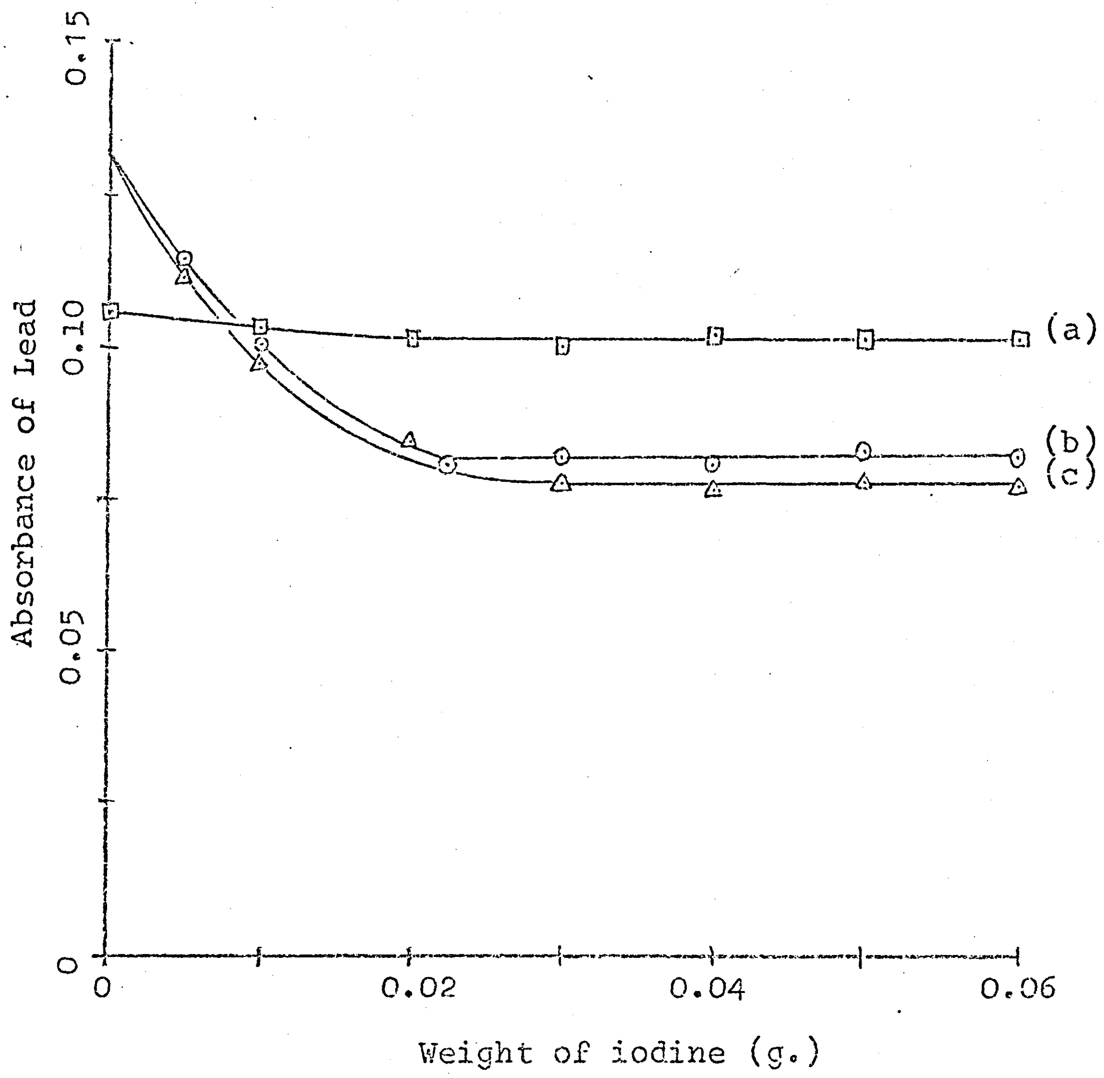

Figure 3.4

The Interference of Iodine

The absorbance of Pb was measured under the conditions shown in Table 3.2.

(a) The extraction of Pb into IBMK and dilution with I_2 in IBMK.

(b) The extraction of Pb into a solution of I_2 in IBMK.

(c) The extraction of Pb and I_2 into IBMK.

into IBMK containing iodine (Plot B) and where both lead and iodine are co-extracted into IBMK (Plot C) are almost identical, the latter illustrating that iodine is extracted into IBMK in preference to the lead. The presence of iodine in the IBMK phase must, therefore, inhibit the extraction of the iodo complex of lead (Plot B). The plateaux of plots B and C do not mark the maximum solubility of iodine in IBMK as iodine was soluble in IBMK in all the proportions tried. Plots B and C are very similar to that of Figure 3.3 where lead is extracted into IBMK in the presence of increasing amounts of copper. The plateau of minimum absorbance is lower in terms of absorbance in the case of copper, the difference representing interference from copper itself. This interference may take the form of either an inhibition of the extraction or an actual interference effect in the determination. In Figure 3.3 the plateau begins at an equivalent iodine concentration of 0.025 g., the same point as in plots B and C of Figure 3.4, indicating that iodine from the reaction -

$$2\ Cu^{2+} + 4\ I^- \longrightarrow 2\ CuI + I_2$$

is the controlling factor in the interference from copper and not copper itself.

In summary, interference from copper operates in two ways, both dependent upon the reaction between copper (11) and iodide ions. The more important factor is the liberation of iodine which inhibits the initial extraction of lead without affecting the atomic absorption determination. Secondary interference comes from copper itself through formation of an IBMK soluble complex which probably inhibits the lead extraction in a way similar to that of iodine.

It is shown in Figure 3.4 that the suppressive effect of iodine reaches a maximum at about 0.03 g. The efficiency of the extraction of lead in the presence of iodine concentrations in this region is discussed in the next section.

3.6.4. The Efficiency of the Extraction of Lead in the Presence of Iodine

The reduction in the efficiency of the extraction of lead in the presence of up to 0.06 g. of iodine was determined by measuring the lead remaining in the aqueous phase after each extraction in the presence of iodine. The lead remaining in the aqueous phase was ascertained by carrying out a second iodide extraction into IBMK, this time omitting iodine.

Calibration was achieved by extracting the lead from 10.0 ml. of lead solution ($10\mu g.ml^{-1}$) into three successive 20 ml. aliquots of IBMK. Each organic extract was sprayed into the flame and the total absorbance of $100\mu g.$ of lead was calculated by summation of the individual absorbances. The total absorbance of each of 25, 50 and $75\mu g.$ of lead in IBMK was determined in the same way and their variation with the lead content shown in Figure 3.5.

The decrease in the extraction efficiency of lead in the presence of iodine was ascertained by preparing a series of solutions containing $100\mu g.$ of lead and increasing amounts of iodine as described in section 3.6.3.1.

The lead was extracted into 20.0 ml. of IBMK (Table 3.5) retaining both the aqueous and IBMK extracts, the latter for spraying into the flame. The aqueous phases were transferred to a second series of separatory funnels adding a further 20.0 ml. aliquot of IBMK to each. After this second

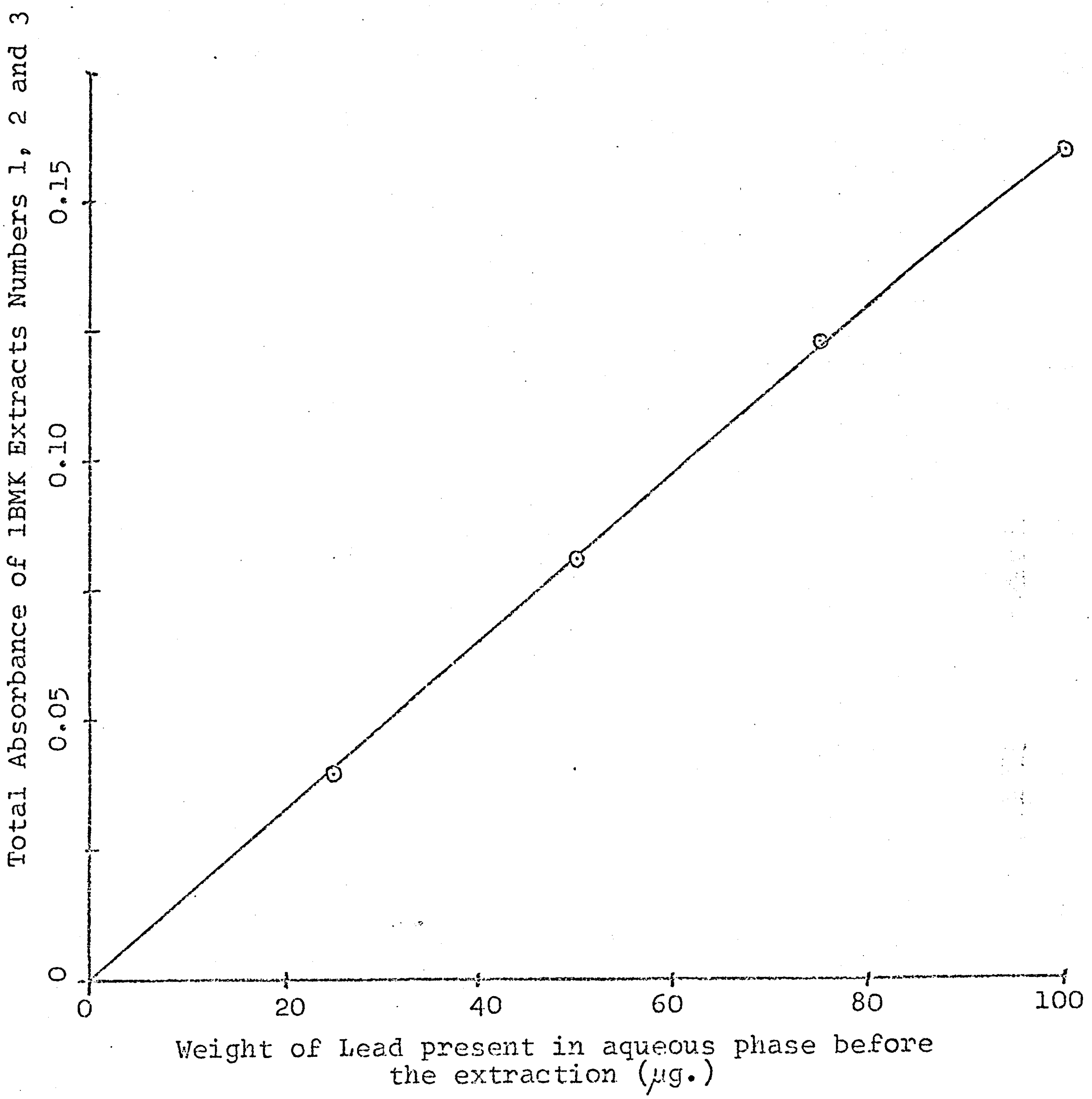

Figure 3.5

Calibration Curve for the Triple Extraction of Lead

The absorbance was measured under the conditions shown in Table 3.2 for the air-acetylene flame at 217.0 nm.

extraction where both the organic and aqueous phases were again retained any further lead remaining in the aqueous phase was extracted into a third aliquot of IBMK, this time retaining only the IBMK extract.

Each extract was sprayed into the flame, recording the absorbances (Table 3.10). The absorbance of the second and third extracts were summed and by relation to Figure 3.5 the concentration of lead remaining in the aqueous phase after the extraction in the presence of iodine (extraction no.1) was found.

TABLE 3.10

The Efficiency of the Extraction of Lead into IBMK with Increasing Concentration of Iodine

g. I_2 in aqueous phase	Absorbance of extraction no. 1	2	3	Total absorbance of extractions 2 + 3	µg. Pb in aqueous phase after 1st extraction (from Figure 3.5)	Efficiency of extraction (%)
0	0.132	0.028	0	0.028	17.7	82.3
0.01	0.107	0.055	0	0.055	34.0	66.0
0.02	0.080	0.085	0	0.085	52.3	47.7
0.03	0.077	0.089	0.004	0.093	58.9	41.1
0.04	0.077	0.091	0.005	0.096	59.3	40.7
0.05	0.079	0.091	0.004	0.095	59.0	41.0
0.06	0.077	0.091	0.005	0.096	59.~~5~~3	40.5

The absorbances were measured under the conditions shown in Table 3.2.

The IBMK phase of the second extract was free from any iodine colour indicating that all iodine had been extracted in the first separation. As expected the amount of lead extracted in the first separation decreased inversely with iodine concentration, levelling out at an efficiency of 40-41%. At the time this reduction in the efficiency of the extraction was thought to be unacceptable although the absorbances were reproducible when measured on the plateau of plots B and C of Figure 3.4.

An attempt to reduce the liberated iodine to iodide before the extraction by adding sodium thiosulphate solution met with little success as the lead absorbance was suppressed in the presence of thiosulphate and a suspension of sulphur was formed in the IBMK phase. This suspension was difficult to remove and rendered the flame unstable when the IBMK extracts were sprayed.

3.6.5. Liberation of Iodine from Alloys

Stainless steels contain up to 0.5% copper. This amount of copper, i.e. 0.01 g. with a sample weight of 2 g., would be expected to liberate 0.02 g. of iodine. Three stainless steel alloys, each containing both copper and lead, were analysed to determine whether the corresponding amount of iodine was liberated by a 2 g. sample. The liberated iodine was determined by measuring the absorption of iodine in 1BMK on the Unicam SP 500 spectrophotometer.

3.6.5.1. Calibration

0.1 g. of iodine were dissolved in 20 ml. of 43% (w/v) potassium iodide and the solution wad diluted to 1 litre with water (100 μg.ml.$^{-1}$ of iodine). A 10.0 ml. aliquot was pipetted into a 250 ml. separatory funnel, and 10 ml. of 43%(w/v) potassium iodide were added before diluting to 150 ml. with water.

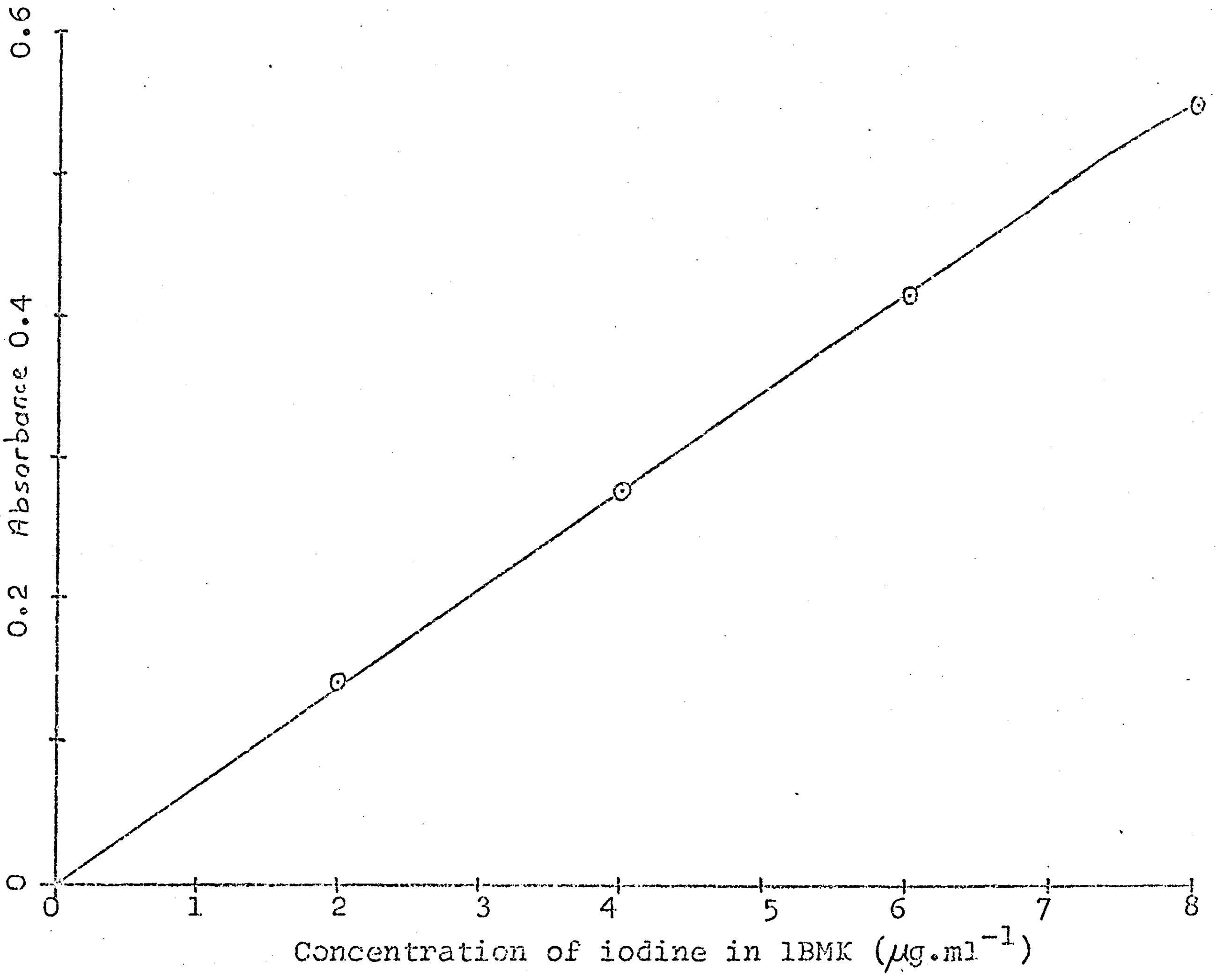

Figure 3.6

Calibration Curve for the Determination of Iodine by Solution Spectrophotometry

20.0 ml. of IBMK were added and the funnel was shaken for one minute. The phases were allowed to separate and the IBMK phase was dried over 0.2 g. of anhydrous sodium sulphate before filtration and dilution of the solution in a graduated flask to 100 ml. with IBMK ($10 \mu g.ml.^{-1}$ of iodine). A portion of this solution was placed in a 1 cm. silica cell and the absorption of the iodine solution was measured over the range 300 to 700 nm. on the Unicam SP 800 Spectrophotometer. One peak was noted in this region, at 367 nm.

A calibration of 0 to $8 \mu g.ml.^{-1}$ of iodine in IBMK was compiled (Figure 3.6) by measuring the absorbance of 5.0, 10.0, 15.0 and 20.0 ml. aliquots of the iodine solution after dilution to 25 ml. with IBMK. The absorbance of each solution was measured on the Unicam SP 500 spectrophotometer at 367 nm. using 1 cm. silica cells.

3.6.5.2. The Determination of Iodine

The iodine liberated by the addition of iodide to three stainless steels containing 0.41, 0.25 and 0.10% of copper respectively was determined as follows:-

2 g. of the alloy were dissolved in 25 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid. The solution was evaporated to dryness, baked for 5 minutes and treated as described in section 3.4.3., page 35, retaining the dried IBMK extract.

The extract (containing x g. of iodine) was diluted to 100 ml. with IBMK. A 5.0 ml. aliquot was pipetted into a second 100 ml. graduated flask and diluted to the mark with IBMK (iodine content $5 \times 10^{-4} x$ g.ml^{-1}). A 10.0 ml. aliquot of this solution was pipetted into a 25 ml. graduated flask and diluted to the mark with 1BMK (iodine content $2 \times 10^{-4}\ x$ g.ml^{-1}). The absorbance of this solution was measured at 367 nm. (Table 3.11). The iodine liberated, i.e. x, was calculated by relation to Figure 3.6.

TABLE 3.11

The Liberation of Iodine in the Analysis of Steels

% Cu in alloy	Equivalent I_2 Concentration (g.)	Absorbance SP 500, 367 nm.	I_2 concentration from Fig. 3.6 (μg.ml^{-1})	g.I_2 liberate
0.41	0.0164	0.405	4.40	0.022
0.25	0.0100	0.510	5.55	0.028
0.10	0.0040	0.392	4.25	0.021

e.g. According to the reaction

$$2\,Cu^{2+} + 4\,I^{-} \longrightarrow 2\,CuI + I_2$$

0.0082 g. of Cu (11) (0.41% Cu) liberates 0.016 g. of I_2. The absorbance of the diluted extract was equivalent to 4.4 g. of iodine (Figure 3.6) and hence

$$2 \times 10^{-4}\, x = 4.4 \times 10^{-6}$$

$$x = \frac{4.4 \times 10^{-6}}{2 \times 10^{-4}} = 0.022 \text{ g. of iodine}$$

In each case more iodine was liberated from the solution of the steel than was expected if the reaction between Cu (11) and iodide was followed. This was thought to be due to incomplete reduction of some metals in the steel matrix. The findings led to the belief that complete freedom from iodine would not be achieved easily. With this in mind the possibility of determining lead in the presence of iodine was pursued.

3.7. Calibration

The interference of copper upon the extraction and determination of lead has been shown to be due mainly to the interaction between copper (11) and iodide liberating iodine into the IBMK. Competition also exists for extraction into IBMK with both copper and iodine being extracted along with lead, the efficiency of the extraction of lead suffering as a result. The percentage of lead extracted, however, does become constant above a certain concentration of both copper and iodine. It is possible to determine lead in the presence of copper if the effects of both interferents can be standardised.

The calibration of an atomic absorption procedure can be achieved in a variety of ways, including calibration from solutions of steels whose lead content is known or using synthetic solutions. In atomic absorption the latter is more acceptable as the reliance upon predetermined standards detracts from the versatility of the technique. In view of the interference problems encountered calibration by the direct extraction of lead is not possible. The calibrant solution must contain either copper, iodine or both. The feasibility of both methods of calibration was ascertained.

Stainless steels generally contain up to 0.5% copper, i.e. less than 0.01 g. in a 2 g. sample. These amounts lie on the gradient of Figure 3.3. Calibration of solutions containing 0 to 0.01 g. of copper would be difficult, extremely accurate additions of copper to the calibrant solutions being needed. Iodine has been found to be liberated from sources other than copper (11). The amounts liberated, 0.02 to 0.03 g., do lie on the plateaux of Figure 3.4 and standardisation by adding, e.g.

0.02 g. of iodine, to the solutions would be acceptable. The addition of iodine would not, however, account for copper interference. A more appropriate standardisation procedure was proposed where copper was added to both calibrants and steels.

If an addition of copper between 0.01 and 0.03 g. is made to both calibrants and steels then the copper content of both will fall on the plateau of Figure 3.3 provided the total copper content, i.e. amount added plus amount in steel, does not exceed 0.03 g. Similarly the amount of iodine liberated will also fall on the plateau of Figure 3.4. The copper addition chosen, 0.012 g. allows for copper contents up to 0.9% in steels. As the iodine liberated by 0.012 g. of copper is 0.024 g. and the maximum released by potassium iodine in the analysis of steel is 0.03 g. then the liberated iodine will also fall on its plateau. These two methods of standardisation were investigated.

3.7.1. Preparation of Calibration Graphs

In the first method the absorbance of the organic extracts from three stainless steels of known lead and copper content were related to a calibration graph compiled from a BCS steel and in the second 0.012 g. of copper were added to both the steels and the calibrant solutions before the extraction of lead.

3.7.1.1. British Chemical Standard Steels

Three 2 g. samples of BCS 334 were treated in a manner similar to that described in section 3.6.5. for the stainless steel alloys. 0, 4.0 and 8.0 ml. aliquots of lead solution ($10\mu g.ml^{-1}$) were added to each of the solutions in the separatory funnels before the lead was extracted into 20.0 ml. of IBMK.

3.7.1.2. Copper

Three 12.0 ml. aliquots of copper (11) solution (10 mg.ml^{-1}) were pipetted into three 250 ml. separatory funnels containing 2.0, 6.0 and 10.0 ml. of lead solution (10 μg.ml^{-1}). The lead was extracted into lBMK as described in Table 3.5.

The absorbance of the lBMK extracts were used to construct calibration curves for each of the two methods (Figure 3.7). Calibration using both BCS 334 and 0.012 g. of copper gave the same plot. The plot, however, was much different from Figure 3.1 where lead alone was extracted into lBMK. In order to ascertain the most suitable calibration method three steels of known lead content were analysed by each of the two procedures and by relation to Figure 3.1.

3.7.2. Pre-analysed Steels

The three stainless steels were analysed by the procedure described in section 3.6.5, extracting the lead into 20 ml. of IBMK. In a second experiment the three steels were analysed as above but 12 ml. of copper solution (10 mg.ml^{-1}) were included in each separatory funnel with the steel solution. The extracts were sprayed into the flame and the absorbance noted (Table 3.12).

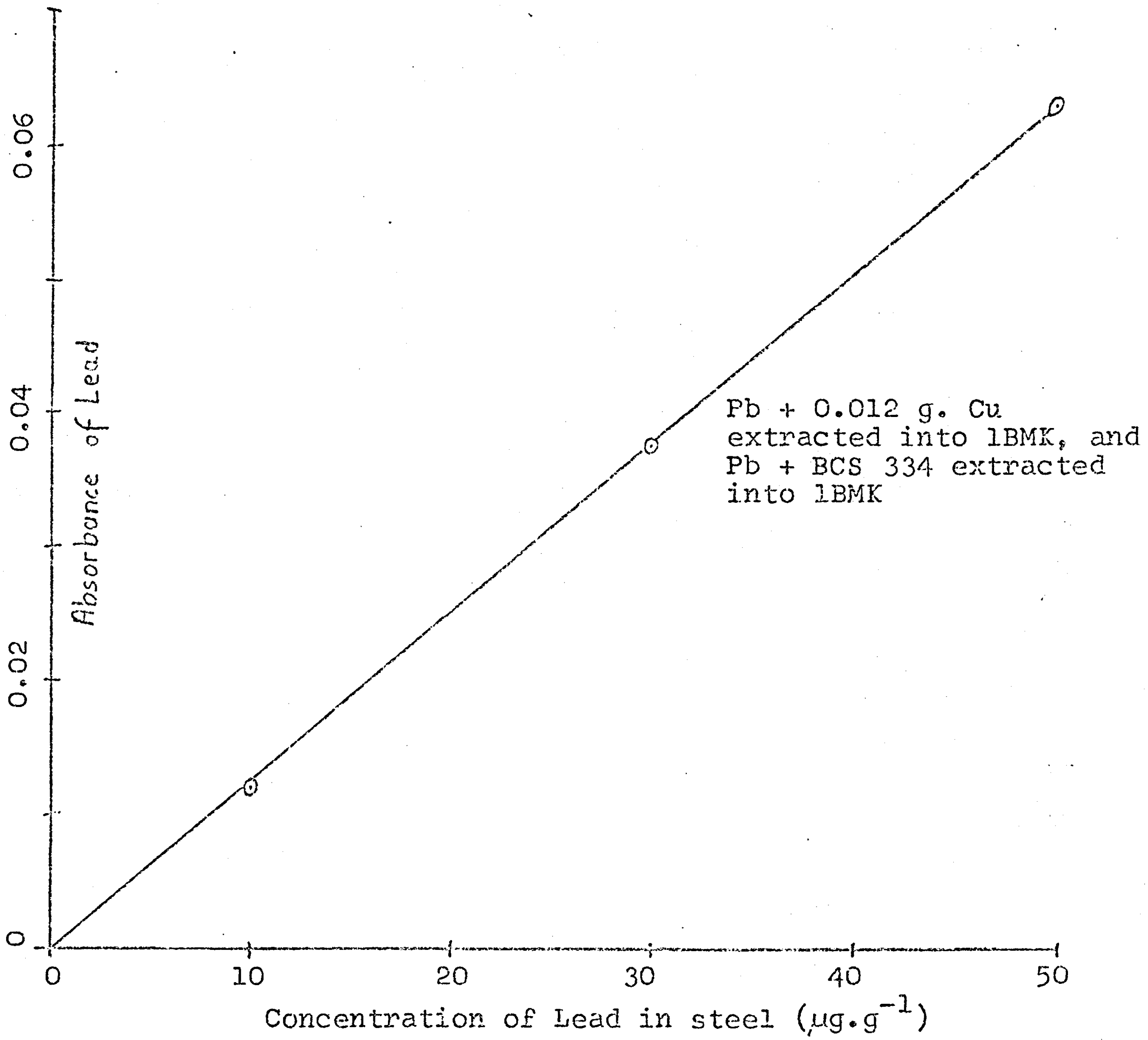

Figure 3.7

Calibration Curve for the Determination of Lead in Steel

The absorbance of Pb was measured under the conditions shown in Table 3.2.

TABLE 3.12

Calibration Procedures

Alloy Number[a]	Absorbance[b] of 1BMK extracts		Concentration of Pb Recovered[c] ($\mu g.g^{-1}$)		
	I	II	A	B	C
1	0.060	0.062	23	48	48
2	0.022	0.020	9	17	17
3	0.038	0.038	15	31	31

[a] The composition of the alloys was -

1. 0.41% Cu, 45$\mu g.g^{-1}$ Pb
2. 0.25% Cu, 15$\mu g.g^{-1}$ Pb
3. 0.10% Cu, 30$\mu g.g^{-1}$ Pb

[b] The absorbance of each extract was measured under the conditions shown in Table 3.2. The Pb was extracted into 1BMK:-

I in the absence of Cu, and

II in the presence of 0.012 g. of Cu.

[c] The absorbance shown in I and II was related to the calibration curves compiled from solutions containing -

A Pb (Figure 3.1),

B 0.012 g. of Cu (Figure 3.7), and

C BCS 337 (Figure 3.7).

The amount of lead detected was determined from the relevant calibration graph (Figures 3.1 and 3.7). In the first column the calibration was from an extraction of lead alone into 1BMK (Figure 3.1). The values obtained were much lower than the actual lead content of the steels. The analysis in the second and third columns where calibration was from either 0.012 g. of copper or from BCS 334 showed close agreement with the actual lead content of the steel. The absorbances of the solutions were almost identical for each analysis procedure.

In the analysis procedure adopted 0.012 g. of copper were added to both steels and calibration solutions before extraction of the lead complex.

3.8. Recommended Procedures

3.8.1. Analysis of Stainless Steels

Dissolve 2 g. of the alloy in 25 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid. Evaporate the solution to dryness and bake until all nitrous fumes have been evolved. Cool and dissolve the residue in 25 ml. of 8M hydrochloric acid with a minimum of boiling. Transfer to a 125 ml. separatory funnel, add 50 ml. of diisopropyl ether and shake for 1 minute. Allow the layers to separate and run the lower aqueous phase into a beaker. Wash the organic phase with three 2 ml. portions of 8M hydrochloric acid and add the washings to the beaker. Evaporate the solution in the beaker to dryness, and redissolve the salts in 25 ml. of water with gentle warming. Add 15 ml. of 50%(v/v) hydrochloric acid and 10 ml. of 6%(w/v) hydroxy~~l~~ammonium chloride. Simmer gently for a few minutes and remove from the hot plate. Allow the beaker to cool and add a further 10 ml. of 6%(w/v) hydroxyammonium chloride.

Transfer the solution to a 250 ml. separatory funnel and dilute to about 135 ml. with water. Add 5 ml. of copper (11) solution (2.4 mg.ml^{-1}) and 10 ml. of 43%(w/v) potassium iodide solution. Pipette 20.0 ml. of IBMK into the funnel, shake for one minute and allow the layers to separate. Discard the aqueous layer and run the lBMK phase into a beaker containing 0.25 to 0.5 g. of anhydrous sodium sulphate. Filter the lBMK phase through a Whatman 541 filter paper into a stoppered polythene bottle and spray into the flame. Read the lead content from the calibration graph.

3.8.2. Calibration Graph

From a burette transfer 0 to 10.0 ml. of lead solution ($10 \mu g.ml.^{-1}$) into 250 ml. separatory funnels. Dilute each to about 120 ml. with water and add 15 ml. of 50%(v/v) hydrochloric acid. Add 5 ml. of copper (11) solution ($2.4\ mg.ml.^{-1}$) and proceed as described above.

3.9. Analysis of Stainless Steel Alloys

Eleven stainless steel alloys, including the three already analysed, and two carbon steels were analysed by the recommended procedures (section 3.8). Their composition together with the analysis quoted by the British Steel Corporation is shown in Table 3.13. The analysis of each steel by relation to the calibration curve compiled from BCS 334 is also shown.

TABLE 3.13

The Analysis of Alloys

No.	Alloy Composition	Lead Content ($\mu g.g^{-1}$)			
		Dithizone[a]	Atomic Absorption		
			R.P.[b]		BCS[c]
1[d]	0.2% Cu	25	23	24	25
2[d]		45	42	44	45
3	9% Ni, 18% Cr, 0.25% Cu	15	13	14	15
4	- " -	35	37	38	35
5	- " -	30	26	24	25
6	- " -	25	23	24	25
7	- " -	35	33	34	30
8	- " -	15	17	15	17
9	- " -	15	14	15	15
10	11% Ni, 18% Cr, 0.2% Cu	55	57	57	60
11	- " -	7	3	5	5
12	11% Ni, 18% Cr, 0.1% Cu	30	31	32	31
13	10% Ni, 18% Cr, 0.4% Cu	45	48	46	48

Notes

[a] Values quoted by B.S.C. using the B.S. dithizone procedure (49).

[b] R.P. - Values obtained by the recommended procedure (section 3.8).

[c] BCS - Values obtained by calibration with BCS 334.

[d] Low-Alloy steels

3.10. Conclusion

The direct determination of lead in steels by atomic absorption spectrophotometry in the range 0 to 100$\mu g.g^{-1}$ has been found to be inpractical due to both the lack of adequate sensitivity and serious interference from the matrix elements in steel.

A determination of lead in steels by atomic absorption has been devised, based on an extraction technique whereby lead is extracted as its tetraiodo complex into IBMK. Of the major and minor elements present in steels only iron and copper have been found to interfere appreciably. Interference by iron was prevented by its prior removal with diisopropyl ether. The interference of copper was the centre of a lengthy study in which it was shown that copper reacts with iodide to liberate iodine into the organic phase. The interference was a combination of the effects of both copper and iodine, the latter inhibiting the extraction of lead. Interference by copper was secondary in nature to that of iodine and was caused by the solubility of a copper-iodide complex in IBMK.

The determination of lead in steels was finally accomplished by the addition of copper to both steels and calibrant solutions before extraction of the lead complex and its subsequent determination by atomic absorption.

The analysis of a number of alloys is quoted each showing excellent agreement with the analysis by the British Standard technique. The method although involving two solvent extraction stages is considerably shorter than the British Standard procedure, more reliable, more precise and is applicable to a wider range of steels.

CHAPTER FOUR

LANTHANUM

4.1. Introduction

Lanthanum, and other rare earth metals, have a high affinity for oxygen and are therefore used as deoxidants of low alloy steels. Deoxidation of steels with rare earth metals is superseding the use of conventional deoxidants because of the undesirable side effects which the metals, such as aluminium, produce. The use of rare earth metals, however, usually as a mixture called Mischmetal, which contains about 50% cerium, 25% lanthanum and 25% of other rare earths plus iron, produces very few detrimental side effects (1,2) and is also an excellent desulphurant; reducing non-metallic inclusions to a minimum.

The absorption of cerium and lanthanum by the steel is important to metallurgists but the methods available for the determination of one of them, lanthanum, are inadequate particularly when considering the small amounts of lanthanum usually involved, up to 0.01% ($100 \mu g.g.^{-1}$).

The usual method used in steelworks for the determination of lanthanum is one of 'difference'. The total rare earth content of the steel is determined by oxalate precipitation, followed by conversion to oxides for subsequent weighing. The rare earth oxides are then redissolved in acid and the cerium content is determined, after its oxidation and removal from the matrix, by reprecipitation of oxalate and subsequent conversion to oxide. The difference between the two weighings is assumed to be that of lanthanum oxide. This method of analysis is very unsatisfactory as the lanthanum analysis amounts to total rare earth analysis minus cerium.

Numerous other methods of determination are available but they are either too insensitive, e.g. colorimetry, or suffer from numerous interferences, e.g. emission spectrometry. Atomic spectroscopy, however, has been used to determine lanthanum in steels (62,63).

Of the atomic spectroscopic techniques atomic absorption has been found too insensitive for the determination of lanthanum in the concentration range required in this study (10 to $100\mu g.g^{-1}$) (64-66). A sensitivity of $100\mu g.ml^{-1}/1\%$ absorption (65) and a detection limit of $80\mu g.ml^{-1}$ (S:N = 1) (66) have been quoted for the nitrous oxide-acetylene flame at 392.8 nm. Flame ~~Atomic~~ emission, however, has been shown to possess ample sensitivity for the determination of small amounts of lanthanum (66-70).

Sudo, Goto and Ikeda (62,63) have described the determination of lanthanum in steels at levels down to 0.01% after prior removal of iron, mercury cathode electrolysis and separation of rare earths first as fluoride and then as oxides, before dissolution for the determination by flame ~~atomic~~ emission. The determination, described by Sudo et al, however, is too insensitive for the determination of lanthanum at concentrations much below $100\mu g.g^{-1}$.

General work on flame ~~atomic~~ emission has disclosed six main bands for lanthanum at wavelengths of 437-442, 541-543, 560-563, 590-593, 740-743 and 791-794 nm. The sensitivities achieved have been quoted for both the oxy-hydrogen and oxy-acetylene flames (67-68), the authors finding that the higher wavelengths gave the more sensitive results particularly when a red sensitive photomultiplier tube was used. The use of the two highest wavelengths was also recommended because of the lower flame background emission apparent in this region of the spectrum (67-68). Detection limits have also been quoted in nitrous oxide-acetylene flames (66, 69,70) for selected wavelengths.

Rains et al (67) have found that much improved sensitivities are possible if an alcohol is added to the lanthanum solution, the authors finding that 50% methanol solutions impart the best increase in signal associated with a low, steady flame background. The use of greater alcohol concentrations although giving better signals require accurate measurement of the alcohol concentration to give reproducible results. Menis, Rains and Dean (67,68) have investigated the effects of other metals on the determination of lanthanum at a variety of wavelengths. They conclude that the degree of interference is very high, e.g. $5\mu g.ml^{-1}$ of chromium has been shown to suppress emission from $100\mu g.ml^{-1}$ of lanthanum by 10%. The authors have also found that interference is reduced by using solutions 50% in methanol and that interference is again less at the higher wavelengths.

Menis et al (68) increased the sensitivity by extraction of lanthanum into IBMK as its 2-thenoyltrifluoroacetone (TTA) complex prior to spraying into the flame. They quantitatively extracted up to $300\mu g$. of lanthanum into 10 ml. of 0.1M TTA in IBMK from a 60 ml. aqueous solution at pH ~5 which also contained 10 ml. of 1M ammonium acetate. Equilibration time was one minute.

The authors found that the pH of maximum extraction was dependent on the acetate concentration, the pH of maximum extraction decreased to 4 when the acetate solution used was decreased to 0.05 molar. They also investigated the effect of other metals on the extraction. Of the metals studied which are present in steels only chromium (Vl) did not interfere. The anions of phosphate and fluoride were also shown to prevent extraction of the TTA complex. Again interferences were a minimum at 743 nm. A summary of TTA extractions (71) has revealed that many other metals besides lanthanum are extractable as TTA complexes.

The sensitivity achieved by Menis et al is ample, $0.05\mu g.ml.^{-1}$ per scale division, for the determination of lanthanum in steels at levels below $100\mu g.g.^{-1}$ if it is extracted into an organic solvent before spraying into the flame. With the use of TTA, however, many interferences are expected from most other metals present in steels.

This chapter describes the determination of lanthanum in steels after extraction with TTA into IBMK and discusses the interference by most metals present in steels. The bulk of these interferents were removed by mercury cathode electrolysis, with a subsequent silver oxide separation to remove metals such as aluminium which were not quantitatively electrolysed into mercury. In the separation the rare earths were precipitated as hydroxides using silver as carrier, the silver being subsequently removed as chloride. After this separation only traces of the interferents remained, these being accounted for in a 'blank' TTA extraction.

The procedure is suitable for the analysis of steels whose lanthanum content is 10 to $80\mu g.g.^{-1}$ and is much more sensitive than either the existing atomic emission method (62,63) or the determination by 'difference' outlined earlier.

4.2. Preliminary Work

A study of the six lanthanum oxide bands was instigated to establish the best wavelength for the determination of lanthanum by atomic emission. In each case a $30\mu g.ml.^{-1}$ aqueous solution of lanthanum was sprayed into the air-acetylene flame under the conditions shown in Table 4.1, the emission from lanthanum being measured in the centre of each oxide band (Table 4.2). The instrumental conditions were arranged such that the emission at the most sensitive wavelength (562 nm.) was measured at a position near to full scale deflection on the recorder. The instrument settings were not altered throughout the remainder of the experiment.

TABLE 4.1

Optimum Instrumental Parameters

Parameter		Water	IBMK
Wavelength	nm.	743	743
Slit width	mm.	0.10	0.10
Burner height	cm.	2.0	1.5
Air pressure	p.s.i.	30	30
Air flow rate	$l.min.^{-1}$	5	5
Acetylene pressure	p.s.i.	5	5
Acetylene flow rate	$ml.min.^{-1}$	800	400

TABLE 4.2

Relative Sensitivities

Wavelength (nm.)	Emission Intensity[a] (mV.)	Relative Sensitivity ($\mu g.ml.^{-1}$)
442	4.40	0.68
542	4.00	0.75
562	8.95	0.34
585	NM	-
743	0.75	4.00
785	0.60	5.00

[a] The emission was measured at the same instrument settings for each wavelength.

NM Signal not measured. A high flame background and severe noise were apparent at 585 nm.

The lanthanum emission at each wavelength was recorded (Table 4.2) and the relative sensitivities calculated. The most sensitive lines suffered from severe noise and a high flame background. The emissions at 743 and 785 nm. were best in this respect, in agreement with the work of Menis et al (82). In view of this and the prospect of less interference, 743 nm. was selected for further study.

The optimum instrumental parameters (Table 4.1) for the determination of lanthanum in aqueous solution at 743 nm. were established in a manner similar to that described for lead. These parameters were used to assess the interference from large excesses of chromium and nickel on the emission from a 10$\mu g.ml.^{-1}$

solution of lanthanum (Table 4.3).

TABLE 4.3

Interference from Chromium and Nickel

Solution	Emission (mV) at 743 nm.
$10\mu g.ml.^{-1}$ La	1
$10\mu g.ml.^{-1}$ La + 10 $mg.ml.^{-1}$ Cr	87
10 $mg.ml.^{-1}$ Cr	76
$10\mu g.ml.^{-1}$ La + 10 $mg.ml.^{-1}$ Ni	12
10 $mg.ml.^{-1}$ Ni	12

As the interference from 1000-fold excesses of both chromium and nickel was severe it was obvious that interference from elements commonly found in steel would present many problems, rendering the direct determination of lanthanum in aqueous solution extremely difficult. Consequently the extraction of lanthanum as its TTA complex into IBMK was investigated.

4.3. The Extraction of Lanthanum into IBMK

The extraction of lanthanum as its TTA complex (68) has already been summarised in section 4.1. The optimum conditions for both the determination and extraction of lanthanum in IBMK were ascertained in the preliminary work described in this section.

4.3.1. Optimum Instrumental Parameters

5.0 ml. of lanthanum solution ($100\mu g.ml.^{-1}$) were pipetted into a beaker. 10 ml. of 1M ammonium acetate were added and the pH was adjusted to 5.0 using 2N hydrochloric acid. The solution was transferred to a 125 ml. separatory funnel and diluted to 60 ml. with water. 10.0 ml. of 0.1M TTA in IBMK were added and the solution was shaken for one minute. The phases were allowed to separate and the upper IBMK phase was run into a 50 ml. graduated flask. The solution was diluted to the mark with IBMK before spraying into the flame. Assuming quantitative extraction of lanthanum then the lanthanum concentration in IBMK was $10\mu g.ml^{-1}$.

This solution was used to ascertain the optimum instrumental parameters for the determination of lanthanum in organic solution, these conditions being shown in Table 4.1.

During the course of this experiment capillary tube blockage occurred. This was found to be due to the crystallisation of TTA while passing through the capillary tube.

4.3.2. Optimum Extraction Parameters

The dependence of the extraction upon the TTA concentration was ascertained, in a manner similar to that described above, by extracting the lanthanum into 0.1M TTA diluted with IBMK (Table 4.4).

TABLE 4.4

Concentration of TTA

Composition of organic phase		Emission (mV.) of organic extract
ml. 0.1M TTA	ml. IBMK	
1.0	9.0	5.75
2.0	8.0	7.00
3.0	7.0	7.00
4.0	6.0	7.15
6.0	4.0	6.82
8.0	2.0	6.20
10.0	0	6.05

The aqueous phase contained $100\mu g$. of lanthanum before extraction. The emission of the IBMK extract was measured under the conditions shown in Table 4.1.

The solutions containing 0.1M TTA in excess of 4 ml. produced unsteady flames and showed a tendency to block the capillary tube. Solutions containing 2, 3 and 4 ml. of 0.1M TTA produced the maximum signal. Consequently 10 ml. of 0.02M TTA in IBMK were used as extractant in the remainder of this work, this being the equivalent of 2 ml. of 0.1M TTA.

The influence of extraction time was decided in the next experiment. 100μg. of lanthanum were extracted into 10.0 ml. of 0.02M TTA as described above by shaking the funnels for 15 to 120 seconds. The results (Table 4.5) indicated that the time of shaking was not critical. The procedure was standardised at 30 seconds.

TABLE 4.5

Equilibration Time

Time (sec.)	Emission (mV.)
15	5.10
30	5.20
45	5.20
60	5.15
90	5.10
120	5.05

The emission from La at 743 nm. was measured under the conditions shown in Table 4.1.

The pH range within which lanthanum was extracted into lBMK was determined in a manner similar to that described above by extracting 100μg. of lanthanum into lBMK from solutions whose pH ranged from 1 to 7.

The pH of maximum extraction was found to be 5 and above (Table 4.6). Extractions at pH values higher than 5 were expected to be of limited use due to the precipitation of the hydroxides of most metals at these high pH values.

TABLE 4.6

The pH of Extraction of La-TTA

pH of Aqueous Solution before Extraction	Emission (mV.)
1.10	0
2.10	0
2.95	0
4.00	1.30
5.05	5.10
6.10	5.20
7.10	5.10

The emission from La was measured under the conditions shown in Table 4.1.

The optimum parameters for the extraction of 0 to 100μg. of lanthanum into IBMK with TTA are summarised in Table 4.7. The efficiency of this system was determined by treatin three solutions containing 100µg. of lanthanum each with TTA, as described in Table 4.7, retaining both the aqueous and IBMK phases, the latter for spraying into the flame. The aqueous phases were treated with two further aliquots of TTA solution retaining each IBMK extract.

TABLE 4.7

Optimum Extraction Parameters

Aqueous Phase	
Total volume	60 ml.
Concentration of lanthanum	0-100µg.
Concentration of acetate ions	10 ml. of 1M ammonium salt
pH	5.0
Organic Phase	10 ml. of 0.02M TTA in IBMK
Time of Shaking	30 seconds

The organic extracts were dried over anhydrous sodium sulphate and stored in stoppered polythene bottles.

The average emission from each of the three successive IBMK extracts, when measured under the conditions shown in Table 4.1, of 4.55, 0.25 and 0.25 mV. respectively and the emission from 0.02M TTA of 0.25 mV. confirmed that the system was quantitative for lanthanum in amounts up to 100µg.

4.3.3. Sensitivity

The lanthanum from a solution containing 50µg. of lanthanum was extracted into TTA as described in Table 4.7 and the solution was used to determine the average sensitivity from five successive sprayings into the flame.

The same instrumental settings were used to determine the sensitivity when a $30\mu g.ml^{-1}$ aqueous lanthanum solution was sprayed into the flame.

The sensitivities achieved were 0.096 and $0.52\mu g.ml^{-1}$ per scale division (0.1 mV.) for IBMK and water based solutions respectively, the determination in organic solution representing an approximately five fold increase in sensitivity over water.

The work described in this section has both confirmed the findings of Menis et al (68) and formed the basis of a procedure whereby up to $100\mu g.g^{-1}$ of lanthanum can be determined in steel after prior extraction into IBMK. However, problems were expected in the co-extraction into IBMK of many metals present in steel with lanthanum.

4.4. Interference from Iron

The interference effects of up to 1 g. of iron, both ferric and ferrous, upon the determination of $100\mu g.$ of lanthanum in organic solution is discussed in this section. A sample weight of 1 g. gives an organic solution containing $10\mu g.ml^{-}$ of lanthanum from steels containing $100\mu g.g^{-1}$ of the rare earth.

4.4.1. Experimental

Suitable aliquots of a solution of the interferent were placed in a 125 ml. separatory funnel with $100\mu g.$ of lanthanum and the lanthanum was extracted into 0.02M TTA as described in Table 4.7 before spraying the lBMK extracts into the flame.

4.4.2. Iron (111)

The interference of up to 1 g. of iron as iron (111) was investigated as described above. Unfortunately iron (111) was not completely retained in solution at pH 5 without the addition of citric acid and the presence of citric acid in the extraction medium inhibited the extraction of lanthanum with TTA.

Upon investigation up to 0.1 g. of iron were found to be retained in solution at pH 5 without the use of citric acid and the variation in the emission from lanthanum after extraction into 0.02M TTA in the presence of 0 to 10 ml. of iron (111) solution (0.01 $g.ml.^{-1}$) is shown in Figure 4.1, plot (a).

In a second experiment the iron solutions alone were treated with TTA, their variation in emission also being represented in Figure 4.1, plot (b).

Figure 4.1 shows that iron at all concentrations is extracted by TTA at pH 5 giving an emission signal (plot b). In addition suppression of the lanthanum signal occurs when iron is present in concentrations greater than 0.02 g. (plot a). As these two curves did not show whether the iron was interfering with the determination or the extraction of lanthanum a third experiment was performed where equal portions of two IBMK solutions containing lanthanum and iron (111) respectively were mixed and sprayed into the flame. The two sets of solutions were prepared by treating six solutions containing 100μg. of lanthanum and six solutions containing 0 to 10 ml. of iron (111) solution (0.01 $g.ml.^{-1}$) as described in section 4.4.1. Plot (c) of Figure 4.1 shows the variation in the emission of these mixed extracts with concentration of iron.

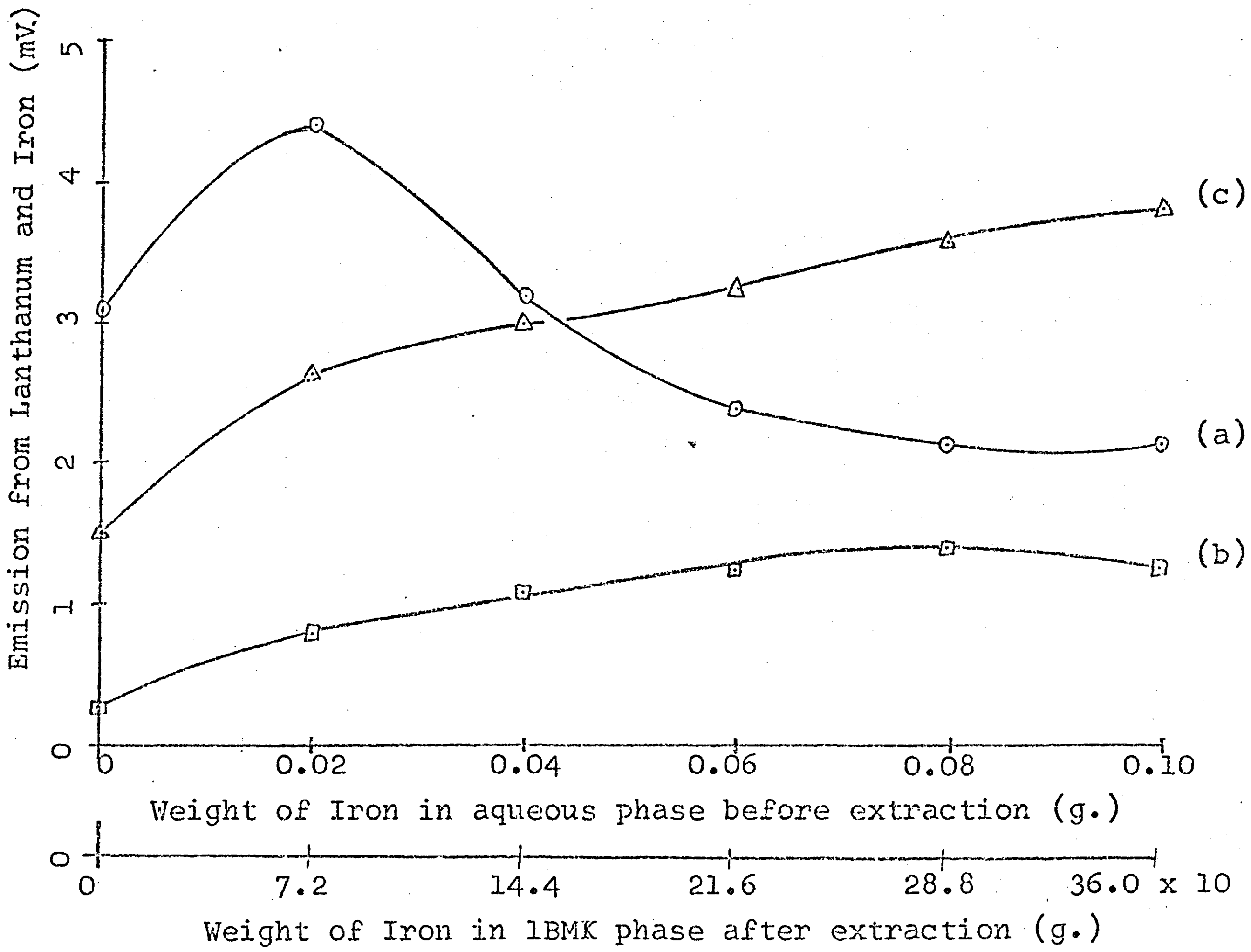

Figure 4.1

The emission of La and Fe was measured at 743 nm. under the conditions described in Table 4.1.

(a) The extraction of La and Fe (111) with 0.02M TTA.

(b) The extraction of Fe (111) with 0.02M TTA.

(c) The extraction of La and Fe (111) into separate 0.02M TTA solutions before the mixing of equal volumes of each extract.

The similarity of plots (b) and (c) shows that emission from lanthanum and iron (111) is additive. As plot (c) does not show any suppression of the lanthanum signal in the presence of iron then the suppression observed in plot (a) is due to inhibition of the extraction of lanthanum by iron.

Figure 4.1 also shows the amount of iron extracted into the organic phase under conditions identical with those for lanthanum. The figures shown represent a 3.6% extraction of iron (111) at pH 5. The amount of iron extracted was ascertained by treating the aqueous solutions retained from the TTA extractions with stannous chloride and potassium dichromate in a method previously described in section 3.4.3. Standardisation was achieved using 10.0 ml. of iron (111) solution (0.1 g.ml.$^{-1}$), the titres of both the standardisation and test solutions being shown in Table 4.8.

TABLE 4.8

The Extraction of Iron with TTA

Volume of 0.1g.ml^{-1} Fe(111) Solution (ml.)	Titre (ml.0.017M $K_2Cr_2O_7$)	Weight of Fe in Aqueous Phase Extraction (g.)	Weight of Fe extracted (g.)	% of Fe extra ted
Standardisation				
10.0	17.33	0.0968	-	-
Test Solutions				
2.0	3.35	0.0187	0.0006	3.31
4.0	6.68	0.0372	0.0014	3.62
6.0	10.00	0.0559	0.0021	3.62
8.0	13.37	0.0746	0.0028	3.62
10.0	16.67	0.0932	0.0036	3.72

4.4.2.1. The pH Range for the Extraction of Iron with TTA

The pH range within which iron was extracted with 0.02M TTA was established by extracting the iron from a series of 5.0 ml. aliquots of iron (111) solution (0.01 g.ml^{-1}) into 10 ml. of the reagent at pH values from 1 to 7, as described in Table 4.7.

The emission from iron at 743 nm. (Table 4.9) showed that iron was extracted over the whole acid pH range with maximum extraction occurring at the lower pHs.

TABLE 4.9

The pH of Extraction of Fe - TTA

pH of Aqueous Phase before Extraction	Emission (mV.)
1.10	3.00
2.00	1.85
3.00	1.25
4.00	1.15
5.00	1.20
6.00	1.25
6.98	1.40

The emission from Fe at 743 nm. was measured under the conditions shown for La in Table 4.1.

4.4.3. Iron (11)

Interference from iron (11) was established by extracting lanthanum from a series of solutions containing both lanthanum and iron (11). Solubility of up to 0.5 g. of iron (11) was achieved at pH 5 without the addition of citric acid. The experiments were carried out in a manner similar to that described in section 4.4.1 using 0 to 5 ml. of iron (11) solution (0.1 $g.ml^{-1}$). The emission from these solutions is shown in Figure 4.2.

With iron (11) a maximum enhancement of signal was reached at iron concentrations of 0.15 g. and above. In practice it was very difficult to maintain a stabilised ferrous solution during the extraction.

In view of the serious nature of the interference from iron it was concluded that all iron must be removed from the aqueous phase before the extraction of lanthanum with TTA. However, before any solvent extraction procedure for the removal of iron was invoked the interference effects of nickel and chromium were ascertained.

4.5. Interference from Nickel and Chromium

The interference effects of 0-0.05 g. of nickel and chromium (0-5% in steels, assuming a 1 g. sample weight) were investigated by carrying out TTA extractions from solutions containing these metals both in the presence and absence of lanthanum.

The experiments were accomplished in a manner similar to that described in section 4.4.1 using 0 to 10 ml. aliquots of nickel, chromium (111) and chromium (V1) solutions (5 $mg.ml^{-1}$) in turn. The variation in emission from the IBMK extracts with concentration of the metal is shown in Figure 4.3.

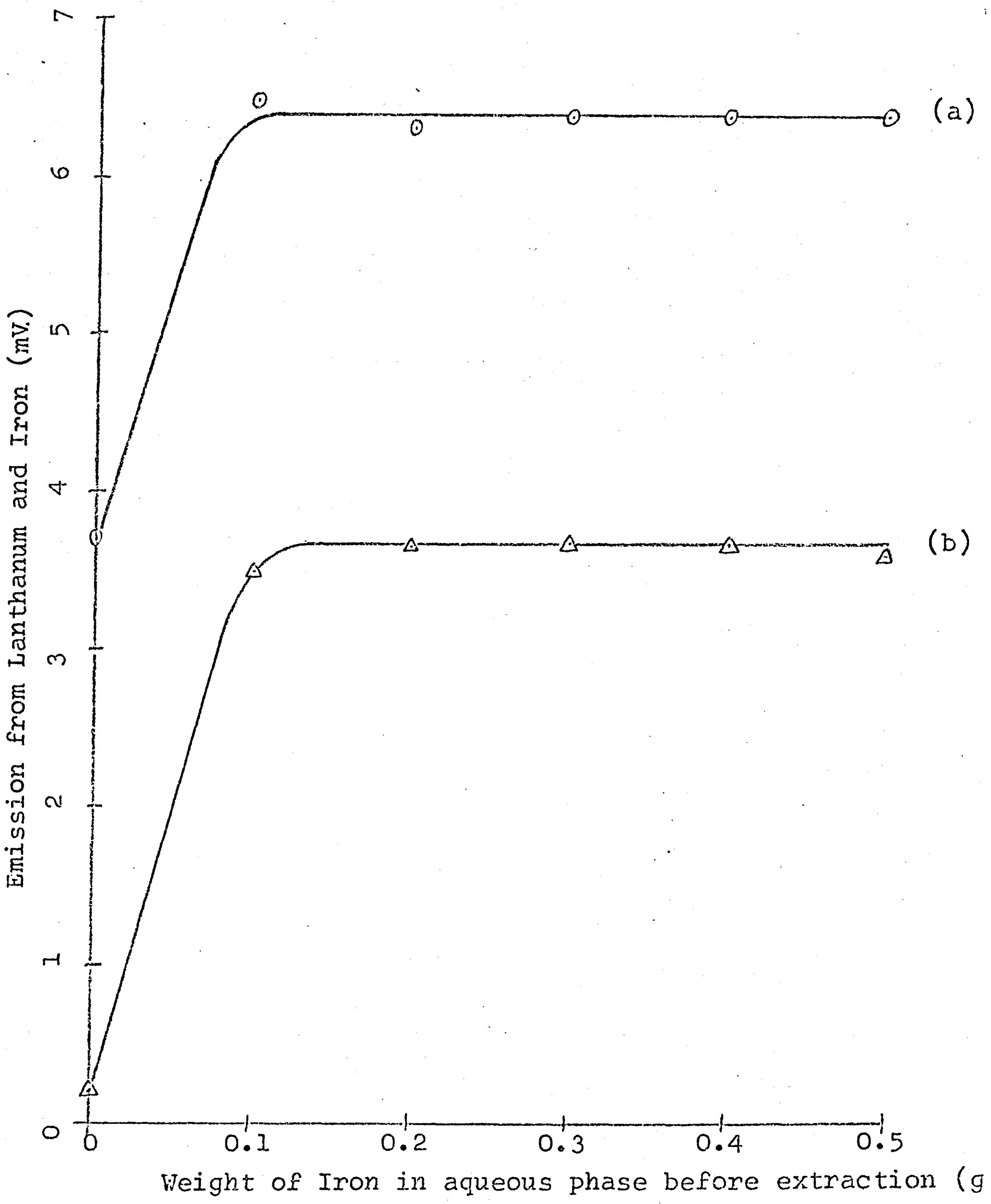

Figure 4.2

The Interference of Iron (11)

The emission from La and Fe was measured at 743 nm. under the conditions described in Table 4.1.

(a) The extraction of La and Fe (11) with 0.02M TTA.

(b) The extraction of Fe (11) with 0.02M TTA.

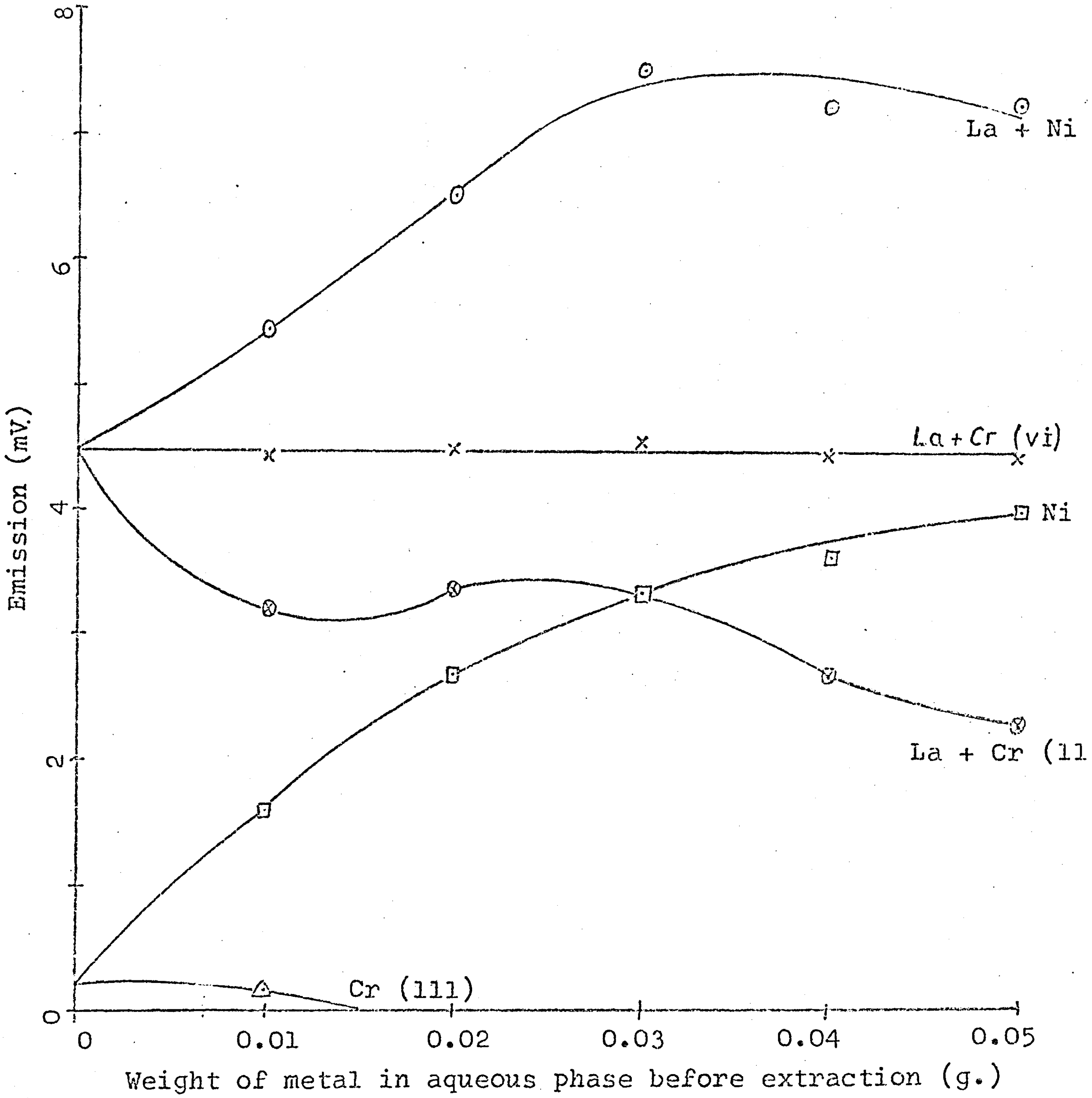

Figure 4.3

The Interference of Nickel and Chromium

The emission of the 1BMK extracts was measured at 743 nm. under the conditions shown in Table 4.1.

Of the two metals only chromium in its higher oxidation state showed no interference on either the extraction or determination of lanthanum. Chromium (111) suppressed the lanthanum emission and nickel showed enhancement. As it was possible to prevent interference from chromium by prior oxidation with ammonium persulphate the interference from chromium was deemed to have been resolved.

The pH range within which nickel was extracted into IBMK was ascertained. Seven aliquots of 4.0 ml. of nickel solution (5 mg.ml.$^{-1}$) were pipetted into separatory funnels and the nickel extracted into 10.0 ml. of 0.02M TTA at pHs from 1 to 7. The aqueous phases were retained and the nickel concentration remaining in the aqueous phases was determined by solution spectrophotometry after formation of the nickel-dimethylglyoxime complex (72).

The results (Table 4.10) showed that like iron, nickel was extracted at all acid pH values, the maximum being at pH3 and above when the percentage extraction was 16.

TABLE 4.10
The pH of Extraction of Ni-TTA

pH of Aqueous Solution before Extraction	Weight of Ni in Aqueous phase after extraction (mg.)	Weight of Ni in 1BMK after extraction (mg.)	% Extraction of Ni
1.20	19.0	1.0	5
2.05	18.0	2.0	10
3.00	16.8	3.2	16
4.00	16.8	3.2	16
5.00	16.8	3.2	16
6.00	16.8	3.2	16
7.00	16.8	3.8	16

In view of the serious interference problems encountered with each of the metals investigated a general method for the removal of the interfering species was sought rather than the removal of each metal in turn.

4.6. Removal of Interferents

Both nickel and iron have been shown to be extracted with TTA throughout the acid pH range. The degree of extraction of these metals is such that for complete removal of the interferent too many extractions would be required. Some specific extractants were tried, including thiocyanate (77) for iron and dimethylglyoxime (72) for nickel, but either too many extractions were required or lanthanum was lost in the process.

Two separation procedures involving precipitation were devised in an attempt to prevent interference by iron and nickel. In the first iron was removed by extraction as thiocyanate and ammonia was added to separate the insoluble rare earth hydroxides from the soluble nickel tetraammine complex. Unfortunately this procedure failed as some nickel was retained by the hydroxide precipitate even after a double separation, causing interference with the determination of lanthanum.

A second precipitation scheme also met with little success. In this scheme, originally devised by Carron et al (7), rare earths were separated as oxalates using calcium as carrier. After removal of the interfering metals the calcium and lanthanum oxalates were dissolved in acid, the lanthanum extracted into IBMK and the extract sprayed into the flame. Interference from calcium was evident but this was standardised by the addition of a known amount of calcium solution. Unfortunately trace amounts of nickel oxalate were precipitated along with the calcium and lanthanum, again causing interference with the extraction and determination. A double separation failed to relieve this problem.

Sudo et al (62,63) in their determination of lanthanum in steels described a mercury cathode electrolysis procedure for the removal of interfering metals. In addition Center et al (78) have described the quantitative mercury cathode electrolysis of a large number of metals, including iron, chromium and nickel, present in steels. A separation by this technique forms part of the British Standard Procedure for the determination of aluminium in steels (76).

Of the metals commonly found in steels all but rare earths, aluminium, titanium, vanadium and some manganese are not separated by mercury cathode electrolysis. The following sections show how mercury cathode electrolysis and a chemical precipitation technique excluded all but trace amounts of the interfering species from the steel solution.

4.7. Mercury Cathode Electrolysis

Five 50 ml. aliquots of iron (111) solution (20 $mg.ml^{-1}$) were placed in electrolysis cells (section 2.1.3) along with 25 ml. of 10%(v/v) sulphuric acid. The electrolytes were diluted to 150 ml. with water, and electrolysed in turn over 50 ml. of mercury for 1, 1.5, 2.0, 2.5 and 3.0 hours respectively at a current of 5 amperes. The aqueous solutions were retained, evaporated until fumes of sulphur trioxide appeared, cooled and 10 ml. of water added to redissolve the residue.

Five 10 ml. aliquots of nickel and chromium(111) solutions (5 $mg.ml^{-1}$) were treated in a similar manner to that described for iron.

The amount of iron, nickel or chromium retained by each electrolyte after electrolysis was then determined by solution spectrophotometry, using thiocyanate (73), dimethylglyoxime (72) and diphenylcarbazide (74) for each metal respectively. The variation in concentration of iron, nickel and chromium remaining in the respective solutions with electrolysis time is shown in Figure 4.4.

Mercury cathode electrolysis for iron, nickel and chromium was found to be virtually quantitative after 3 hours when 140μg. of iron, 25μg. of nickel and 40μg. of chromium remained in the electrolyte. The interference by these amounts of metals was expected to be minimal and was confirmed by extracting the lanthanum into IBMK from solutions containing 100μg. of lanthanum and 150, 28 and 50μg. of iron (111), nickel and chromium (111) respectively. A fourth solution contained 100μg. of lanthanum and 25 ml. of 10%(v/v) sulphuric acid.

No difference was found in the emission of the extracts containing the metal interferents from that containing lanthanum alone indicating the eminent suitability of mercury cathode electrolysis for the elimination of the bulk of the interferents present with lanthanum in steels. However, the emission from lanthanum extracted in the presence of sulphuric acid was negligible. Sulphuric acid had prevented the extraction of lanthanum and thus a chemical separation for this acid was required.

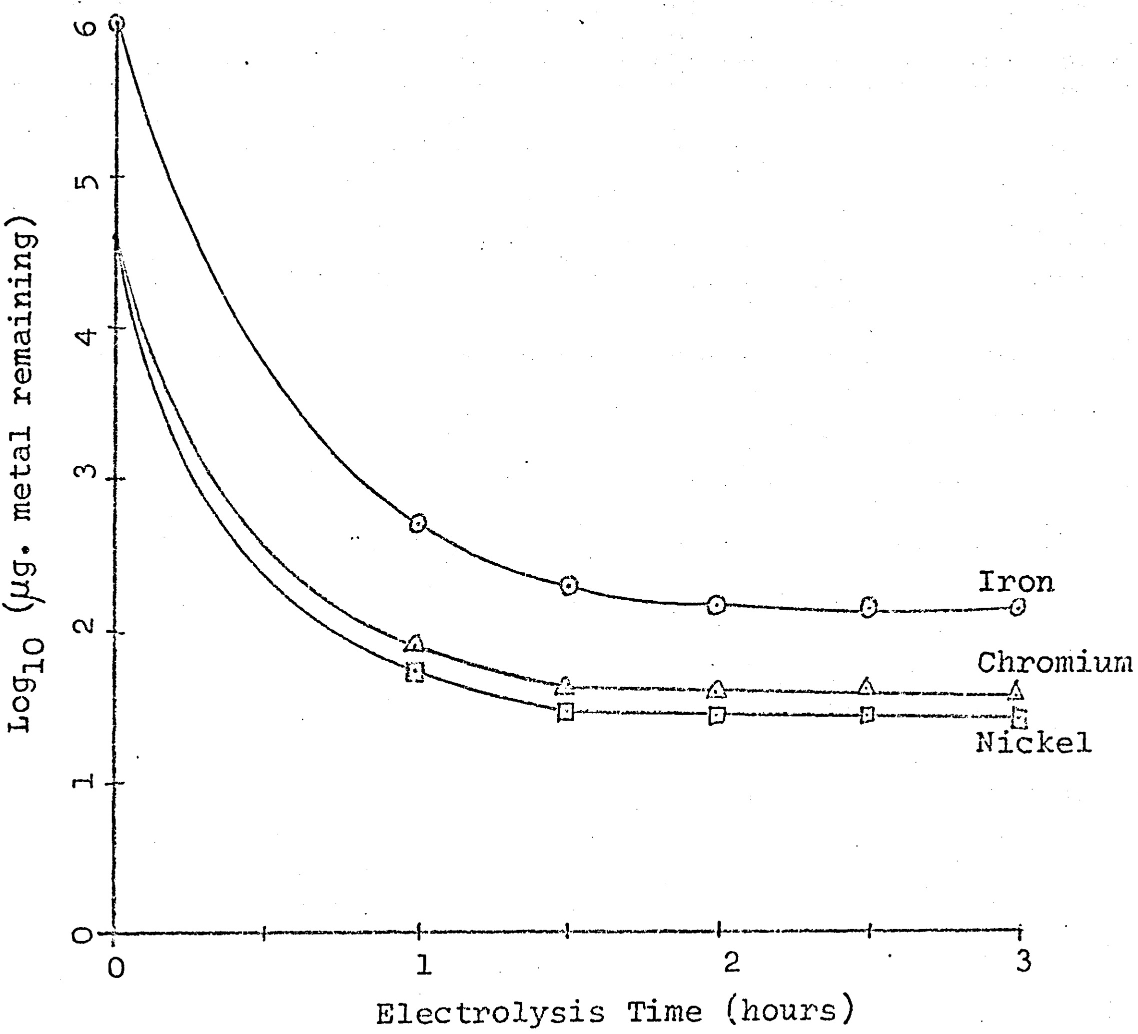

Figure 4.4

The Mercury Cathode Electrolysis of Iron, Chromium and Nickel

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THE DETERMINATION OF TRACE AMOUNTS OF LANTHANUM IN LOW-ALLOY STEELS BY FLAME EMISSION SPECTROPHOTOMETRY

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The presence of trace amounts of rare earth elements improves the ductility and impact strengths of heat-treated carbon steels[1,2] and also potentially aids in successful deoxidation and desulphurisation of the steel. Lanthanum is present in certain steels after Mischmetal addition, usually at less than the 0.005% level.

Atomic absorption spectrophotometry does not provide the sensitivity required for the determination of lanthanum at this level of concentration[3-5]. For example, Amos and Willis[5] quote a 1% absorption value of 100 p.p.m. in a nitrous oxide–acetylene flame at the 392.8-nm line. Flame emission spectrophotometry, however, has been employed for the determination of lanthanum. Ishida[6] determined lanthanum in minerals and glasses using the oxide band emission at 440 and 560 nm and an air–acetylene flame. Menis *et al.*[7] studied the flame spectrophotometric determination in an oxygen–acetylene flame. These workers obtained sensitivities for the various oxide bands in aqueous, aqueous methanolic, and 4-methyl-2-pentanone (hexone) solutions and concluded that 743 and 791 nm were suitable wavelengths to use, partly because of the very small background radiation of the flame and partly because interferences were lessened at these wavelengths. They also suggested an extraction at pH 1.5 with 2-thenoyltrifluoroacetone (TTA) before extraction of lanthanum with TTA in hexone from an acetate buffer at pH 5.0 when thorium, uranium, copper and iron are present as major components. A 100-fold increase in sensitivity was obtained when the organic phase was sprayed into the oxygen–acetylene flame compared with when an aqueous solution was sprayed.

It was decided to investigate the possibility of determining lanthanum in steels by flame emission spectrophotometry in an air–acetylene flame. Iron and nickel were found to interfere severely with the lanthanum emission intensity both from aqueous solution and from hexone solution after extraction with TTA. No simple solvent extraction or precipitation procedure could be designed to overcome these interferences and therefore mercury cathode electrolysis was attempted. Traces of iron and nickel remained in solution after electrolysis for 1 h and these still caused interference. However, under the conditions selected for the extraction of lanthanum as the TTA complex into hexone, the residual iron and nickel were extracted only to a small extent. It was therefore possible to make use of a "blank" extraction from solution of pH 2.5 to overcome this slight interference. Manganese, which is not quantitatively deposited in mercury, also interferes but this can be removed by a simple chemical procedure following the electrolysis. The method was applied to the recovery of lanthanum added to B.C.S. steels and to the determination of lanthanum in steels of known lanthanum content.

EXPERIMENTAL

Apparatus

A Unicam SP90 atomic absorption spectrophotometer was used in the emission mode with a Meker burner for air–acetylene.

Electrochemical analyzer (Baird and Tatlock).

Standard instrumental conditions

Wavelength 743 nm	Air pressure 30 p.s.i.; flow 5 l min^{-1}
Slit width 0.10 mm	Acetylene pressure 5 p.s.i.; flow 0.4 l min^{-1}.
Burner height 15 mm	

Reagents

All the reagents used were of analytical-reagent grade.

Standard lanthanum solution (100 *p.p.m.*). Dissolve 0.117 g of high-purity lanthanum oxide in the minimum amount of 2 *M* nitric acid and evaporate just to dryness. Dissolve the residue in water and dilute to 1 l. Store in a polythene bottle.

Mixed acid. Mix 3 parts of water, 6 parts of concentrated nitric acid and 1 part of concentrated sulphuric acid.

Analysis of low-alloy steels

Dissolve 1.00 g of the alloy in 40 ml of mixed acid, evaporate to dryness and dissolve the residue in 25 ml of water. Evaporate to dryness and dissolve the residue in 25 ml of 10% (v/v) sulphuric acid. Cool and dilute to 150 ml with water. Add 50 ml of mercury and electrolyse for 90 min at a current of 5 A. Evaporate the aqueous solution to *ca.* 50 ml, add 5 ml of 0.1 *M* silver nitrate and 10 ml of 10% (w/v) ammonium persulphate solution, and simmer for 5 min. Cool, add 50% (w/v) sodium hydroxide solution until alkaline, add a further 2 ml and simmer for 1 min. Cool and filter through No. 541 filter paper. Wash the beaker and filter paper twice with 1% (w/v) sodium hydroxide solution and several times with water. Finally wash the filter paper with 75 ml of hot 5% (v/v) nitric acid solution. Add 5 ml of concentrated hydrochloric acid to the filtrate and simmer. Filter through No. 541 filter paper and wash the precipitate twice with 5% (v/v) hydrochloric acid solution. Evaporate the solution to dryness, cool and redissolve in 5 ml of water.

Add 10 ml of 1 *M* ammonium acetate solution, adjust the pH to 5.0 with 2 *N* nitric acid or 2 *N* ammonia solution and transfer to a separating funnel. Add 10 ml of 0.02 *M* TTA in hexone and shake for 30 sec. Allow the two phases to separate. Transfer the aqueous phase to another separating funnel and adjust the pH to 2.5 by adding a predetermined quantity of 1 *M* hydrochloric acid*. Add 10 ml of 0.02 *M* TTA in hexone and shake for 30 sec. Dry both organic phases over sodium sulphate and spray each into the flame. Subtract the emission reading of the extract of the pH 2.5 solution from the emission reading of the extract of the pH 5.0 solution, and read off the lanthanum content from the calibration graph.

Preparation of calibration graph

Transfer 0, 2, 4, 6 and 8 ml of 10-p.p.m. lanthanum solution (prepared by appropriate dilution of the standard lanthanum solution) into a series of separating

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* Adjust the pH to 2.5, in the first instance, by dropwise addition of 1 *M* hydrochloric acid from a burette. The amount added can be used for all subsequent additions at this stage.

funnels, add 10 ml of 1 *M* ammonium acetate solution and continue as described above. The calibration curve is linear for 0–8 p.p.m. of lanthanum in the organic layer.

RESULTS AND DISCUSSION

Preliminary investigations in aqueous solution

A preliminary study of the sensitivities of various lanthanum oxide band emissions (442, 544, 562, 585, 743 and 785 nm) in the air–acetylene flame showed that the bands at 442, 544 and 562 nm were the most sensitive but the emission intensity obtained at 743 nm gave the most stable reading. This is in agreement with the results of Menis *et al.*[7] who used oxy–acetylene flames. In view of this and the prospect of less interference, 743 nm was selected for further study. Optimal conditions in aqueous solution were essentially the same as those given in the experimental section except that the optimal acetylene flow was 0.8 l min^{-1} and the optimal burner height was 20 mm. Large excesses of chromium and nickel caused severe interference at 743 nm as well as at 445 and 542 nm. It was obvious that, although sufficient sensitivity was obtainable from aqueous solutions, interference from elements commonly found in steels would present many problems.

Extraction of lanthanum with 2-thenoyltrifluoroacetone (TTA) into hexone

Poskanzer and Foreman[8] have summarized the extraction of many metals with TTA from acetate solution into hexone. They found that lanthanum was completely extracted by a solution of 0.1 *M* TTA in hexone from a 1 *M* acetate solution buffered at pH 5. A prior extraction at pH 1.5 was recommended when large amounts of iron were present. In the present work it was found desirable to extract with 0.02 *M* TTA in hexone as, on spraying the more concentrated solution, instability of the emission readings and capillary blockage occurred.

Quantitative extraction of up to 100 μg of lanthanum into 10 ml of 0.02 *M* TTA in hexone was obtained on shaking the 2 phases for 30 sec. A hexone extract containing 5.0 p.p.m. of lanthanum gave an emission intensity reading of 52 divisions on the recorder. This corresponds to a sensitivity of 0.096 p.p.m. of lanthanum per scale division (1 mV) and is an approximately 5-fold increase in sensitivity over that obtainable from aqueous solution.

Interference from chromium, nickel and iron

If a 1-g sample weight is taken, a steel containing 0.01 % of lanthanum extracted into 10 ml of hexone gives a solution containing 10 p.p.m. of lanthanum. On addition of chromium, nickel and iron, in amounts corresponding to up to 5, 5 and 60% respectively in steel, to the aqueous solution before extraction, severe interference was found from chromium(III), nickel, iron(II) and iron(III). Chromium(VI) caused no interference. Chromium(III) caused suppression of the lanthanum signal whereas both nickel and iron(II) caused enhancement. Experiment showed that the interference of nickel on lanthanum was purely of a spectral type. In the case of iron(III), the interference followed an unusual pattern. The results indicated that iron(III) inhibited the extraction of lanthanum in addition to interfering spectrally. It was obvious, therefore, that traces of nickel and iron interfered with the proposed procedure and needed to be removed before the extraction of lanthanum.

Removal of interfering elements

Solvent extraction. Nickel and iron are extracted by TTA throughout the acidic pH range but the number of extractions required for complete removal is too great to make a preliminary extraction an attractive proposition. Other systems were investigated, including thiocyanate for iron and dimethylglyoxime for nickel, but either too many extractions were required for complete removal or lanthanum was lost in the process.

Precipitation. Ammonia was used to separate the insoluble lanthanum hydroxide from the soluble nickel tetrammine complex, but some nickel was retained in the hydroxide precipitate even after a double precipitation and caused interference with the lanthanum emission intensity after extraction. Carron *et al.*[9] have described a separation technique based on the precipitation of rare earth oxalates with calcium as carrier. This technique was attempted but met with little success, as enough nickel oxalate was formed to cause interference in the subsequent extraction and determination of lanthanum.

Mercury cathode electrolysis. Mercury cathode electrolysis removes quantitatively several of the elements likely to be found in steels, *e.g.* iron, chromium, nickel, molybdenum[10]. Elements such as aluminium and rare earths are not deposited in the mercury and remain completely in solution. Indeed, this separation technique forms part of the British Standard Method for the determination of aluminium in steels[11]. Electrolysis from dilute sulphuric acid at a current of 5 A, removed almost completely iron, nickel, chromium and molybdenum in the amounts likely to be present in steel from a 1-g sample. However, when the initial amounts of iron and nickel were 1 g and 0.05 g, respectively, 140 μg of iron and 25 μg of nickel were detected in the aqueous solution even after electrolysis for 3 h.

These trace amounts of iron and nickel were not enough to interfere with the determination of lanthanum when each element was present separately. However, the presence of sulphate ion inhibited the extraction of lanthanum as its TTA complex. Manganese was not quantitatively removed from solution by electrolysis and interfered with the lanthanum emission. Aluminium, which is not electrodeposited, also caused interference. After the electrolysis stage, therefore, it was necessary to separate lanthanum from sulphate ions, manganese and aluminium. Manganese was oxidised to permanganate with ammonium persulphate, and lanthanum hydroxide was precipitated with silver as a carrier. The silver was subsequently removed by precipitation as chloride, leaving a solution containing rare earths in addition to minute traces of other metals. Lanthanum was extracted into hexone as its TTA complex after the mercury cathode electrolysis stage and chemical separation. At this point, it was found that although trace amounts of iron and nickel, remaining after electrolysis, did not cause interference when present individually, some kind of cumulative interference was observed when these elements were present together as in a steel sample. This small interference was eliminated by use of a blank extraction.

Blank extraction

Lanthanum is extracted from aqueous solution by TTA into hexone at pH values greater than 3 and quantitatively at pH 5. An extraction at pH 5 extracts all the lanthanum plus small quantities of iron and nickel. Approximately 15% of the nickel and 4% of the iron were found to be extracted by 0.02 *M* TTA into hexone from

TABLE I

RECOVERY OF LANTHANUM ADDED TO STANDARD STEELS

Alloy	*Lanthanum added* (%)	*Lanthanum found* (%)
BCS 255/1	0.0010	0.0009
BCS 329	0.0030	0.0029
BCS 251/1	0.0040	0.0041
BCS 215/2	0.0050	0.0053

aqueous solution of pH 5. The percentage extractions for iron and nickel did not vary much over the whole acid pH range. Although it has been stated above that the interference of iron was rather unusual, certainly at these levels it was completely spectral and was definitely not an inhibiting one. By carrying out a second extraction at pH 2.5, one obtains a hexone extract containing no lanthanum and amounts of iron and nickel approximately equal to the amounts present in the lanthanum extract from the pH 5 solution. The difference in emission from these two solutions when sprayed into the flame is due solely to the lanthanum content of the solution.

Recovery of lanthanum by the proposed method

Lanthanum was added to four British Chemical Standard Steels and the steels were subjected to the proposed method. Table I shows the recoveries of lanthanum obtained. The amounts of lanthanum added and found are shown as equivalent per cent in the steel.

TABLE II

THE DETERMINATION OF LANTHANUM IN LOW-ALLOY STEELS

Alloy	*Lanthanum content* (%)[a]	*Proposed method* (%)
A1	0.0010	0.0013
A2	0.0020	0.0018
A3	0.0015	0.0014
A4[b]	0.0010	0.0008

[a] Values provided by the British Steel Corporation. Total rare earth content was determined by oxalate precipitation, cerium was isolated and determined by oxalate precipitation, and the difference quoted as lanthanum.

[b] High-speed steel.

Application to low-alloy steels

Results for the determination of lanthanum in three low-alloy steels and one high-speed steel by the proposed method are shown in Table II. These results are considered perfectly satisfactory. Although the method involves mercury cathode electrolysis there seems no reason why it should not be acceptable to the steel industry since the currently accepted method for aluminium involves this separation technique. With regard to time of analysis, six samples can be analysed in rather less than a working day.

The authors acknowledge with thanks B.S.C. (Special Steel Products Division) for provision of the steel samples and for a maintenance grant for one of us (M.E.H.).

SUMMARY

A method is described for the determination of 0.001–0.008 % of lanthanum in steels by flame emission spectrophotometry. After sample dissolution the bulk of the interfering elements are removed by mercury cathode electrolysis. A hydroxide precipitation of lanthanum with silver as carrier is followed, after dissolution of the precipitate, by extraction as its 2-thenoyltrifluoroacetone complex into isobutyl methyl ketone from aqueous solution buffered at pH 5. The organic phase is sprayed into an air–acetylene flame and the emission intensity measured at 743 nm. A "blank" extraction from aqueous solution of pH 2.5 is used to eliminate slight interferences from iron and nickel remaining after the electrolysis stage.

RÉSUMÉ

On décrit une méthode pour le dosage du lanthane dans les aciers (0.001 à 0.008%) par spectrophotométrie d'émission de flamme. On élimine les éléments pouvant gêner par électrolyse sur cathode de mercure. On procède ensuite à une précipitation d'hydroxyde de lanthane en présence d'argent, comme entraîneur, dissolution du précipité et extraction sous forme de son complexe avec la 2-thénoyltrifluoroacétone dans l'isobutylméthylcétone, en milieu tampon pH 5. La phase organique est vaporisée dans une flamme air–acétylène; l'intensité de l'émission est mesurée à 743 nm. On effectue une extraction à blanc à pH 2.5 pour éliminer les légères interférences du fer et du nickel restant après électrolyse.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von 0.001–0.008% Lanthan in Stählen durch Flammenemissionsspektrophotometrie beschrieben. Nach Auflösung der Probe wird die Hauptmenge der störenden Elemente durch Elektrolyse mit einer Quecksilberkathode entfernt. Das Lanthan wird mit Silber als Träger als Hydroxid gefällt und nach Wiederauflösung des Niederschlages als 2-Thenoyltrifluoraceton-Komplex aus wässriger, auf pH 5 gepufferter Lösung mit Methylisobutylketon extrahiert. Die organische Phase wird in eine Luft–Acetylen-Flamme gesprüht und die Emissionsintensität bei 743 nm gemessen. Durch "Blind"-Extraktion aus wässriger Lösung von pH 2.5 werden geringe Störungen durch Eisen und Nickel, die nach der Elektrolysestufe verblieben sind, eliminiert.

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THE DETERMINATION OF TRACE AMOUNTS OF LEAD IN HIGH-ALLOY STEELS BY SOLVENT EXTRACTION AND ATOMIC ABSORPTION SPECTROSCOPY

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SCHOLES[1] has reviewed the application of atomic absorption spectroscopy (a.a.s.) to the determination of elements, including lead, in steels. There are few problems in the determination of lead at the 0.005% level and above in cast iron, mild and low-alloy steels. However, large amounts of chromium and nickel, as present in high-alloy steel, interfere[2,3]. The interferences are difficult to interpret and therefore a preliminary solvent extraction stage is necessary for the determination of lead in high-alloy steels.

CHAKRABARTI *et al.*[4] extracted lead as the tetraiodoplumbate ion, into methyl isopropyl ketone in the determination of trace amounts of lead in water by a.a.s. DAGNALL AND WEST[5] have studied the extractions of lead oxinate and lead diethyldithiocarbamate into methyl isobutyl ketone (hexone) and determined lead by a.a.s. in some commercially available products such as chocolate samples, beer and gasoline. WEST *et al.*[6] have also determined trace amounts of lead in steels, brass and bronze alloys after extraction of tetraiodoplumbate into hexone. In the case of steel samples they found it necessary to remove iron by preliminary solvent extraction. They found that a 5–6-fold increase in sensitivity was obtained on spraying the hexone layer into the flame after iodide extraction of the lead and noted no interference from 1000-fold molar amounts of several cations including iron(III), chromium(III) and copper(II). However, most of the samples analysed were mild steels.

It was thought, at first, that a method for the determination of trace amounts of lead in high-alloy steels should be straightforward after prior removal of the iron and subsequent extraction of lead as its iodo complex into hexone. On examination of the method, however, small amounts of iron(III) and copper(II) produced an appreciable interference, in conflict with the findings of WEST *et al.*[6]. This is attributed mainly to the formation of iodine which inhibits the extraction of lead. The percentage extraction of lead, however, becomes constant above a certain amount of liberated iodine. Copper, extracted into the hexone layer, shows slight interference with the lead absorbance, quite apart from the effect of liberating iodine and consequent inhibition of the lead extraction. This interference, however, also becomes constant above a certain amount of copper. The method proposed here to overcome these difficulties involves adding a constant amount of copper both to the steel solutions and to the calibration solutions before extraction into hexone. The effects of copper and liberated iodine are then constant between the steel samples and the calibration solutions. Although the method involves two solvent extraction procedures it is still very much quicker than the standard dithizone method[7] and the results obtained for the determination of lead in eight high-alloy steels are considered perfectly satisfactory.

EXPERIMENTAL

Apparatus

A Unicam SP 90 atomic absorption spectrophotometer and a lead hollow cathode lamp were used.

Standard instrumental conditions

Air–propane (used for studies in aqueous solution).

Wavelength	217.0 nm	Air	pressure	30 p.s.i.
Slit width	0.10 mm		flow	5 l min^{-1}
Burner height	1.4 cm	Propane	pressure	10 p.s.i.
Lamp current	6 mA		flow	0.4 l min^{-1}

Air–acetylene (used for studies in organic phase after solvent extraction).

Wavelength	217.0 nm	Air	pressure	30 p.s.i.
Slit width	0.10 mm		flow	5 l min^{-1}
Burner height	0.4 cm	Acetylene	pressure	10 p.s.i.
Lamp current	6 mA		flow	0.6 l min^{-1}

Reagents

All the reagents used were of analytical-reagent grade.

Standard lead solution (100 p.p.m.). Dissolve 0.1599 g of AnalaR anhydrous lead nitrate in distilled water and make up to 1 l with water. Store in a polythene bottle.

Standard copper solution (0.24% w/v). Dissolve 0.24 g of copper foil in the minimum volume of 50% (v/v) nitric acid with gentle heating. Add 10 ml of concentrated hydrochloric acid, evaporate to dryness and bake until all nitrous fumes have been evolved. Cool and dissolve the residue in 25 ml of distilled water. Transfer to a 100-ml graduated flask and dilute to the mark with water. Store in a polythene bottle.

Analysis of high-alloy steels

Dissolve 2.00 g of the alloy in 25 ml of concentrated hydrochloric acid and 5 ml of concentrated nitric acid. Evaporate the solution to dryness and bake until all nitrous fumes have been evolved. Cool and dissolve the residue in 25 ml of 8 *M* hydrochloric acid with a minimum of boiling. Transfer to a 125-ml separating funnel, add 50 ml of diisopropyl ether and shake for 1 min. Allow the layers to separate and run the lower aqueous layer into a beaker. Wash the organic layer with three 2-ml portions of 8 *M* hydrochloric acid and add the washings to the beaker. Evaporate the solution in the beaker to dryness, and redissolve the salts in 25 ml of distilled water with gentle warming. Add 15 ml of 50% (v/v) hydrochloric acid and 10 ml of 6% (w/v) hydroxylammonium chloride. Simmer gently for a few minutes and remove from the hot plate. Allow to cool and add a further 10 ml of 6% (w/v) hydroxylammonium chloride.

Transfer to a 250-ml separating funnel and make up to about 135 ml with distilled water. Add 5 ml of standard copper solution and 10 ml of 43% (w/v) potassium iodide solution. Pipette 20 ml of hexone into the funnel, shake for 1 min and allow the layers to separate. Discard the aqueous layer and run the hexone layer into a beaker containing 0.25–0.5 g of anhydrous sodium sulphate. Filter the hexone solution through a Whatman 541 filter paper into a stoppered polythene bottle and spray into the flame. Read off the lead content from the calibration graph.

Preparation of calibration graph. From a burette transfer 0, 2, 4, 6, 8, 10 ml of 10-p.p.m. lead solution (prepared by appropriate dilution of the standard lead solution) into separate 250-ml separating funnels. Dilute each to about 120 ml with distilled water and add 15 ml of 50% (v/v) hydrochloric acid. Add 5 ml of standard copper solution and 10 ml of 43% (w/v) potassium iodide solution, and continue as described above. The calibration graph is linear from 0 to 5 p.p.m. lead in the hexone layer.

RESULTS AND DISCUSSION

Preliminary investigations in aqueous solution

An air–propane flame was found to be more sensitive than an air–acetylene flame. Optimum sensitivity (1% absorption) in the former flame was 0.28 p.p.m. lead compared with 0.43 p.p.m. in the latter flame. In both flames the resonance line at 217.0 nm was found to be more sensitive than the one at 283.3 nm.

All of the following information in this section was obtained with the air–propane flame for the resonance line at 217.0 nm. All solutions contained 5 p.p.m. lead. Both a 5000-fold amount of chromium and a 3000-fold amount of nickel increased the absorbance of a 5-p.p.m. lead solution. In addition, solutions with these high concentrations of chromium and nickel gave positive absorbances even in the absence of lead. The "blank" absorbances were inconsistent and difficult to interpret. These results are in agreement with those of other workers[2,3] for an air–acetylene flame.

Organic solvents are well known to enhance the absorbance of many elements in atomic absorption spectroscopy[8]. It was thought that the use of an aqueous organic solution, in addition to increasing the sensitivity of the method, might possibly eliminate the interference of chromium and nickel. Although enhancement was observed, the effect was far less marked than with some other elements. A solution containing 20% (v/v) n-propanol enhanced the absorbance by a factor of 1.6 relative to aqueous solution. This was the largest enhancement found in a study of the effects of 0–60% (v/v) methanol, ethanol, n- and iso-propanol. This limited enhancement for lead has been observed by several other workers[4,5,9]. Both chromium (5000-fold amount) and nickel (3000-fold amount) gave severe positive interference in 20% (v/v) n-propanol. In addition, as with the results in aqueous solution, positive absorbances were obtained even in the absence of lead.

It became obvious, at this stage, that to determine lead in high-alloy steels containing high concentrations of chromium and nickel, a preliminary solvent extraction stage, to isolate the lead, is necessary.

The extraction of lead as tetraiodoplumbate into methyl isobutyl ketone

On spraying the organic layer, after extraction of lead as tetraiodoplumbate into hexone, into the air–propane flame, the background noise became excessive. In an attempt to reduce this noise by lowering the propane flow rate, the flame simply "lifted off" the burner. The background noise, however, on spraying the extract into an air–acetylene flame, under the conditions described in the experimental section, was minimal. All subsequent work was carried out with the air–acetylene flame.

DAGNALL *et al.*[10], in a study of the determination of lead spectrophotometrically with 4-(2-pyridylazo)-resorcinol, established optimum conditions for the extraction of lead as its iodo complex into hexone, the results being more promising than extraction into methyl isopropyl ketone[11]. They found that optimum extraction was obtained from a solution which was 5% in hydrochloric acid and 7% in potassium iodide. By consideration of the absorbance of the hexone layer after extraction of lead, the optimum conditions obtained in the present work were from a solution which was 5% in hydrochloric acid and which contained 4 ml of saturated potassium iodide in a total aqueous volume of 150 ml; this amount of iodide is equivalent to 10 ml of 43% (w/v) potassium iodide solution as stated in the procedure. No further extraction was obtained after 1 minute of shaking. Some lead remained in the aqueous phase after a single shaking. Atomic absorption measurement of the hexone and aqueous layers after one, two and three extractions, indicated that only 82% of the lead was extracted after one extraction. This was consistently found to be the case. A hexone extract containing 4.1 p.p.m. lead gave an absorbance of 0.132 which corresponded to a sensitivity (1% absorption) of 0.14 p.p.m. This is approximately a 3-fold increase in sensitivity over aqueous solutions in the air–acetylene flame under optimum conditions.

Interference from chromium, nickel and iron

Assuming a 2-g sample weight, a steel containing 0.01% lead extracted into 20 ml of hexone gives a solution containing 10 p.p.m. lead (approximately, in view of the incomplete extraction). On addition of sufficient chromium and nickel to the aqueous solution to correspond to 25 and 20%, respectively, in steel, no interference on the lead absorbance was observed after the extraction procedure. This is to be expected as neither chromium nor nickel is extracted. However, on extracting a solution containing lead and iron(III) corresponding to 60% in steel, a severe depression of the absorbance was obtained and a red coloration of the hexone layer was observed. Iron(II), however, produced no such red colour and no interference. In view of the large amounts of iron(III) present in the aqueous solution after steel dissolution, a preliminary separation of iron was deemed necessary.

The solvent extraction separation of iron from hydrochloric acid solution is well documented[12,13]. No detailed investigations were carried out but a single shaking of a solution, 8 *M* in hydrochloric acid, with diisopropyl ether proved to be satisfactory for the removal of most of the iron. A trace of iron(III) remained in the aqueous phase after the extraction which caused depression of the lead absorbance in the hexone layer after iodide extraction. However, the addition of hydroxylammonium chloride reduced the iron(III) to iron(II) and no interference then occurred.

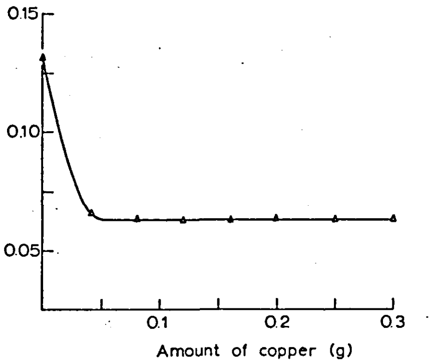
Interference from other elements

The interference of other elements found in minor amounts in steels was then investigated. As in the study of the interferences of chromium, nickel and iron, a number of other elements, in amounts corresponding to their maximum possible concentration in steel, were added to a solution of lead and extracted into hexone after addition of hydroxylammonium chloride. The lead content of the hexone layer in this study was 5 p.p.m. (actually 4.1 p.p.m., in view of 82% extraction). This corresponds to 0.005% lead in steel based on a 2-g sample weight after extraction into 20 ml of hexone. The concentration (equivalent percentage in steel) of each element studied is given in parenthesis after the element. There was no interference from manganese (10%), aluminium (10%), molybdenum (5%), cobalt (2%), vanadium (2%), niobium (2%), titanium (1%), boron (1%), sulphur (0.5%) and phosphorus (0.5%). Interference was considered to have occurred if the lead absorbance altered by more than ±4% from its value in the absence of interferent. This is considered a satisfactory precision for lead in the region of 0.005% in steel.

Copper(II), however, produced severe depression of the lead absorbance (Fig. 1). As in the case of iron(III), on extraction of copper(II) into hexone a red colour was observed in the organic extract. This was thought to be due to liberated iodine, according to the reaction:

$$2\,Cu^{2+}+4\,I^{-} \rightarrow 2\,CuI+I_2$$

Attempts to prevent the interference of copper by addition of ethylenediaminetetraacetic acid were unsuccessful.



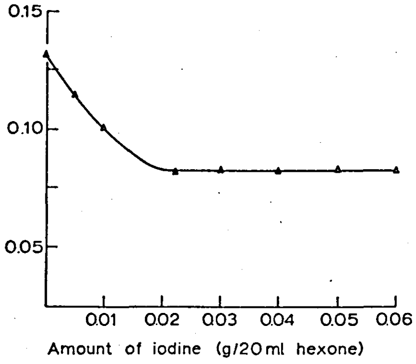


Fig. 1. Effect of copper in the aqueous phase on the lead absorbance after extraction into methyl isobutyl ketone.

Fig. 2. Effect of iodine in the methyl isobutyl ketone layer on the lead absorbance after extraction.

Interference of iodine

The partition coefficient of iodine between hexone and water is very high; no iodine could be detected spectrophotometrically in the aqueous phase after shaking with hexone. The effect of extracting lead into hexone containing various amounts of added iodine is shown in Fig. 2. The similarity with the effect of copper (Fig. 1) was noted. In an attempt to elucidate whether the interference of iodine was spectral, chemical or otherwise, lead was extracted into 20 ml of hexone and increasing volumes of a solution of iodine in hexone were added to the organic extract each time. The volume was adjusted to 25 ml with hexone in each case, the solutions containing 3.3 p.p.m. lead and 0–0.1 g iodine per 25 ml of hexone. None of the solutions showed any variation in absorbance. In other words iodine, liberated in the presence of copper, must inhibit the extraction since iodine itself does not interfere with the lead absorbance. This was shown to be the case by examination of the aqueous phase after extraction of lead with hexone containing increasing amounts of iodine. The amount of lead remaining in the aqueous phase increased as the amount of iodine increased.

The amounts of iodine liberated on extraction of lead plus varying amounts of copper, were determined spectrophotometrically, and the equation proposed earlier was confirmed. The "flame" absorbances obtained, however, on extracting lead plus added copper (Fig. 1) were consistently found to be lower than those obtained on extracting lead into hexone containing iodine (Fig. 2). It is assumed that copper extracted into hexone interfered slightly with the lead absorbance. The effect shown in Fig. 1, therefore, is explained in the following way. Copper present in the aqueous solution, before extraction with hexone, liberates iodine which inhibits the extraction of lead. The percentage extraction of lead, however, becomes constant above *ca.* 0.024 g of iodine liberated in the 20 ml of hexone. The copper which is extracted into hexone[14] causes a slight depression of the absorbance. This interference also becomes constant above a certain level of copper (in view of the parallel nature of the plateaux of Figs. 1 and 2). It is estimated that the effect of copper becomes constant above 0.01 g present in the aqueous solution before extraction. The solution to this problem is obvious. One needs to ensure that the amount of copper present in both the sample and the calibration solutions, before extraction, is such that on extraction, the amount of iodine liberated falls on the plateau of Fig. 1. The amount of copper must also exceed 0.01 g, since up to this amount copper interferes with the lead absorbance. These conditions are achieved by adding 5 ml of the standard copper solution (equivalent to 0.012 g of copper) to the aqueous solution before the final extraction.

On extracting steels without the added copper, 0.02–0.03 g of iodine was consistently found in the hexone layer. All of this cannot have been formed from the

TABLE I

RESULTS FOR THE DETERMINATION OF LEAD IN HIGH-ALLOY STEELS BY ATOMIC ABSORPTION SPECTROSCOPY

Alloy		*Lead content*		
		Dithizone method[a] *(%)*	*A.a.s.*[b] *(%)*	*A.a.s.*[c] *(%)*
1[d]	0.20% Cu	0.0025	0.0025	0.0025
2[d]		0.0045	0.0040	0.0045
3	9% Ni, 18% Cr, 0.25% Cu	0.0015	0.0015	0.0015
4		0.0035	0.0035	0.0035
5		0.0030	0.0025	0.0025
6		0.0025	0.0025	0.0025
7		0.0035	0.0035	0.0030
8	11% Ni, 18% Cr, 0.20% Cu	0.0015	0.0015	0.0015
9		0.0055	0.0055	0.0060
10		0.0007	0.0003	0.0005

[a] Values quoted by the British Steel Corporation.
[b] Values obtained by the recommended procedure.
[c] Values obtained by calibration with B.C.S.334 (containing 0.10% copper) with lead additions. No copper was added to either the steel samples or calibration solutions before extraction in this case.
[d] Low-alloy steels.

copper present in the steels (normally of the order of 0.25%). The total amount of iodine liberated from the steels with added copper, however, never exceeded 0.06 g and hence falls on the plateau. It is suggested that in analysing steels with high copper contents, care should be exercised in calibrating the method.

Application to high-alloy steels

Results for the determination of lead in eight high-alloy steels by the proposed procedure are shown in Table I. The analyses of two low-alloy steels are also included. The values obtained by reference to a calibration curve prepared from B.C.S.334 (containing 0.10% copper) with lead additions are also shown. No copper was added to the steel samples in this case. The results are considered satisfactory and the method, although involving two solvent extraction stages, is considerably shorter than the standard dithizone method.

The authors acknowledge with thanks the British Steel Corporation (Special Steel Products Division) for provision of the steel samples and for a maintenance grant for one of us (M.E.H.)

SUMMARY

A method is described for the determination of 0.001–0.01% lead in high-alloy steels by atomic absorption spectroscopy following solvent extraction. After sample dissolution, the bulk of the iron is removed by extraction with diisopropyl ether and residual traces of iron(III) are reduced with hydroxylammonium chloride. Lead is extracted as tetraiodoplumbate into methyl isobutyl ketone and the organic extract is sprayed into the flame. Iodine, which is liberated during the iodide extraction, particularly in the presence of copper, inhibits the extraction of lead, and the copper which is extracted also produces slight interference. Both the effects can be standardised by the addition of 0.012 g of copper to the aqueous solution before the iodide extraction in both the steel samples and the lead solutions for calibration.

RÉSUMÉ

On décrit une méthode pour le dosage de 0.001 à 0.01% de plomb dans les aciers, par spectroscopie par absorption atomique, après extraction dans un solvant. Après dissolution de l'échantillon, le fer est éliminé par extraction avec l'éther diisopropylique; les traces de fer(III) résiduelles sont réduites par le chlorhydrate d'hydroxylamine. Le plomb est extrait comme tétraiodoplombate dans la méthylisobutylcétone; l'extrait organique est vaporisé dans la flamme. L'iode formé, spécialement en présence de cuivre, gêne l'extraction du plomb; le cuivre qui est extrait produit également une légère interférence.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von 0.001–0.01% Blei in hochlegierten Stählen durch Atomabsorptionsspektroskopie nach vorhergehender Solventextraktion beschrieben. Nach Auflösung der Probe wird die Hauptmenge Eisen durch Extraktion

mit Diisopropyläther entfernt, die restlichen Eisen(III)-Spuren werden mit Hydroxylammoniumchlorid reduziert. Blei wird als Tetrajodoplumbat mit Methylisobutylketon extrahiert und der organische Extrakt direkt in die Flamme gesprüht. Jod, das während der Jodidextraktion besonders in Gegenwart von Kupfer freigesetzt wird, beeinträchtigt die Bleiextraktion; auch das extrahierte Kupfer stört etwas. Beide Effekte können dadurch standardisiert werden, dass die wässrige Lösung vor der Jodidextraktion sowohl bei den Stahlproben als auch bei den Blei-Eichlösungen mit 0.012 g Kupfer versetzt wird.

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THE DETERMINATION OF TRACE AMOUNTS OF BISMUTH IN STEELS BY SOLVENT EXTRACTION AND ATOMIC ABSORPTION OR ATOMIC FLUORESCENCE SPECTROMETRY

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Headridge and Richardson[1], in a method for the determination of 0.0001–0.01% of bismuth in steels, have shown the need to employ solvent extraction to concentrate the bismuth before its determination by atomic absorption spectrometry. The bismuth was extracted as the iodide complex into isobutyl methyl ketone (MIBK). Good results for the determination of 2–130 μg Bi g^{-1} in cast irons and stainless steels were obtained. The method, however, involves the addition of ascorbic acid to reduce iron(III) and this makes it necessary to add iron to the standard calibration solutions. In addition, a distillation step, to concentrate the organic phase, is incorporated, which is rather time-consuming. More recently, Burke[2] has described a method for the determination of microgram amounts of antimony, bismuth, lead and tin in aluminium, iron and nickel-base alloys by non-aqueous atomic absorption spectrometry. This method involves the quantitative extraction of these elements from a solution which is 10% in hydrochloric acid, 6% in potassium iodide and 2% in ascorbic acid into a 5% solution of trioctyl phosphine oxide (TOPO) in MIBK. Excellent results have been obtained and this procedure promises to be a very useful one.

Ammonium 1-pyrrolidinedithiocarbamate (APDC) has received increasing attention for the extraction of metals before their determination by atomic absorption spectrometry (a.a.s.)[3–5]. Lau *et al.*[6] have made a detailed study of APDC as a reagent for bismuth and have shown the feasibility of both spectrophotometric and atomic absorption spectrometric determination of bismuth in the presence of a large number of diverse ions. The possibility of applying their procedure to the determination of bismuth in highly-alloyed steels has therefore been examined.

In view of the current interest in the potential usefulness of atomic fluorescence spectroscopy (a.f.s.), it was decided to examine the possibility of determining bismuth in steels by a.f.s. in addition to a.a.s. Several workers[7–9] have investigated the fluorescence characteristics of bismuth under a variety of conditions. Bismuth fluorescence has been excited with an iodine electrodeless discharge tube[7] and in later work[8] with an electronically modulated bismuth electrodeless discharge tube. In this latter work a method was described for the determination of bismuth in aluminium alloys by a.f.s. No problem was encountered from scattered radiation and the results obtained were in good agreement with those obtained by a solution spectrophotometric method.

In the present work, it was established that the method of Lau *et al.*[6], with only minor modification, can be applied to the determination of bismuth in highly-alloyed steels and that perfectly satisfactory results are obtained whether the organic phase after extraction is subjected to a.a.s. or a.f.s.

EXPERIMENTAL

Apparatus

A Unicam SP90 atomic absorption spectrophotometer and a bismuth hollow-cathode lamp were used for the atomic absorption measurements.

Standard instrumental conditions

Wavelength	223.1 nm	Air pressure	30 p.s.i.
		flow	5 l min^{-1}
Slit width	0.05 mm		
Burner height	0.4 cm	Acetylene pressure	15 p.s.i.
		flow	0.3 l min^{-}
Lamp current	12 mA		

For the atomic fluorescence measurements a Jarrell-Ash 82-529 Maximum Versatility Flame Spectrometer was used. Some modification to this instrument was required. It was found that the major contribution to noise came from the photomultiplier tube. The zero control was not capable of completely backing off this noise when the P.M. was operated at high voltages. A 10 kΩ variable resistor was incorporated into the zero control circuit to enable this "backing off" to be effectively carried out at high P.M. voltages.

An argon-hydrogen-oxygen flame, burning on a Hetco total-consumption burner was used for the fluorescence measurements. This flame was selected because of its low background[10] and low quenching characteristics[10,11]. A bismuth electrodeless discharge tube (E.M.I.) was operated in an E.M.S. 214L ¼ wave cavity (Electro-Medical Supplies Ltd.) and powered by a Microton 200 Mk II microwave generator (2450 MHz, Electro-Medical Supplies Ltd.). The tube, which was operated at 55 W in the unmodulated mode, was placed at right angles to the optical axis of the spectrometer as in the normally accepted position for fluorescence studies. No mirrors or lenses were used and the cavity was placed near the flame (*ca.* 5 cm). An asbestos shield effectively prevented stray light from the tube from falling on the entrance slit of the monochromator.

Standard instrumental conditions

Wavelength	306.8 nm	Argon pressure	20 p.s.i.
		flow	8 l min^{-1}
E.D.T. power	55 W		
Entrance slit	0.1 mm	Oxygen pressure	10 p.s.i.
		flow	0.5 l min^{-1}
Exit slit	0.15 mm	Hydrogen pressure	10 p.s.i.
		flow	2 l min^{-1}
Burner height	6.5 cm		

Reagents

All reagents used were of analytical-reagent grade,

Bismuth solution A (100 gg Dissolve 0.10 g of pure bismuth in 25 ml of water and 40 ml of concentrated nitric acid, and dilute to 1 1with water.

Bismuth solution B (10 gg ml~x). Dilute 10.0 ml of bismuth solution A to 100 ml with water.

APDC solution. Dissolve 0.4108 g of APDC in 100 ml of water. Filter before use. (A fresh solution should be prepared weekly.)

Masking agent. Dissolve 50 g of disodium EDTA and 294 g of trisodium citrate in 267 ml of concentrated ammonia solution and dilute to 1 1with water.

Sodium citrate solution (30% w/v). Dissolve 300 g of trisodium citrate in 250 ml of water. Dilute to 1 1with water.

All solutions were stored in polythene bottles.

Analysis of steels

Dissolve 1.00 g of the steel in 20 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid. Evaporate the solution down to *ca.* 5 ml and add 20 ml of water followed by 10 ml of 30% trisodium citrate solution. Add concentrated ammonia until the solution is alkaline and then add a solution of 7 g of disodium EDTA in 70 ml of hot water. Evaporate the solution to *ca.* 30 ml. Transfer to a 125-ml separating funnel, add 10 ml of masking agent solution, and 10 ml of APDC solution. Dilute to 60 ml with distilled water and add 10 ml of MIBK (Note). Shake for 2 min and allow the layers to separate. Discard the aqueous layer and filter the MIBK layer through a Whatman 540 filter paper containing 1 g of anhydrous sodium sulphate into a stoppered polythene bottle. Spray into the flame and read off the bismuth content from the calibration graph.

Note. It may prove more satisfactory to extract with 20 ml of MIBK if an atomic fluorescence measurement is taken. Longer spray times are required for the a.f.s. determination, hence a volume of 10 ml is sometimes inadequate for duplicate readings. This in no way detracts from the a.f.s. method.

Preparation of calibration graph

From a burette transfer 0, 2, 4, 6, 8 and 10 ml of bismuth solution B into separate 125-ml separating funnels. Add 10 ml of masking solution and 10 ml of APDC solution to each. Dilute to 60 ml with distilled water and continue as described above. The calibration graphs, both in atomic absorption and atomic fluorescence, are linear from 0 to 10 *gg* ml-1 bismuth in the MIBK layer. If extraction of bismuth into 20 ml of MIBK is carried out for a.f.s., the calibration graph is linear from 0 to 5 *gg* ml-1.

RESULTS AND DISCUSSION

Extraction of bismuth-APDC complex and interferences

Lau *et al.6* have shown that the bismuth-APDC complex can be quantitatively extracted into chloroform or MIBK from solutions of pH 0 to 12. Since the dithiocarbamates are generally unselective reagents, these authors made a detailed study of the reactions of a large number of ions with APDC in the presence and absence of EDTA and cyanide as masking agents. In the presence of EDTA, citrate and cyanide, no ion in up to at least 40-fold amounts interfered with the atomic absorption determination of bismuth on spraying the MIBK layer into the flame.

In view of the large amounts of chromium, nickel and particularly iron present in a steel sample, it was thought necessary to increase the amount of EDTA present in the aqueous phase to complex all the iron. In addition, it was hoped to perform the determination in the absence of cyanide if possible. If cyanide is absent, copper will form an APDC complex which might interfere. The amount of APDC used in the extraction was therefore increased from that used by Lau *et al.* to ensure complete complexing of bismuth and copper. If a 1-g sample weight is taken, a steel containing 0.005% bismuth extracted into 10 ml of MIBK gives a solution containing 5 *fig* Bi ml-1. A number of elements, commonly found in steels, in amounts corresponding to their maximum possible concentration in steel, were added to an aqueous solution containing 50 *fig* of bismuth and the bismuth was extracted into MIBK. The concentration (equivalent percentage in steel) of each element studied is given in parenthesis after each element. There was no interference from iron (100%), chromium (25%), nickel (25%), manganese (10%), molybdenum (5%), vanadium (2%), copper (0.5%), tin (0.5%), aluminium (10%) and cobalt (2%).

Atomic fluorescence of bismuth

It is well known that the bismuth resonance line at 306.8 nm is the most intense fluorescence line[7] but it is generally not used because of the proximity of the hydroxyl band emission which might prove troublesome in an unseparated flame with an unmodulated source. On modulation at 50 Hz, the stability and intensity of the output from the bismuth source was found to decrease and generally proved troublesome. This is in agreement with the findings of Hobbs *et al.*[8]. In view of the low background of the argon-hydrogen-oxygen flame[10], it was hoped that complications caused by variations in the flame background would be minimal and indeed this was found to be the case. Maximum intensity of the source was obtained at a power of 50-55 W in the unmodulated mode. Maximal bismuth fluorescence and minimal background were obtained with a low flow rate of oxygen. Increasing the flow rate of hydrogen increased the fluorescence marginally but also increased the background. It was hoped that since a solvent extraction stage had been incorporated into the procedure, little or no interference from matrix elements would result. This was found to be the case and no interference from elements commonly found in steels was observed. The interference study was carried out in an identical way to that described above for a.a.s. It seems likely that if bismuth is to be determined directly in an aqueous phase with large amounts of other elements present, then a hotter flame may well be required.

Detection limits and linearity of calibration curves

The atomic absorption curve was found to be linear in the range 0-10 *fig* Bi mb1 in the organic phase with a 1% absorption value of 0.18 *fig* ml-1. The detection limit, defined as that concentration of bismuth in the organic solution which produces a signal:noise ratio of 1:1, was found to be 0.06 *fig* ml-1 in a.a.s.

In atomic fluorescence the-curve was again linear in the range 0-10 pg ml-1 with a detection limit, defined as before, of 0.012 pg ml-1. A comparison of the detection limits of the two techniques shows that atomic fluorescence is approximately five times more sensitive than atomic absorption for bismuth in organic solutions.

Recoveries of bismuth by the proposed methods

Bismuth was added to seven steels known not to contain bismuth and the steels were analysed by the proposed method. The results obtained by both atomic absorption and atomic fluorescence are shown in Table I.

TABLE I

RECOVERY OF BISMUTH ADDED TO STEELS

Sample	*Steel*					*Bismuth added (pg)*	*Bismuth found (pg)*	
	% Element						*A.a.s.*	*A.f.s.*
	Ni	*Cr*	*Mo*	*Cu*	*Mn*			
1	12	17	2	0.15	1.5	30	31	31
2	–	1	-	0.10	0.5	10	9	11
3	10	18	0.5	0.25	1	5	5	5
4		1	-	0.20	1	30	30	31
5	10	18	1	0.30	1	10	9	10
6	10	18	1	0.20	1	5	5	5
7	10	18	1	0.20	1	10	9	10

TABLE II

THE DETERMINATION OF BISMUTH IN STEELS

Alloy	*Bismuth content*0 *(m 9~*)*	*Proposed methods (pg g l)*	
		A.a.s.	*A.f.s.*
1]	1	1, 1	1.5, 1.5
■18% Cr, 4% Ni	50	51, 51	50, 51
3	68	70, 70	68, 70
4	105	107, 106	104, 106

“ Values quoted by the British Steel Corporation which represented the average of analyses by other methods, including square-wave polarography, and dithizone and iodide extraction-spectrophotometry.

Application to high-alloy steels

Results for the determination of bismuth in four high-alloy steels by the two methods are shown in Table II. These results are considered perfectly satisfactory.

In conclusion it is considered that this method is an attractive alternative to previously published methods for bismuth in steels. There is very little to choose between the two methods described here. However, for the determination of even lower amounts of bismuth in alloys, *e.g.* at the 0.1 /<g g_1 level, the a.f.s. method, which is more sensitive, offers more scope and is likely to be the method of choice.

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SUMMARY

A method is described for the determination of 0.0001-0.01% bismuth in high-alloy steels by either atomic absorption spectrometry or atomic fluorescence spectrometry after solvent extraction. After sample dissolution, the bismuth is extracted by ammonium pyrrolidine dithiocarbamate into MIBK and the organic phase is sprayed into an air-acetylene flame (atomic absorption) or an argon-hydrogen-oxygen flame (atomic fluorescence). Extraction of possible interfering elements is prevented by the addition of EDTA and citrate ion. Results for the analysis of four stainless steels are presented.

RESUME

Une methode est proposee pour le dosage du bismuth (de 0.0001 a 0.01%) dans des aciers. On procede soit par spectroscopie d'absorption atomique, soit par spectrometrie de fluorescence atomique. Apres dissolution de l'echantillon, le bismuth est extrait par le pyrrolidinedithiocarbamate d'ammonium dans la methylisobutylcetone. La phase organique est vaporisee dans une flamme air-acetylene (absorption atomique) ou dans une flamme argon-hydrogene-oxygene (fluorescence atomique). Des interferences peuvent etre evitees par addition d'EDTA et de citrate.

ZUSAMMENFASSUNG

Es wird eine Methode fiir die Bestimmung von 0.0001-0.01% Wismut in hochlegierten Stahlen durch Atomabsorptionsspektroskopie oder Atomfluoreszenzspektrometrie beschrieben. Nach Auflosung der Probe wird das Wismut durch Ammoniumpyrrolidindithiocarbamat in MIBK extrahiert und die organische Phase in eine Luft-Acetylen-Flamme (Atomabsorption) oder eine Argon-Wasserstoff-Sauerstoff-Flamme (Atomfluoreszenz) gespruht. Die Extraktion von moglicherweise storenden Elementen wird durch Zugabe von EDTA und Citrat verhindert. Die Ergebnisse der Analyse von vier rostfreien Stahlen werden vorgelegt.

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4.8. Interference from Manganese and Aluminium

The interference of manganese and aluminium on the extraction and determination of lanthanum as its TTA complex was studied as manganese and aluminium are two of the metals occurring in appreciable amounts in steel which are not removed by mercury cathode electrolysis.

In this study 10 ml. each of manganese and aluminium solutions (1 mg.ml^{-1}) were added to two separatory funnels containing 100µg. of lanthanum. The lanthanum was extracted into TTA and sprayed into the flame. The emission from the two solutions was much lower than that of lanthanum extracted alone, and hence a separation of these two metals from lanthanum was required.

4.9. Separation with Silver

The trace amounts of iron, chromium and nickel remaining after mercury cathode electrolysis were not enough to interfere with the determination of lanthanum when present separately. However the presence of other metals not removed by electrolysis and of sulphuric acid have been shown to cause interference. A silver oxide separation was developed to separate manganese, aluminium and sulphate ions from the rare earth solution after electrolysis.

Manganese (11) is oxidised to permanganate by boiling with persulphate ions in the presence of silver nitrate. A caustic soda addition to this solution will precipitate silver oxide, rare earth hydroxides and some manganese dioxide leaving in solution sulphate ions, sodium aluminate and any remaining sodium permanganate. If the precipitate is filtered and silver and rare earth metals redissolved in nitric acid then the silver can be removed as silver chloride by addition of hydrochloric acid, leaving a solution containing only rare earth metals. The scheme is summarised in Figure 4.5.

It was found necessary to add an excess of silver nitrate in the initial precipitation to ensure that all rare earth hydroxides were precipitated. Similarly the amount of nitric acid used to redissolve the hydroxides was limited as manganese dioxide was soluble in nitric acid.

4.9.1. Manganese Dioxide

In order to minimise the solubility of manganese dioxide in dilute nitric acid 0.01 to 0.02 g. samples of manganese dioxide were boiled with 5 to 50% nitric acid for five minutes. The amount of manganese dioxide dissolved in the aqueous solution was then determined by atomic absorption in a procedure similar to that used in the determination of manganese in steels (37).

From the analysis of the test solutions (Table 4.11) it was evident that manganese dioxide was soluble in all proportions of nitric acid. As the solubility was least in hot 5% nitric acid this solvent was selected for use in the procedure adopted.

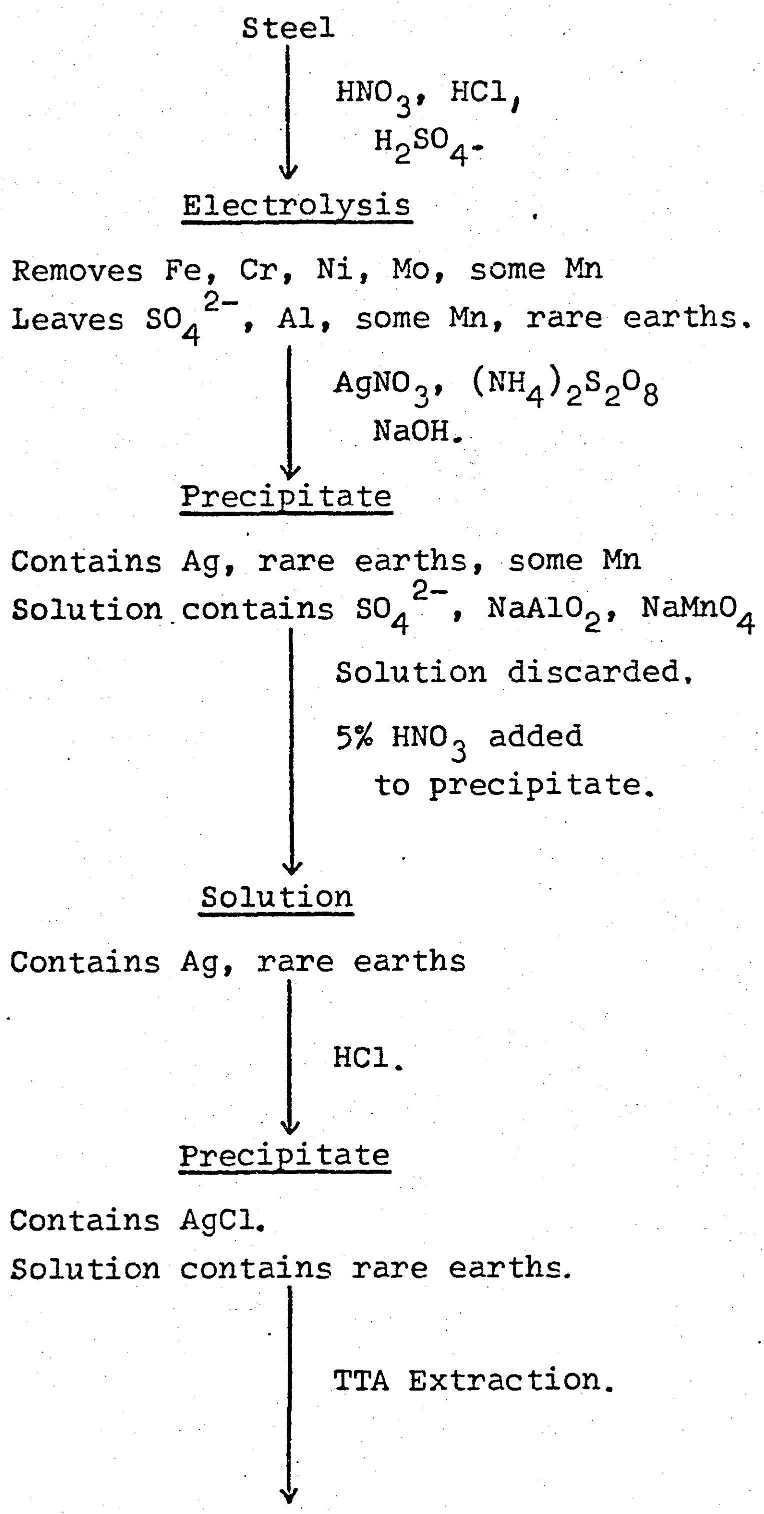
TABLE 4.11

The Solubility of Manganese Dioxide in Nitric Acid

%(v/v) HNO_3	Weight of MnO_2 (g.)	Weight of MnO_2 Dissolved (μg.)	Solubility of MnO_2 %	mg./100ml.
5	0.0186	1266	6.80	2.53
10	0.0192	1502	7.83	3.00
20	0.0174	1660	9.54	3.32
30	0.0159	1976	12.41	3.95
40	0.0197	2510	12.79	5.02
50	0.0165	2675	16.21	5.35

FIGURE 4.5

The Silver Oxide Separation



Steel

↓ HNO_3, HCl, H_2SO_4.

Electrolysis

Removes Fe, Cr, Ni, Mo, some Mn
Leaves SO_4^{2-}, Al, some Mn, rare earths.

↓ $AgNO_3$, $(NH_4)_2S_2O_8$ NaOH.

Precipitate

Contains Ag, rare earths, some Mn
Solution contains SO_4^{2-}, $NaAlO_2$, $NaMnO_4$

↓ Solution discarded. 5% HNO_3 added to precipitate.

Solution

Contains Ag, rare earths

↓ HCl.

Precipitate

Contains AgCl.
Solution contains rare earths.

↓ TTA Extraction.

Tests were conducted to establish the least volume of 5% nitric acid required to dissolve the oxide/hydroxide precipitates formed, a volume of 75 ml. finally being selected for use in the procedure.

4.9.2. Adopted Procedure

Evaporate the aqueous solution after electrolysis to ca. 50 ml., add 5 ml. of 0.1M silver nitrate and 10 ml. of 10%(w/v) ammonium persulphate, and simmer for 5 min. Cool, add 50%(w/v) sodium hydroxide until the solution is alkaline, add a further 2ml. and simmer for 1 minute. Cool and filter through a Whatman 541 filter paper. Wash the beaker and filter paper twice each with 1%(w/v) sodium hydroxide and three times with water. Wash the paper with 75 ml. of hot 5%(v/v) nitric acid, add 5 ml. of concentrated hydrochloric acid to the filtrate and simmer. Filter the precipitate through a Whatman 541 filter paper and wash the paper twice with 5%(v/v) hydrochloric acid. Evaporate the solution to dryness, cool and redissolve the salts in 5 ml. of water.

The procedure was tested at every stage to ensure that the interferent had been removed without loss of lanthanum. The silver oxide separation was finally tested by the analysis of solutions containing manganese, aluminium and sulphuric acid.

Table 4.12 shows the composition of the solutions and the emission from lanthanum after the solutions were treated as described above and after extraction of the lanthanum with TTA (Table 4.7). Very little difference in emission was evident for solutions 1, 2, 3, 4 and 6 confirming the feasibility of the silver oxide separation. The emission from the fifth solution was much lower than the rest, indicating a cumulative interference effect by these metals.

TABLE 4.12

The Separation of Manganese and Aluminium

Solution No.	Weight of Metal in Solution[a] (mg.)			Volume of 25% H_2SO_4 (ml.)	Emission[b] (mV.)
	Mn	Al	La		
1	-	-	0.10	-	4.50
2	10	-	0.10	-	4.35
3	-	10	0.10	-	4.40
4	-	-	0.10	25	4.30
5	10	10	0.10	25	3.65
6	0.10 mg. La (TTA extraction only)				4.55

[a] Solutions of the metals were prepared individually in nitric acid and mixed together before analysis.

[b] The emission from La at 743 nm. was measured under the conditions shown in Table 4.1.

In a second experiment a series of solutions (Table 4.13) was subjected to the whole analysis procedure of mercury cathode electrolysis, separation with silver oxide and extraction of lanthanum into TTA. The solutions were prepared by mixing individual solutions of the metals before evaporating them to dryness, redissolving in 25 ml. of 10%(w/v) sulphuric acid and transference to the electrolysis cells.

TABLE 4.13

The Analysis of Synthetic Solutions of Steel

Solution No.	mg. Metal in Solution									Emission (mV.)
	Mn[a]	Ni[a]	Cr[a]	Mo[b]	V[b]	Cu[a]	Sn[a]	Al[a]	La[c]	
1									0.07	3.40
2		50							0.07	3.55
3			50						0.07	3.40
4				50					0.07	3.50
5[d]		50	50	10					0.07	6.20
6[d]	10	50	50	10					0.07	4.90
7[d]		50	50	10				1	0.07	6.30
8[d]	10	50	50	10	1	0.5	0.5	1	0.07	5.60
9	0.07 mg. La (TTA extraction only)									3.45

[a] Addition was by pure metal dissolved in HCl or HNO_3.

[b] Addition was by metal oxide - MoO_3, V_2O_5.

[c] Lanthanum was added as 7.0 ml. of lanthanum solution ($10\mu g.ml^{-1}$).

[d] Iron was added to these solutions to bring the total metal content to 1000 mg.

The emission at 743 nm. was measured under conditions shown in Table 4.1.

The emission of the 1BMK extracts were measured (Table 4.13), the emissions of the solutions containing each interferent singularly showing little deviation from solution number 9, where lanthanum was subjected to the TTA extraction only, indicating that interference had been eliminated from these metals. The solutions (numbers 5 and 8) containing more than one interferent did show interference again caused by a kind of cumulative effect.

4.10. The Separation of Metals

The separtion of six metals from lanthanum by the combined techniques was investigated to ascertain the amount of the metals remaining after electrolysis and after the silver oxide precipitation.

The amounts of iron, nickel and chromium remaining were determined as described in section 4.7.1. and manganese as described in section 4.9.1. Molybdenum was determined as thiocyanate (75) after extraction into isoamyl alcohol and the absence of aluminium in the final solution was confirmed using Alizarin S. The findings are summarised in Table 4.14.

TABLE 4.14

Metals Remaining after Electrolysis and Separation

Metal	Weight present before electrolysis (g.)	Weight of metal present (µg.) After Electrolysis	After Separation
Fe	1	150	150
Ni	0.05	25	25
Cr	0.05	40	ND
Mn	0.01	A	88
Al	0.01	A	ND
Mo	0.01	62	ND

A = All remaining

ND = Non detected

A blank extraction was developed to overcome the problem caused by the cumulative interference from the metal traces remaining after electrolysis and silver separation.

4.11. Blank Extraction

Solutions of TTA in IBMK extract lanthanum at pH values greater than 3 (Table 4.6). At pH values above 5 the extraction is quantitative provided the amount of interferent is insufficient to inhibit the extraction of lanthanum. Extractions at pH 5 have been shown to extract other metals as well as lanthanum, for instance, about 4% of iron (Table 4.9) and 16% of nickel (Table 4.10) are extracted into 0.02M TTA. As the percentage of iron and nickel extracted does not vary significantly over the pH range 2 to 7 a second extraction at pH 2.5 would, therefore, extract approximately the same amounts of interferents as at pH 5, but would not extract lanthanum.

In practice it was found easier to carry out the extraction at pH 5 first before adding a pre-determined quantity of hydrochloric acid to reduce the pH to around 2.5 for the second extraction. The procedure was illustrated using aqueous solutions which contained 50 and 70μg. of lanthanum and 5 mg. of nickel, as this amount of nickel has been shown to cause interference with the determination of lanthanum (Figure 4.3) but not to inhibit the extraction.

5.0 ml. of lanthanum solution (10μg.ml.$^{-1}$) were pipetted into two separatory funnels after adding 1 ml. of nickel solution (5 mg.ml.$^{-1}$) to one of them. Two 7.0 ml. aliquots of the lanthanum solution were pipetted into two further separatory funnels, again adding 1 ml. of the nickel solution to one of them. The lanthanum was extracted into 0.02M TTA and both the aqueous and organic extracts were retained.

1M hydrochloric acid was added to each aqueous phase until the pH was 2.5. The solution was returned to the separatory funnels and 10.0 ml. of 0.02M TTA added. The funnels were shaken for 30 secs. and the phases allowed to separate, retaining the IBMK phases as before. Each IBMK extract was dried over anhydrous sodium sulphate and sprayed into the flame.

TABLE 4.15

The Determination of La in the Presence of Ni

µg. La	mg. Ni	Emission (mV.)			µg. La
		pH 5	pH 2.5	true	detected
70	-	3.30	0	3.30	-
50	-	2.40	0	2.40	-
70	5	3.70	0.30	3.40	70
50	5	2.80	0.40	2.40	50

The emission from the lBMK extracts was measured at 743 nm. under the conditions shown in Table 4.1.

The emission of each extract (Table 4.15) was used to calculate the true lanthanum emission from the relationship:-

true lanthanum emission = emission (pH 5.0) - emission(pH 2.5)

Emission readings from the extracts at pH 2.5 were only observed from the solutions containing nickel and when subtracted from the emissions of the pH 5 extracts they equalled the emissions from the two calibrant solutions. Interference from nickel had been alleviated using this procedure.

4.12. Recommended Procedures

4.12.1. Analysis of Steels

Dissolve 1.00 g. of the steel in 40 ml. of mixed acid (a), evaporate the solution to dryness and dissolve the residue in 25 ml. of water. Evaporate the solution to dryness and dissolve the residue in 25 ml. of 10%(w/v) sulphuric acid. Cool, transfer to the electrolysis cell and dilute the solution to 150 ml. with water. Add 50 ml. of mercury to the cell and electrolyse for 90 min. at 5 amperes. Evaporate the aqueous solution to ca. 50 ml., add 5 ml. of 0.1M silver nitrate and 10 ml. of 10%(w/v) ammonium persulphate and simmer the solution for 5 min. Cool, add 50%(w/v) sodium hydroxide to the solution until alkaline. Add a further 2 ml. and simmer for 1 min. Cool the solution and filter through a Whatman 541 filter paper. Wash the beaker and filter paper twice each with 1%(w/v) sodium hydroxide and three times with water. Finally pour 75 ml. of hot 5%(v/v) nitric acid through the filter paper retaining the filtrate. Add 5 ml. of concentrated hydrochloric acid to the filtrate and simmer for 2 min. Filter through a Whatman 541 filter paper and wash the filter paper twice with 5%(v/v) hydrochloric acid. Evaporate the filtrate to dryness, cool and redissolve in 5 ml. of water.

Add 10 ml. of 1M ammonium acetate, adjust the pH to 5.0 using either 2N nitric acid or 2N ammonia solution and transfer to a 125 ml. separatory funnel. Dilute the solution to 60 ml. with water. Add 10.0 ml. of 0.02M TTA and shake for 30 secs Allow the phases to separate and transfer the lower, aqueous phase to a second 125 ml. separatory funnel and add 1M hydrochloric acid to adjust the pH to 2.5 (b). Add 10.0 ml. of 0.02M TTA and shake for 30 secs. Allow the phases to separate. Dry the organic phases from both extractions over 0.2 to 0.5 g. of anhydrous sodium sulphate and spray the extracts into the flame. Subtract the emission reading of the extract of the pH 2.5 solution from the emission reading of the pH 5.0 extract, and read the lanthanum content from the calibration graph.

4.12.2. Preparation of Calibration Curve

Transfer 0, 2.0, 4.0, 6.0, 8.0 and 10.0 ml. of lanthanum solution ($10\mu g.ml^{-1}$) into a series of 125 ml. separatory funnels. Add 10 ml. of 1M ammonium acetate and continue as described above.

Note (a) For steels containing tungsten the tungstic oxide precipitate is filtered through a Whatman 541 filter paper.

(b) The amount of 1M hydrochloric acid for the pH adjustment to pH 2.5 is pre-determined for each fresh solution of the acid by adding the 1M acid to the solution dropwise from a burette, noting the volume taken. This volume is then added to all subsequent determinations using this acid solution.

4.13. Analysis of Alloys

4.13.1. Preparation of Calibration Curve

A calibration graph for 0 to $10\mu g.ml^{-1}$ of lanthanum in IBMK was prepared as directed in section 4.12.2.

The variation of the true emission from each solution with concentration of lanthanum, shown in Figure 4.6, is linear from 0 to $80\mu g.g.^{-1}$ of lanthanum in steel.

4.13.2. Analysis of Synthetic Alloys

The feasibility of the recommended procedures

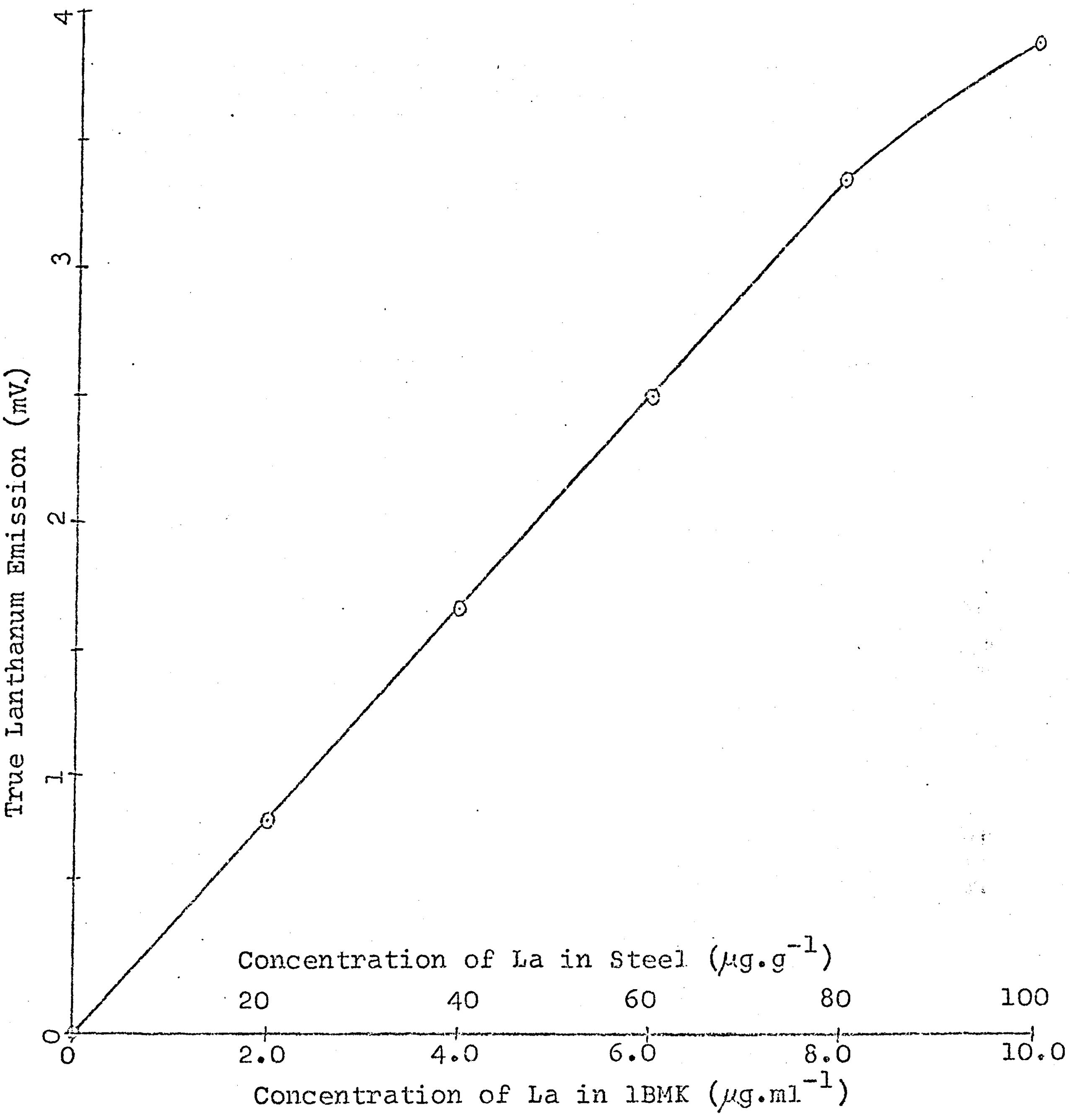


Figure 4.6

Calibration Curve for the Determination of Lanthanum in Steels was established by the analysis of the four solutions (5, 6, 7 and 8) originally described in Table 4.13.

TABLE 4.16

The Recovery of Lanthanum from Synthetic Steel Solutions

Solution Number[a]	Emission (mV.)[b]			La content (μg.g.$^{-1}$)	
	pH 5	pH 2.5	True	Actual	Recovered
5	3.60	0.50	3.10	70	74
6	2.90	0.20	2.70	70	65
7	3.00	0.20	2.80	70	68
8	3.20	0.20	3.00	70	71

[a] See Table 4.13.

[b] The emission of the IBMK extracts were measured at 743 nm. under the conditions shown in Table 4.1.

The emission of the IBMK extracts (Table 4.16) were related to the calibration curve (Figure 4.6) and the lanthanum content was determined. The analysis was considered perfectly satisfactory at this level of lanthanum.

4.13.3. The Analysis of Steels

Lanthanum was added to four British Chemical Standard Steels and the lanthanum content was determined by the recommended procedure, the results of which are shown in Table 4.17

TABLE 4.17

The Analysis of Pre-Analysed Steels

Alloy	Lanthanum Content ($\mu g.g.^{-1}$)		Emission[b] (mV.)			La detected ($\mu g.g^{-1}$)
	of steel[a]	added	pH 5	pH 2.5	True	
BCS 255/1	0	10	0.55	0.20	0.35	9
BCS 329	0	30	1.65	0.50	1.15	29
BCS 251/1	0	40	2.35	0.65	1.70	41
BCS 215/2	0	50	2.45	0.30	2.15	53
1	10	40	2.35	0.20	2.15	13
2	20	-	1.15	0.50	0.65	18
3	15	-	0.75	0.20	0.55	14
4[c]	10	40	2.25	0.30	1.95	8

[a] Value quoted by British Steel Corporation or BCS certificate.

[b] The emission from the IBMK extracts at 743 nm. was measured under the conditions shown in Table 4.1.

[c] Tool steel containing tungsten.

Four steels, three of which were low alloy and the fourth a tool steel, were also analysed as described in recommended procedures (Table 4.17). The steels and original analysis were provided by British Steel Corporation, the values representing determination by the 'difference' method.

4.14. Conclusion

The determination of lanthanum in steels by the procedure normally used in steelworks has been shown to be very unsatisfactory. Of the atomic spectrophotometric techniques available only ~~atomic~~ flame emission possessed adequate sensitivity for the determination of trace amounts of lanthanum in steels. In this investigation flame ~~atomic~~ emission was used in conjunction with a solvent extraction system to determine lanthanum in steels within the concentration range 10 to 80μg.g.$^{-1}$. The system chosen for this study, TTA, quantitatively extracted up to 100μg. of lanthanum into IBMK in one shaking improving the sensitivity five fold over water.

A number of interferences from matrix elements was encountered upon the extraction and determination of lanthanum. The severity of the interferences enforced the prior removal of the matrix elements using a combined mercury cathode electrolysis and silver separation technique.

In the procedure the bulk of the matrix metals were removed by electrolysis leaving only metals, such as aluminium and manganese, which were not transferred into the mercury under electrolysis. Aluminium and manganese were separated from the rare earth metals by treatment with sodium hydroxide after adding silver as carrier, the silver being easily removed as chloride before the extraction of lanthanum. Unfortunately the traces of the metals remaining in solution with lanthanum were enough to interfere with the determination of lanthanum. The extent of the interference by these metals was measured in a 'blank' TTA extraction and subtracted from the emission initially measured to give a signal representing the actual lanthanum content of the steel.

This technique allows the determination of trace amounts of lanthanum in steel. The results of the analysis of four such steels is included in this chapter, the analysis being considered perfectly satisfactory at the levels of lanthanum involved. In practice six samples were analysed in about six hours, the analysis time and precision representing a tremendous improvement over the existing method by 'difference'.

CHAPTER FIVE

SILVER

5.1. Introduction

Trace amounts of silver have been found to precipitate at grain boundaries within stainless steel causing cracking of the steel during rolling. The determination of silver in steels in concentrations up to 0.001% ($10 \mu g.g^{-1}$) is achieved by extraction of silver dithizonate into chloroform. In the method the colour of the test extraction is compared visually with dithizone extracts containing a known amount of silver. The procedure (79) on which this is based when adapted for the determination of silver in steels suffers from a number of disadvantages, the principal one being the lack of sensitivity to silver concentrations less than $1 \mu g.g^{-1}$. Secondly the presence of copper, which also forms a coloured dithizone complex, prevents the accurate matching of the colour of the test solution with that of the standards.

Atomic absorption has been shown to be twice as sensitive as atomic emission for silver (66). Since atomic fluorescence at the present time does not show much improvement in sensitivity over absorption, due to the lack of high intensity spectral sources for silver, atomic absorption was selected for this study of silver with the hope that a more rapid and reliable method for the determination of low levels of silver would be developed.

It has been shown (81) that, of the two main resonance lines of silver (328.1 nm. and 338.1 nm.) 328.1 nm. is the more sensitive, a 1% absorption value of 0.05μg.ml.$^{-1}$ in the air-acetylene flame being quoted by Hwang et al (80). A study of the interference of a large number of cations and anions has been carried out in the air-propane flame (43). No interference was encountered upon 5μg.ml.$^{-1}$ of silver from 1000 fold excesses of iron, chromium, nickel and copper. An enhancement of absorbance was noted for silver when determined in aqueous solutions containing miscible organic solvents.

The atomic absorption determination of silver in water immiscible organic solvents has been studied. T.S. West et al (43, 82) have extracted silver di-n-butylammonium salicylate into IBMK reporting very little interference from 1000 fold molar excesses of many metals including iron, chromium and nickel. The only notable exception was mercury which they prevented by adding anthranilic acid-diacetic acid (AADA).

P.W. West et al have described the extraction of silver dithizonate into ethyl propionate (ETP). In their reports they extracted the silver from EDTA solutions (83) and from tartrate solutions (84), discovering a 3 to 5 fold increase in signal when the ETP extracts were sprayed into the air-acetylene flame.

It would appear from the sensitivities quoted (e.g. 80, 81) that the direct determination of silver in steels in aqueous solution in amounts less than 10μg.g.$^{-1}$ is not possible, particularly when considering the large excess of other metals present with silver. An extraction of silver into an organic solvent would undoubtedly produce sufficient sensitivity to enable the determination of up to 10μg.g.$^{-1}$ of silver in stainless steels.

This chapter discusses four solvent extraction systems for silver ; TTA, diethyldithiocarbamate, di-n-butylammonium salicylate and dithizone; and shows how sufficient sensitivity for the determination of up to $10\mu g.g.^{-1}$ of silver in steels was achieved using the latter two systems. Of these two systems the salicylate extraction suffered from serious interference problems of an unusual nature; an explanation of one type of interference being included in this chapter. The extraction of silver with dithizone into ETP formed the basis of a method for the determination of silver in steels producing a procedure more reliable and more precise than the existing one.. The only notable interference accompanying this extraction came from chromium (VI) which, in the perchloric acid medium used, oxidised the dithizone. The relief of this problem using sulphur dioxide is also discussed in this chapter.

5.2. Preliminary Investigation

The work described in this preliminary study led to the optimisation of the instrumental parameters for the determination of silver in aqueous solution and investigated the effects of miscible solvents and iron, nickel and chromium upon the absorbance of silver.

5.2.1. Optimisation of Instrumental Parameters

The instrumental parameters for the aqueous determination were optimised (Table 5.1) in a manner similar to that described for lead in chapter 3. The wavelength chosen for this study of silver was that of the most intense resonance line at 328.1 nm. (81).

TABLE 5.1

Optimum Instrumental Parameters

Parameters		Water	IBMK	ETP
Wavelength	nm.	328.1	328.1	328.1
Burner height	mm.	7	7	8
Slit - entrance	mm.	0.025	0.025	0.025
- exit	mm.	0.025	0.025	0.100
Lamp current	mA.	2.5	2.5	2.5
Air pressure	p.s.i.	30	30	30
Air flow rate	$l.min.^{-1}$	5	5	5
Acetylene pressure	p.s.i.	10	10	10
Acetylene flow rate	$ml.min.^{-1}$	800	600	600

5.2.2. The Adsorption of Silver onto Glassware

The adsorption of silver onto glassware has been discussed in various publications (82,83), the authors preventing this by coating the glassware with a silicone preparation. In the investigation described in this chapter preventive treatment was not given to the glassware as adsorption of silver was not evident even from $2\mu g.ml.^{-1}$ solutions which had been stored in a variety of glassware for up to 2 days.

5.2.3. The Effects of Miscible Solvents, Iron, Chromium and Nickel

The enhancement of the absorption of silver by two water miscible solvents, n-propanol and ethylmethylketone, was studied. These two solvents were chosen as they had already been shown in a previous publication (43) to give the greatest enhancement. In this study a 70% enhancement of signal was achieved with solutions either 50% in n-propanol or 30% in the ketone. The use of the ketone, however, was limited due to its relative immiscibility with water.

The effect of 30,000 fold excesses of iron, nickel and chromium on $5\mu g.ml.^{-1}$ of silver in aqueous solution was ascertained, all three solutions showing an enhancement of the silver signal of only 5% rendering the direct determination of silver in steel just feasible. Unfortunately the difficulty in preparing solutions of this salt concentration and the blockage of the capillary tube which they caused prohibited this.

Because of the inadequate sensitivity achieved for silver in water, $0.12\mu g.ml.^{-1}$ for a 1% absorption, and the problems described above a suitable solvent extraction system for silver was sought.

5.3. Extractions with 2-Thenoyltrifluoroacetone

During the work on the determination of lanthanum it was observed that 2-thenoyltrifluoroacetone (TTA) also formed a complex with silver. With a view to its possible inclusion in an analysis scheme for silver the extractability of the silver - TTA complex was investigated.

The pH range within which the silver - TTA complex was extracted into IBMK, the optimum concentrations of TTA and ammonium acetate and the shaking time were ascertained in a manner similar to that described in the preceding chapter for lanthanum. The results are summarised in Table 5.2 and Figure 5.1, the former showing the most suitable extraction conditions into IBMK for the silver - TTA system and the latter showing the variation in the extraction of silver with pH. The absorbance of the lBMK extracts were measured under the conditions stipulated in Table 5.1 for aqueous solution. The acetylene flow, however, was reduced to 600 ml.min.$^{-1}$ to prevent 'lift-off' of the flame.

TABLE 5.2

The Extraction of Silver with TTA

Aqueous Phase	
Volume	50 ml.
Concentration of Silver	0-100μg.
Concentration of 1M ammonium acetate	2.5 ml.
pH	7
Organic Phase	
20.0 ml. of 0.04M TTA in IBMK.	
Time of Shaking	1 minute

The organic extract is dried over anhydrous sodium sulphate and stored in a stoppered polythene bottle.

Maximum extraction of silver by 0.1M TTA occurred between pH 7 and 8 (Figure 5.1). The extraction dropped sharply at pHs higher than 8, probably due to the formation of the stable silver ammine complex. In addition emulsions were formed in both the aqueous and organic phases in extractions carried out at pH values greater than 10.

The percentage extraction of 100μg. of silver into IBMK with TTA was determined by treating the aqueous solution with five successive 20 ml. aliquots of 0.04M TTA.

The average absorbance of the extracts (Table

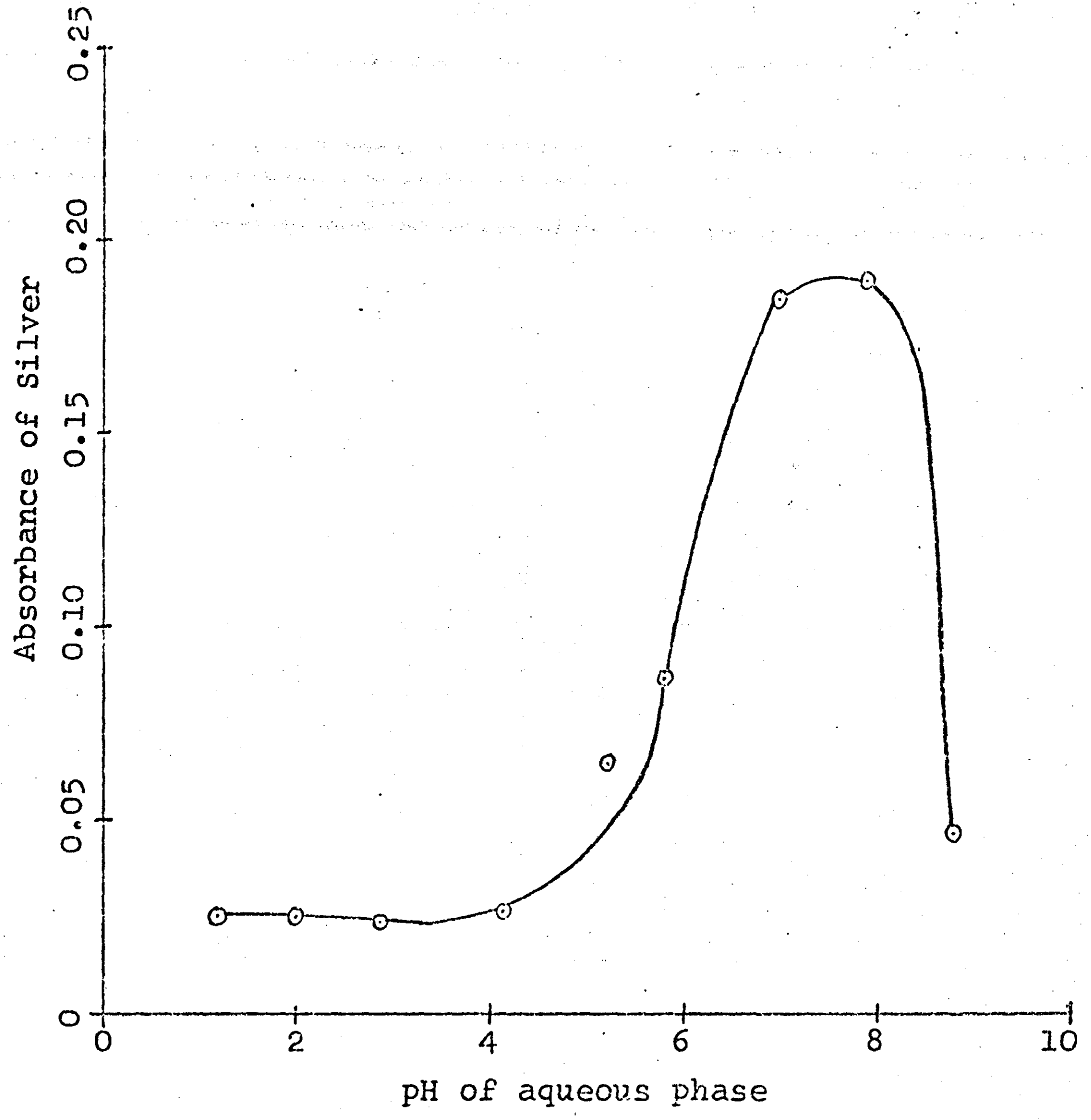


Figure 5.1

The Variation in the Extraction of Silver into 0.1M TTA with pH

The aqueous phase contained 125µg. of Ag before extraction.

The absorbance of the IBMK extracts were measured under the conditions shown in Table 5.1.

5.3) revealed that only 53% of the silver were extracted in one equilibration with TTA assuming quantitative extraction after three shakings. Clearly a solvent extraction procedure separating only 53µg. of silver from the original 100µg. is of little use in the analysis of steel involving very small quantities of silver.

TABLE 5.3

The Percentage Extraction of Silver-TTA

Extraction Number	Absorbance	% Extraction
1	0.174	53.2
2	0.092	28.1
3	0.061	18.7
4	0.039	0
5	0.029	0
(0.04M TTA)	0.032	-

The absorbance of Ag was measured under the conditions shown in Table 5.1 for 1BMK.

5.4. The Extraction of Silver as Diethyldithiocarbamate

The extraction of silver diethyldithiocarbamate into organic solvents, such as carbon tetrachloride and benzene, is well documented (e.g. 85,86). These solvents are unsuitable in the flames normally used in atomic spectroscopy because of instability and the liberation of toxic gases. An attempt was made to extract the silver complex into more suitable solvents such as ETP, amyl acetate and IBMK. Unfortunately this met with little success as either silver was not extracted at all or the system required many extractions to be quantitative. Attention was turned, therefore, to the extraction of silver with di-n-butylammonium salicylate.

5.5. The Extraction of Silver with Di-ni-butylammonium Salicylate

Belcher, Dagnall and West (43) have examined the atomic absorption determination of silver after its extraction into IBMK with di-n-butylammonium salicylate. Their procedure using 'hexone reagent "A"' was investigated as the sensitivity quoted was ample for the determination of up to $10\mu g.g^{-1}$ of silver in steels.

5.5.1. pH of Maximum Extraction

Belcher et al, in their work, did not ascertain the pH of maximum extraction of the silver-salicylate complex. This was determined in the following experiment:-

3.0 ml. aliquots of silver solution ($5\mu g.ml^{-1}$) were pipetted into a series of 250 ml. separatory funnels adding 5 ml. of 5M sodium nitrate and 5 ml. of 20%(w/v) sodium acetate to each. Nitric acid was added to each solution to adjust the pH to pre-selected values within the range 1 to 8, the pH of the solution being accurately measured after diluting the solutions to 200 ml. with water. 10.0 ml. of salicylic acid, di-n-butylamine solution (SABA) were added and the funnel was shaken for one minute. The phases were allowed to separate and the upper, IBMK extracts were sprayed into the flame measuring the absorbance of silver under the conditions stated in Table 5.1 for IBMK. Maximum extraction of silver occurred at pH 5 and above (Table 5.4).

TABLE 5.4

The pH of Extraction of Ag/SABA

pH of Aqueous Solution	Absorbance
1.40	0.032
2.40	0.032
3.30	0.032
4.25	0.040
5.15	0.357
6.05	0.362
6.60	0.360
7.90	0.361

5.5.2. The Percentage Extraction of Silver

The efficiency of this solvent extraction system was established by extracting 15μg. of silver into IBMK at pH 6 in the manner described above. Both the organic and aqueous extracts were retained, any silver remaining in the aqueous extract being transferred into IBMK by two further shakings with 10 ml. of SABA. The absorbance of each of the three IBMK extracts sprayed into the flame, when measured as shown for IBMK in Table 5.1, were 0.360, 0.030 and 0.030 respectively and the absorbance of SABA solution was 0.030.

The experiment, carried out in triplicate, confirmed that the system was quantitative for silver in one extraction, providing ample sensitivity, 0.015μg.ml.$^{-1}$ for a 1% absorption, for the determination of up to 10μg.g.$^{-1}$ of silver in steels, particularly when viewed with the prospect of little interference as the work of Belcher et al (43) has suggested.

5.5.3. Interference Study

The extraction of silver with SABA has been shown to occur quantitatively at pH 5 and above. In common with the solvent extraction of lead and lanthanum at these pH values problems were expected in attaining pH 5 without hydroxide precipitation. These difficulties were relieved in this investigation by substituting sodium citrate for the sodium acetate used in the experiments so far.

An initial study of the effects of up to 50000, 25000 and 25000 fold excesses of iron (111), nickel and chromium (111) respectively on the extraction revealed some peculiar shaped interference curves. In an attempt to explain one of the curves the plots were represented in terms of the ionic strength (I) of the solution instead of concentration of interferent. The ionic strength (87) was calculated from the relationship -

$$I = 0.5 \sum C_i Z_i^2$$

where C_i = molar concentration of the species, i, and

Z_i = electronic charge on that species,

and included contributions from the sodium citrate, the metal compound and the sodium hydroxide added to attain the pH of 5. The contribution to the ionic strength from the silver nitrate solution was considered negligible.

5.5.3.1. Experimental

The procedure for the interference study of iron (111) is described below. A study of the effects of nickel, manganese (11) and chromium (111) was carried out in a method identical with that described for iron.

0, 4.0, 7.0, 10.0, 14.0 and 19.0 ml. of 0.5M

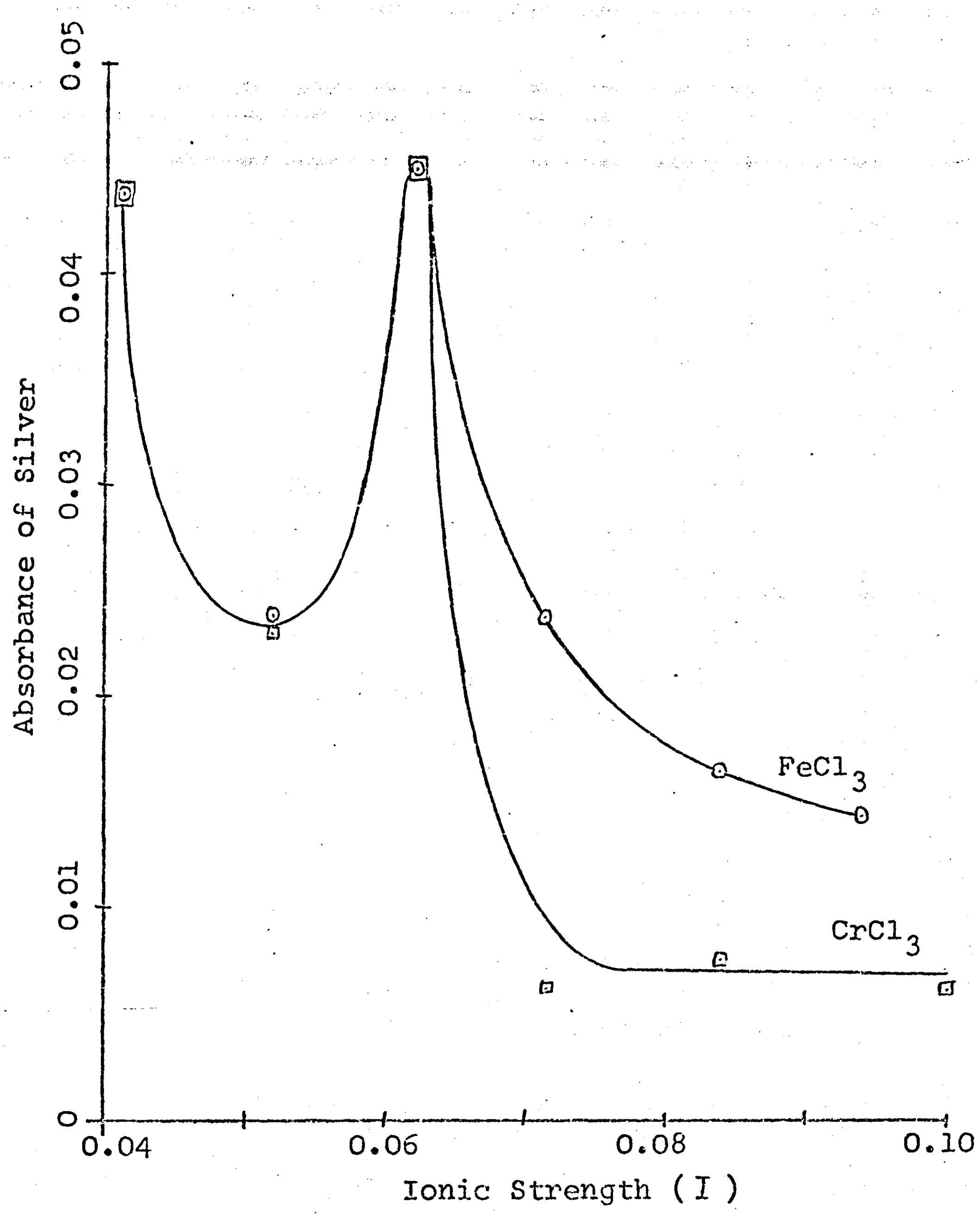


Figure 5.2

The Interference of Iron and Chromium

The aqueous phase before extraction contained 15μg. of silver and 0.0068M Citrate $^{3-}$.

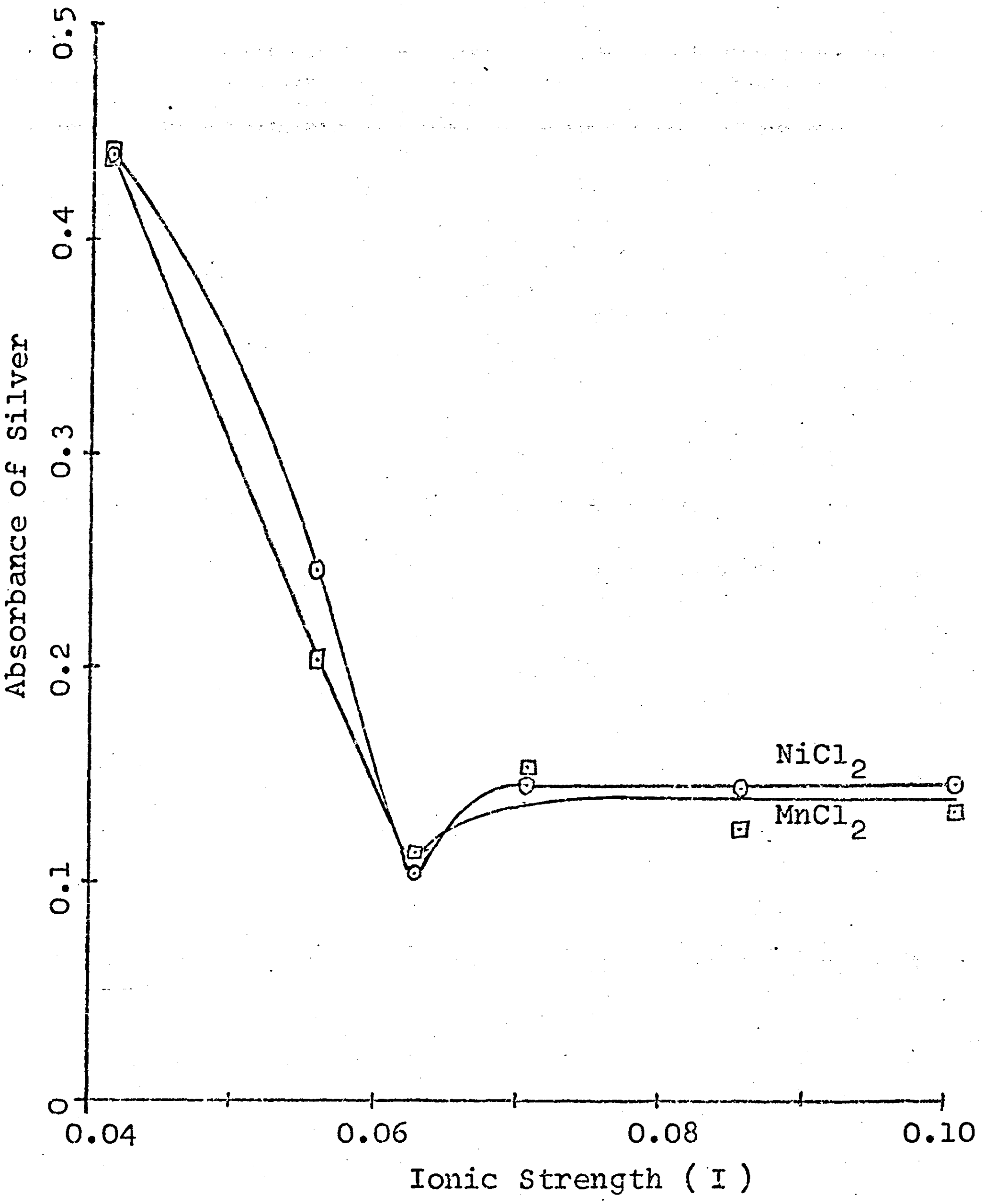


Figure 5.3

The Interference of Nickel and Manganese

The aqueous phase before extraction contained 15μg. of Ag and 0.0068M Citrate $^{3-}$.

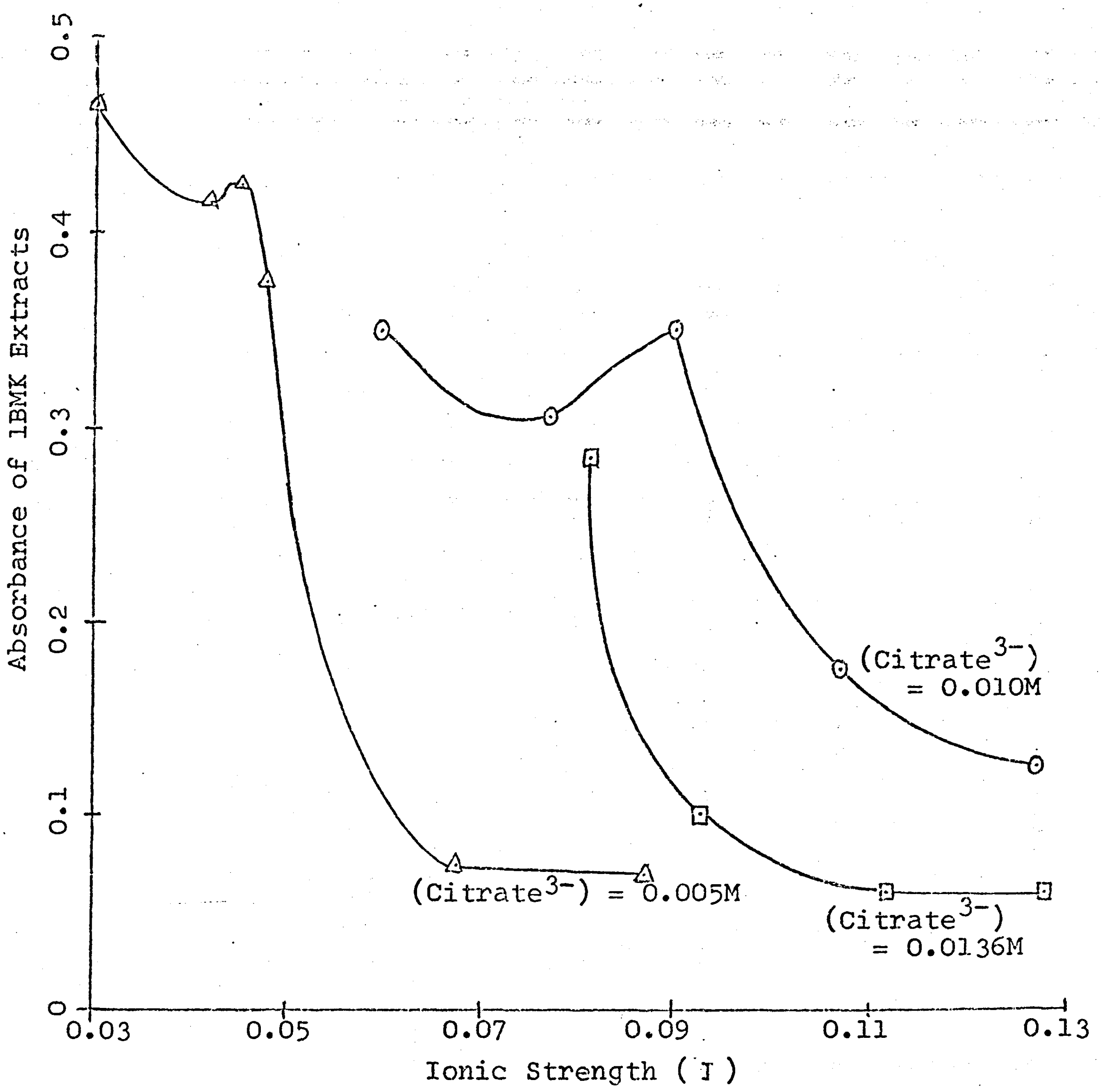


Figure 5.4

The Influence of Ionic Strength upon the Interference of Iron

The aqueous phase before extraction contained 15μg. of silver and 0.005, 0.010 and 0.010M Citrate^{3-} in each of the three curves respectively.

ferric chloride were added to each of six separatory funnels containing 15μg. of silver and 10 ml. of 20%(w/v) sodium citrate. The solutions were diluted to 150 ml. with water and 0.1M sodium hydroxide was added to each solution from a burette until the pH measured between 5.0 and 5.5. The solutions were diluted to 200 ml. with water and the silver was extracted into 10.0 ml. of SABA solution by shaking the funnels for one minute each. The organic extracts were sprayed into the flame and the absorbance noted (Table 5.5). The variation in the absorbance with total ionic strength for the electrolyte is shown in Figure 5.2.

TABLE 5.5

Calculation of Ionic Strength

Volume of 0.5M $FeCl_3$ (ml.)	Molarity of Fe	Volume of 0.1M NaOH (ml.)	Total Ionic Strength	Absorbance[a]
0	0	0	0.041	0.440
4	0.002	0	0.053	0.236
7	0.0035	2.0	0.062	0.447
10	0.005	5.0	0.0715	0.240
14	0.007	12.0	0.084	0.167
19	0.0095	16.0	0.094	0.113

[a] The absorbance of Ag was measured under the conditions shown in Table 5.1 for IBMK.

The ionic strength was derived as follows:-

$$I = 0.5\left((cz^2)_{FeCl_3} + (cz^2)_{Na_3\ Citrate} + (cz^2)_{NaOH}\right)$$

e.g. For the addition of 10.0 ml. of 0.5M ferric chloride:-

$$(cz^2)_{FeCl_3} = (0.005 \times 3^2) + (3 \times 0.005 \times 1^2) = 0.060$$

$$(cz^2)_{Na_3\ Citrate} = (3 \times 0.0068 \times 1^2) + (0.0068 \times 3^2) = 0.082$$

(10 ml. of 20%(w/v) sodium citrate is equivalent to 0.0068 moles.)

$$(cz^2)_{NaOH} = (0.0005 \times 1^2) + (0.0005 \times 1^2) = 0.001$$

$$\therefore I = 0.5\ (0.060 + 0.082 + 0.001) = 0.0715.$$

The variation in absorbance with ionic strength for a second 1:3 electrolyte, chromic chloride, is also shown in Figure 5.2. Similarly the variation for the two 1:2 electrolytes, nickel chloride and manganous chloride, is shown in Figure 5.3. The absorbances and ionic strengths were compiled using a 0.5 molar solution of the chromic salt and 1 molar solutions of the nickel and manganese salts.

In a further experiment the interference of iron on the extraction of silver was investigated at sodium citrate concentrations of 0.005, 0.010 and 0.0136 moles instead of the 0.0068 moles used initially. The absorbances of the IBMK extracts were measured under the conditions shown in Table 5.1 and their variation with the ionic strength of the ferric chloride electrolyte is shown in Figure 5.4.

5.5.3.2. Discussion

The variation in the interference of the metals upon the extraction of silver with SABA is very similar for the two groups of metals studied: i.e. nickel and manganese, and, iron and chromium: the plots for the first pair (Figure 5.3) being almost identical. The first part of the plots for iron and chromium (Figure 5.2) are also identical, the deviation above an ionic strength of ca. 0.07 being due to the insolubility of relatively high concentrations of chromium (111) in solutions of pH 5 and above.

In every case investigated the extraction of silver into IBMK decreased as the ionic strength increased. Secondly, the effects can be classified into electrolyte types, i.e. 1:2 or 1:3, and lastly it is interesting to note that the plots all show an outstanding feature at an ionic strength of 0.062; i.e. either a maximum or a minimum. A possible explanation for these findings is presented here in terms of iron.

The interference from ferric chloride, in terms of ionic strength, upon the extraction of silver into IBMK at different concentrations of citrate ions is shown in Figures 5.2 and 5.4. In the first of these where the citrate concentration is 0.0068 moles (Figure 5.2) a maximum occurs at an ionic strength of 0.062, corresponding to an iron concentration of 0.0035 moles. This concentration of iron is nearly half of the citrate concentration and may indicate a particular compound formation, e.g.

$$Fe^{3+} + 2\ Citrate^{3-} \longrightarrow (Fe(Citrate)_2)^{3-}.$$

If this is the case any variation in the citrate concentration present will cause a corresponding shift in the peak of maximum extraction of silver by SABA. Figure 5.4. shows the interference of iron at citrate concentrations of 0.0136, 0.010 and 0.005 moles.

Two of the three plots show peak absorbance at ionic strengths of 0.045 and 0.09 equivalent to 0.0025 and 0.005 moles of iron. These correspond to citrate concentrations of 0.005 and 0.010 moles; i.e. again double the iron concentration;

indicative that some type of compound formation is occurring. The third plot, where the citrate concentration is 0.0136 moles, does not show a maximum as the point of zero extraction of silver is reached before the critical iron concentration.

If some type of compound formation is occurring then why does this effect the extraction of silver? It has already been established that the extraction of silver decreases as the ionic strength increases then, if a compound of the type indicated in the above reaction is being formed, the ionic strength of the solution is decreased by the formation of one ion from three ions. A reduced ionic strength means an increase in the extraction efficiency thus giving a maximum on the curve.

This postulate explains the effect of iron. A similar one will explain chromium interference as well but not the minimum absorbance observed in Figure 5.3. for nickel and manganese.

5.5.3.3. Anthranilic acid, diacetic acid (AADA)

The use of this reagent to prevent interference by other metals on the extraction of silver with SABA has been described (43,82). Unfortunately when this reagent was used to overcome the interference of as little as 0.1 g. of iron then AADA in excess of 1 g. was required. The further use of this reagent was prohibited by its high cost of preparation.

The investigation discussed in this section has shown the extraction of silver with SABA to be both quantitative at pH values above 5 and sufficiently sensitive for the determination of trace amounts of silver in steel. A study of the interference effects of a number of metals commonly found in steels revealed peculiar interference curves which could be divided into two groups dependent upon the stoichiometry of the metal compound used. A possible explanation of one type of interference was presented here. The findings of the interference study, however, were not in conflict with those of West et al (43, 82) as their study involved less concentrated solutions of the interferents. The problems encountered led to the investigation of dithizone as a more suitable complexant for the solvent extraction of silver.

5.6. The Extraction of Silver with Dithizone

P. W. West et al (83,84) have described the extraction of silver dithizonate into ethyl propionate (ETP) from an aqueous solution buffered at pH 3 to 4 with tartaric acid. Initial studies using this system revealed that the concentration of dithizone required for maximum extraction of silver, 0.02% in ETP, produced a noisy signal and unsteady flame. The noise prevented measurement of the absorbance of silver at the concentrations required, furthermore a single extraction of silver proved unreliable with regards to efficiency as, sometimes two or more extractions were required.

These findings, contrary to those of the original authors who used the system to determine traces of silver in water, led to the investigation of the dithizone system already used for the determination of silver in steels, namely that of Jones and Newman (79).

Jones et al described the extraction of up to 20μg. of silver into either chloroform or carbon tetrachloride from 3.5M perchloric acid using a dithizone solution of 0.001%.

Ascorbic acid was also added to the aqueous solution to retard the oxidation of dithizone. In the studies described in this chapter ETP was used as solvent as ETP has better flame characteristics than either chloroform or carbon tetrachloride.

5.6.1. Preliminary Investigations

The optimum instrumental conditions for the determination of silver in ETP were established for the air-acetylene flame in a manner similar to that described for lead in chapter 3 after extracting 15 μg. of silver into 10 ml. of 0.001% dithizone. The aqueous phase of 25 ml. contained the silver, 8 ml. of concentrated perchloric acid and 5 ml. of 1%(w/v) ascorbic acid and the time of shaking was 1 minute. The optimum instrumental parameters are summarised in Table 5.1.

The most suitable conditions for the extraction of silver were investigated in the following sequence; perchloric acid concentration, dithizone concentration and aqueous volume. The results are shown in Tables 5.6, 5.7 and 5.8 respectively and a summary of the optimum conditions is shown in Table 5.9.

TABLE 5.6

Optimum Perchloric Acid Concentration

Volume of concentrated $HClO_4$ (ml.)	Colour of ETP extract	Absorbance
0	Green	0.281
2.5	Green	0.296
5.0	Green	0.296
7.5	Dark green	0.196
10.0	Brown	0.050
12.5	Dark brown	0.050

The absorbances were measured under the conditions shown in Table 5.1 for ETP.

TABLE 5.7

Optimum Concentration of Dithizone

Concentration of Dithizone in 10 ml. of ETP (μg.)	Absorbance
40	0.177
80	0.286
120	0.350
160	0.350
200	0.350

The absorbance of the organic extracts were measured under the conditions shown in Table 5.1 for ETP.

TABLE 5.8

Optimum Aqueous Volume

Aqueous Volume (ml.)	Absorbance
25	0.290
50	0.340
75	0.370
100	0.400
150	0.420
200	0.537
250	0.540

The absorbance of the organic extracts were measured under the conditions shown in Table 5.1 for ETP.

TABLE 5.9

Optimum Extraction Parameters for Silver Dithizonate

Aqueous Phase

Volume	200 ml.
Concentration of silver	0-15µg.
Concentration of 40%(v/v) perchloric acid	10 ml.
Concentration of 1%(w/v) ascorbic acid	5 ml.

Organic Phase

10.0 ml. of 0.002%(w/v) dithizone in ETP.

Time of Shaking 1 minute

The organic extract is dried over anhydrous sodium sulphate and stored in a stoppered polythene bottle.

Optimum perchloric acid concentration was between 2.5 and 5.0 ml. of the concentrated acid (Table 5.6), additions in excess of this resulted in oxidation of the dithizone and decreased extraction efficiency. Maximum extraction of silver into 10 ml. of ETP occurred in the presence of dithizone concentrations of 120µg. and above (Table 5.7). The flame instability observed in earlier studies with this reagent was not noticed at the concentrations used here.

In the work of Jones and Newman the aqueous volume was 25 ml., however a volume of 200 ml. and above was found to achieve maximum extraction of the silver dithizonate into ETP (Table 5.8).

The percentage extraction of silver from three solutions containing 10µg. of silver was ascertained by treating each solution as described in Table 5.9 with three successive 10 ml. aliquots of the dithizone solution. The average absorbance of each of the three ETP extracts were 0.530, 0.032 and 0.030 and the absorbance of 0.002%(w/v) dithizone was 0.030. The extraction of silver was 99.7% efficient in one shaking and quantitative in two, the sensitivity for a 1% absorption being 0.0083μg.ml.$^{-1}$ representing a 14 fold increase over the determination in water.

The preliminary investigation into silver dithizonate has disclosed ample sensitivity for the requirements of this study, although the conditions used for the extraction are somewhat different from those described by Jones and Newman.

5.6.2. Interference from Matrix Elements

The extraction described by Jones et al using dithizone has been found in practice to be relatively free from interferences when applied to the analysis of steel, the only notable interference occurring with copper.

In this study interference from iron was also encountered when the silver extractions were carried out in the presence of iron (111) which had been prepared by dissolving iron in hydrochloric and nitric acids. The nitric acid in these solutions was not completely evaporated allowing the partial extraction of ferric nitrate into ETP. The ferric nitrate, once in the ETP, oxidised the dithizone preventing the extraction of the silver complex. When the solutions of iron were evaporated in the presence of perchloric acid no further problems of this nature were encountered allowing the determination of up to 10μg. of silver in the presence of 1 g. of iron.

The effect of eight elements, likely to be found in stainless steels, upon the extraction and determination of silver was investigated by adding each of the metals in turn to silver, in amounts equivalent to the maximum likely to be found in steels. In the experiment the metal or metal oxide was dissolved in a suitable solvent before adding 5.0 ml. of silver solution (2μg.ml^{-1}) and 10 ml. of concentrated perchloric acid to each solution. The solvent was evaporated until copious white fumes were evolved from the acid. Fuming was continued for 5 mins, the solution cooled and 50 ml. of water added. The solution was simmered for 2 mins, cooled and transferred to a 250 ml. separatory funnel. 5 ml. of 1%(w/v) ascorbic acid were added and the solution was diluted to 200 ml. with water. 10.0 ml. of 0.002%(w/v) dithizone were added and the solution shaken for 1 min, before collecting the ETP phase for drying and spraying into the flame.

TABLE 5.10

An Interference Study

Metal	Weight of metal added (mg.)	Metal or metal compound added	Absorbance[a]	Weight of silver recovered[b] (µg.)
Silver alone	10µg.	-	0.530	10.0
Iron	1000	Fe	0.535	10.4
Nickel	200	Ni	0.520	9.7
Manganese	10	Mn	0.530	10.0
Molybdenum	50	MoO_3	0.526	9.8
Titanium	20	Ti	0.534[c]	10.3
Aluminium	20	Al	0.525	9.8
Copper	10	Cu	0.530[d]	10.0
Chromium	250	Cr	0.055	1
Chromium	250	Cr	0.525[e]	9.8

[a] The absorbance of Ag was measured under the conditions shown in Table 5.1 for ETP.

[b] The amount of Ag recovered was calculated by relation to the absorbance of 10µg. of Ag when subjected to the dithizone extraction only.

[c] The oxide of Ti precipitated during the analysis.

[d] The dithizone concentration was 0.004%.

[e] The Ag was extracted after reduction of Cr (V1) with SO_2.

The amount of each element added is shown in Table 5.10 together with the absorbance and amount of silver recovered. Interference was deemed to have occurred if the amount of silver recovered differed by more than 4% from the amount added. Of the eight elements investigated only copper and chromium were found to interfere with the extraction and determination of silver. The study revealed that copper was co-extracted with silver into ETP under the conditions shown in Table 5.9. yielding a brick red ETP phase. However, when the dithizone concentration was increased to 0.004% the organic phase remained green, resolving the problem of copper.

The interference by chromium was found to be due to the formation of dichromate ions when the solution containing chromium was treated with perchloric acid. Contact between the dichromate solution and the organic phase spontaneously oxidised the dithizone, preventing the extraction of silver. To solve the problem either the chromium had to be removed from the matrix or reduction to chromium (111) was required. In theory the former method seemed easier as chromium can be evaporated as volatile chromyl chloride on addition of concentrated hydrochloric acid to the fuming perchloric acid mixture. However, in practice, the method was tedious and required too much hydrochloric acid to be effective.

In the method selected gaseous sulphur dioxide was bubbled through the hot perchlorate solution for 1 minute before the extraction of silver. This procedure was enough to reduce the bulk of the chromium to its trivalent oxidation state and to restore the original green colour to the solution. The excess sulphur dioxide was removed by simmering the solution for five minutes.

At this stage a procedure for the determination of silver in stainless steels was proposed.

5.7. Recommended Procedures

5.7.1. Analysis of Stainless Steels

Dissolve 1 g. of the steel in 15 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid. Add 10 ml. of concentrated perchloric acid and evaporate the solution until white fumes were evolved from the perchloric acid. Continue fuming for 5 min., cool and dissolve the residue in 50 ml. of water. Heat the solution to boiling and bubble gaseous sulphur dioxide through the hot solution for 1 min. Simmer the solution for 5 min., cool, add 5 ml. of 1%(w/v) ascorbic acid, dilute to 200 ml. with water and transfer to a 250 ml. separatory funnel. Add 10.0 ml. of 0.004%(w/v) dithizone in ETP to the funnel, shake for 1 min. and allow the layers to separate. Discard the aqueous phase and run the ETP phase into a beaker containing 0.2 to 0.5 g. of anhydrous sodium sulphate. Filter the solution through a Whatman 541 filter paper into a stoppered polythene bottle and spray into the flame under the conditions shown in Table 5.1 for ETP. Read off the silver content from the calibration graph.

5.7.2. Preparation of Calibration Curve

Pipette 0, 1, 2, 3, 4 and 5.0 ml. aliquots of silver solution ($2\mu g.ml.^{-1}$) into 200 ml. graduated flasks adding 10 ml. of 40%(v/v) perchloric acid and 5 ml. of 1%(w/v) ascorbic acid before diluting to the mark with water. Transfer the solutions to 250 ml. separatory funnels, add 10.0 ml. of 0.004%(w/v) dithizone in ETP and proceed as described above.

A typical calibration graph is shown in Figure 5.5, being linear up to silver contents of about 8μg.g.$^{-1}$.

5.8. The Analysis of Alloys

The proposed method was subjected to a recovery test where various amounts of silver were added to four highly alloyed steels. The composition of the steels is shown in Table 5.11 and the amount of silver detected by relation of the absorbance of the ETP extracts to Figure 5.5 is shown in Table 5.12.

TABLE 5.11

The Composition of Alloys

Alloy		Composition of Alloy[a]				
	Percentage	Ni	Cr	Mo	Mn	Ti
BCS 336		10	18	2.5	1	
No.1		10	18	1		0.5
2		12	18	2	1.5	
3		11	18	3	1.5	

[a] In the analysis 0, 1.5, 3.0 and 4.5 ml. of silver solution (2μg.ml.$^{-1}$) were added to each alloy.

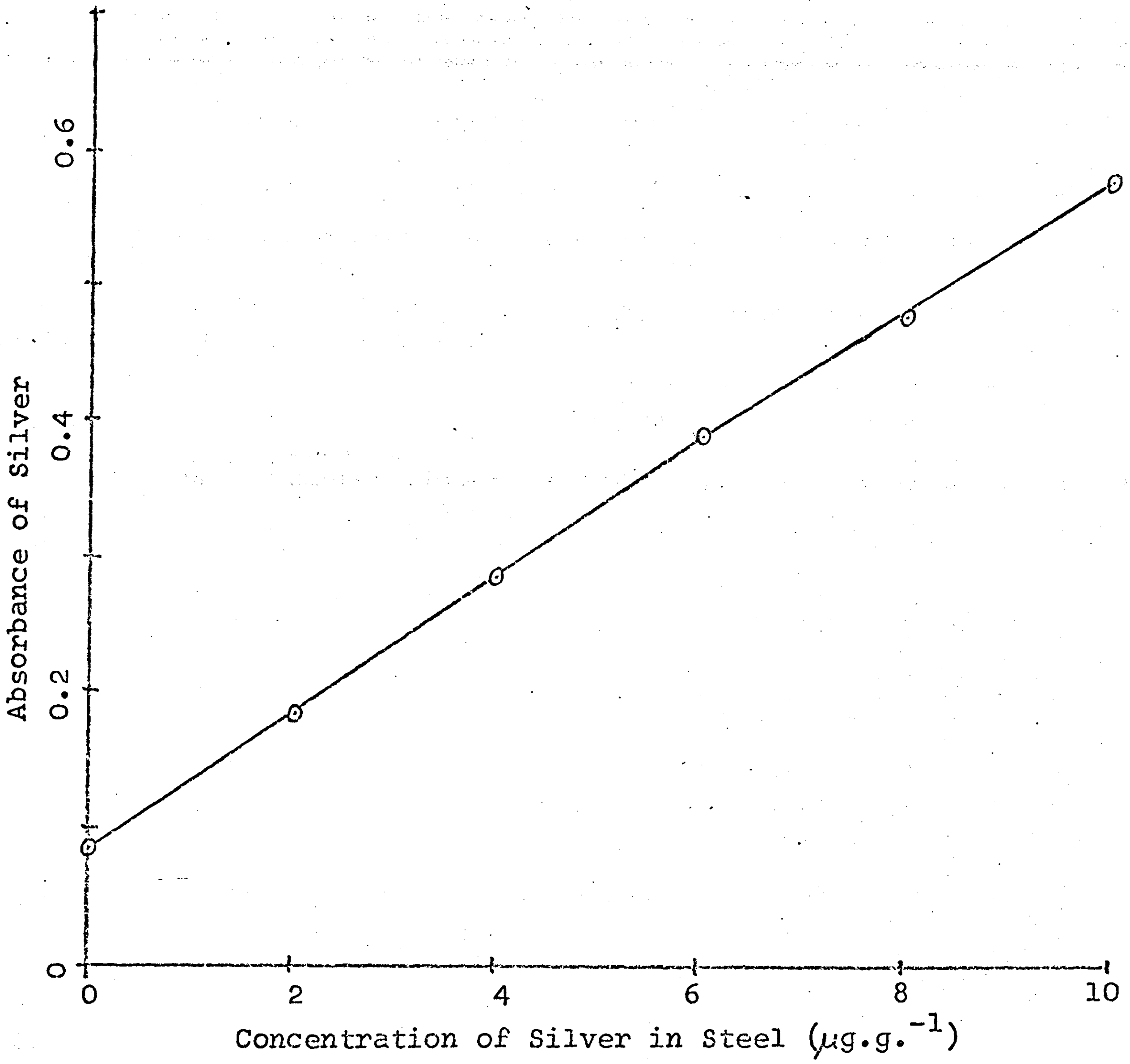


Table 5.5

Calibration Curve for the Determination of Silver in Steel

TABLE 5.12

The Recovery of Silver

Alloy and Weight of Silver added (µg.)		Absorbance[a]	Concentration of Silver ($\mu g.g.^{-1}$) Recovered	Actual	Recovery of Silver (%)
BCS 336	0	0.103	0.30		
	3	0.270	3.65	3.35	112
	6	0.415	6.50	6.20	103
	9	0.510	9.00	8.70	97
Alloy 1	0	0.218	2.62		
	3	0.392	6.05	3.45	115
	6	0.505	8.90	6.30	105
	9	0.565	11.60	9.00	100
Alloy 2	0	0.120	0.60		
	3	0.270	3.65	3.05	103
	6	0.436	7.00	6.40	107
	9	0.527	9.85	9.25	103
Alloy 3	0	0.160	1.40		
	3	0.318	4.60	3.20	110
	6	0.450	7.30	5.90	98
	9	0.531	10.00	8.60	96

[a] The absorbance of Ag was measured under the conditions shown in Table 5.1 for ETP.

The results were considered satisfactory at the levels of silver involved (i.e. 0.1 to 10$\mu g.g.^{-1}$ in steel), the standard deviation of the errors of the twelve analyses containing silver being 0.39$\mu g.g.^{-1}$. The tests also showed that the steels did contain a very small amount of silver although no confirmatory data was available. In an attempt to compare the atomic absorption analysis with that used in steelworks the four steels were analysed using the method of Jones and Newman (79). The results of this comparison are shown in Table 5.13, the figures obtained in the method of Jones et al being from titres of 0, 0.3, 0.1 and 0.2 ml. of silver solution (10μg.ml^{-1}) respectively. The method of the above authors, when applied to steel analysis, is very limited with regard to sensitivity and precision, partly because of the very small titres involved and partly because of indistinct colour changes of the dithizone solutions.

TABLE 5.13

The Determination of Silver in Steels

Alloy	Adaptation of the Method by Jones et al (79) (μg.g^{-1})	Atomic Absorption Procedure (μg.g^{-1})
BCS 336	0	0.3
Alloy 1	3	2.6
2	1	0.6
3	2	1.4

The results of this comparative study did confirm the presence of silver in three of the alloys, though to a lesser degree of precision. With regards to reproducibility of the atomic absorption procedure nine solutions containing 6μg. of silver were analysed by the prescribed method, the standard deviation of the errors being 0.06μg. of silver.

5.9. Conclusion

The direct determination of silver in steels in the range 0.1 to 10μg.g^{-1} by atomic absorption spectrophotometry is not feasible because of the difficulties involved in the atomisation of highly concentrated matrices. Four solvent extraction systems for silver were investigated, two being rejected as unsuitable because too many extractions were involved for quantitative separation.

Of the two remaining systems both showed ample sensitivity for the requirements of this study. The interference of iron and three other metals commonly found in steel upon the extraction of silver with one of the reagents, SABA, revealed curiously shaped curves which could be classified into two groups dependent upon the oxidation state of the metal being investigated. A possible explanation of the interference pattern of one of these groups, iron (111) and chromium (111), is presented in this chapter in terms of iron. The postulate describes the formation of a complex within the solution between iron (111) and citrate ions. The use of this extractant for silver was discontinued as these interference problems proved difficult to overcome without recourse to preliminary separation.

The extractions with dithizone from perchloric acid solutions were virtually quantitative in one shaking with the only notable interferent being chromium (Vl). Chromium in its highest oxidation state spontaneously oxidised the dithizone preventing the extraction of silver. This problem was easily relieved by prior reduction of the chromium using sulphur dioxide. This chapter describes this extraction procedure and shows the analysis by atomic absorption of four alloys to which silver had been added and compares this analysis with the procedure currently used in steelworks laboratories. The atomic absorption method, although requiring a similar analysis time, is more sensitive and more precise than the usual method.

CHAPTER SIX

BISMUTH

6.1. Introduction

Bismuth, like lead, is a residual metal in steel, trace amounts being absorbed from the steelmaking materials. The problems associated with bismuth are again similar to lead but their effects on the mechanical properties are much more disastrous; a BISRA Committee (4) found that as little as 0.0045% of bismuth in stainless steels reduced the ductility to zero.

The methods for the determination of these trace amounts of bismuth are as varied as they are numerous and range from square-wave polarography (88) to a variety of solution spectrophotometric techniques, the most notable ones being dithizone (89) and iodide (16). The determination of bismuth in stainless steels by these techniques involves the prior removal of the bulk of the matrix elements and hence the analysis time is usually lengthy.

The physical techniques of X-ray fluorescence and emission spectrometry are of little use in the determination of bismuth in these small amounts.

The various techniques described are the subject of a current BISRA Committee to find a suitable standard procedure for the determination of trace amounts of bismuth in stainless steel.

The determination of bismuth in steels by atomic spectroscopy is well documented particularly for atomic absorption (90-93). In the first report (90) bismuth was determined in aqueous solution after dissolution of the steel in acid, with 0.01% marking the lower determinable limit. The other papers were concerned with the extraction of bismuth into an organic solvent prior to spraying into the flame, in so doing obtaining lower limits of detection. Each author indicated the lack of sensitivity for the direct determination of bismuth in amounts less than 0.01% ($100\mu g.g^{-1}$) in stainless steels. Detection limits (S:N = 2) for the determination of bismuth in aqueous solutions have been quoted in the oxy-acetylene flame as $1\mu g.ml^{-1}$ (94) and as $0.4\mu g.ml^{-1}$ in the air-propane flame (95).

West et al have studied the atomic fluorescence spectroscopy of bismuth and have obtained a detection limit of about $0.05\mu g.ml^{-1}$ (S:N = 1) in a variety of flames (95-97) finding little interference from 500 fold excesses of many metals, including iron, chromium and nickel. A recent paper of West et al (96) has described the direct determination of 0.2 to 0.6% of bismuth in aluminium alloys by atomic fluorescence.

Two EDL light sources have been used in their studies, the better detection limits being obtained with a bismuth EDL at 306.8 nm. An iodine EDL has also been used as an alternative excitation source for bismuth as its very intense line at 206.16 nm. overlaps the 206.17 nm. bismuth transition. The use of this source allows the excitation of bismuth atoms to a very high energy state from which fluorescence, at a variety of wavelengths, can be observed without any problems of source light reflection into the monochromator being observed. The best detection limits using this source have been obtained at 302.5 nm. where, in the argon-hydrogen flame, the signal was twice that at 306.8 nm (97). West et al have made a rigorous study of this cool flame using an iodine source, the low background emission enabling a detection limit to be achieved which equalled those obtained in the separated air-propane and air-acetylene flames. In general, however, the best detection limit for a particular flame has been obtained with a bismuth EDL.

In atomic emission sensitivity for bismuth is much inferior to atomic absorption, Figures of 3.3 and $6.4 \mu g.ml.^{-1}$ per scale division being quoted for the air-hydrogen and oxy-acetylene flames respectively at 223.1 nm (98).

The determination of bismuth after extraction into an organic solvent has been achieved by both atomic fluorescence (95) and absorption (91-93). In the former technique West et al extracted bismuth as its complex iodide into IBMK, the detection limit showing a three fold improvement over water. The iodo-bismuth system has also been used in atomic absorption (91,93).

Headridge and Richardson (91) determined 2 to $130 \mu g.g.^{-1}$ of bismuth in steels by extracting its iodide complex into IBMK quoting a 100% extraction in one shaking and noting no interference from the other metals in steel. The method, however, is rather time consuming as the aqueous phase, before extraction of bismuth, requires a triple evaporation to dryness and treatment with ascorbic acid to reduce the iron. The bismuth is extracted into 50 ml. of IBMK and involves a distillation procedure to concentrate the organic phase in order to achieve adequate sensitivity. Iron is also added to the calibration solutions, a practice which detracts from the versatility of atomic absorption.

Bismuth, in the range 3 to $50\mu g.g^{-1}$, has been determined in steels by Kisfaludi et al (92) after extraction as dithizonate into carbon tetrachloride. The method, unfortunately, suffers from a number of disadvantages, the main one being the unsuitability of carbon tetrachloride in flame techniques. Cyanide is also used as complexant for interfering metals and again there is a need to reduce iron to its ferrous state.

In a report published since this study began Burke (93) used a combined solvent extraction technique to determine a number of trace metals, including bismuth, in aluminium, iron and nickel based materials. The author described the extraction of the iodo-bismuth complex into IBMK containing trioctylphosphine oxide obtaining a 12 fold increase in signal over aqueous solutions, using only a 10 ml. IBMK phase, instead of the 50 ml. required elsewhere (91). Burke, however, also experienced interference from iron (111) as well as from nitrates.

In summary, the determination of 1 to $100\mu g.g^{-1}$ of bismuth in stainless steels is not feasible in atomic emission whether in aqueous or organic solution, nor is it feasible in aqueous solution by atomic absorption. Atomic fluorescence can be used to determine this amount of bismuth if the separated air-acetylene or the cool argon-hydrogen flames are used although interference from the matrix would undoubtedly be encountered, especially in the latter flame. With the problems of matrix interference in mind the solvent extraction of bismuth was again thought to hold the key to the determination of trace amounts of bismuth in steels.

Of the solvent extraction techniques for the determination of bismuth in steels already discussed in this chapter all were prone to interference from iron. Lau, Droll and Lott (99) have studied the extraction of bismuth with ammonium 1-pyrrolidinedithiocarbamate (APDC) into IBMK, the reagent already being used to determine a variety of metals by atomic absorption (e.g. 100,101) as well as bismuth by solution spectrophotometry (102). Lau et al discovered that the extraction of bismuth was virtually quantitative within the pH range 0 to 12 noting many interferences in the absence of masking agents. In the presence of EDTA and citrate only copper, silver and thallium were co-extracted and if cyanide ions were also present, then, only thallium was co-extracted with bismuth. Under these conditions the authors found no interference from metals commonly found in steels when present in 40 fold molar excesses of over $1.393\mu g.ml.^{-1}$ of bismuth and quote a 1% absorption sensitivity of $8.2\mu g.ml.^{-1}$.

The extraction method of Lau, Droll and Lott is the subject of the investigation described in this chapter whereby bismuth is determined in stainless steels by both atomic absorption and atomic fluorescence spectrophotometry. In the recommended procedure cyanide was omitted from the extraction medium as copper was the only metal masked by cyanide which was present in steels in appreciable amounts. Interference from copper was alleviated in this study by adding a sufficient amount of APDC to complex all bismuth and all copper. Under these conditions all bismuth and some copper were extracted into the IBMK phase. The amount of copper extracted was found to be insufficient to interfere with both the extraction and determination of bismuth.

This chapter also discloses the superior sensitivity of atomic fluorescence over absorption for bismuth in both aqueous and organic solutions. In atomic fluorescence a bismuth EDL was selected as excitation source for the metal in an argon-hydrogen flame as it was felt that the detection limit of $0.05\mu g.ml.^{-1}$ (S:N = 1) obtained by West et al (97) in the same flame using an iodine EDL could be surpassed.

6.2. Atomic Absorption

The determination of bismuth by atomic absorption was carried out on a Unicam SP 90 atomic absorption spectrophotometer. Details of this instrument, the ancillary equipment and reagents used are presented in chapter 2.

6.2.1. Preliminary Studies

These studies enabled the sensitivities and detection limits for the aqueous, atomic absorption determination of bismuth to be ascertained after prior optimisation of the instrumental conditions (Table 6.1). Of the two wavelengths studied, 223.1 and 306.8 nm., the shorter wavelength showed a 5 fold improvement in sensitivity over that at 306.8 nm.

The table also shows the optimum instrumental settings for use with organic solutions. These were ascertained after extracting bismuth into 10.0 ml. of IBMK by shaking the IBMK for 2 min. with a 60 ml. aqueous solution containing 10.0 ml. of bismuth solution ($10\mu g.ml.^{-1}$), 10 ml. of masking agent and 6 ml. of APDC solution.

TABLE 6.1

Optimum Instrumental Parameters - Atomic Absorption

		Aqueous Solution		Organic Solution	
Wavelength:-		223.1 nm.	306.8 nm.	223.1 nm.	306.8 nm.
Parameter					
Lamp current	mA.	12	5	12	5
Burner height	mm.	1	1	4	6
Slit width	mm.	0.01	0.05	0.05	0.10
Acetylene pressure	p.s.i.	15	15	15	15
Acetylene flow rate	$ml.min.^{-1}$	800	800	300	300
Air pressure	p.s.i.	30	30	30	30
Air flow rate	$l.min.^{-1}$	5	5	5	5
Sensitivity					
$\mu g.ml.^{-1}$/1% Abs.		0.8	4.0	0.18	0.92
Detection Limit (S:N = 1)					
$\mu g.ml.^{-1}$		0.2	1.0	0.06	0.23

The optimisation procedures in both the aqueous and organic solutions were carried out in a manner similar to that described in chapter 3 for lead.

The optimum conditions for the extraction of bismuth with APDC were ascertained at 223.1 nm. by measuring the variation in the absorbance of the bismuth extracts with the pH of the aqueous phase and with the total aqueous volume. In the first experiment a series of solutions were prepared in a similar way to those described above. The pH of the solution was adjusted to preselected values in the range 4 to 10 by adding nitric acid to the separatory funnels. The bismuth was extracted into 10 ml. of IBMK and the IBMK extracts were sprayed into the flame. The absorbances (Table 6.2) confirmed the extractability of bismuth with APDC over the pH range 4 to 10.

TABLE 6.2

The pH of Extraction of Bi-PDC

pH	Absorbance
4.30	0.225
5.20	0.220
6.10	0.210
7.10	0.200
8.00	0.210
9.00	0.200
10.00	0.210

The aqueous phase contained 100µg. of bismuth before the extraction.

The absorbance of the organic extracts were measured at 223.1 nm. under the conditions shown in Table 6.1.

The bismuth from a series of solutions containing 100µg. of bismuth in aqueous volumes ranging from 50 to 200 ml. was extracted into 10.0 ml. of IBMK as described above. The pH of the aqueous solution was 10. The absorbance of the dried IBMK extracts decreased inversely with the aqueous volume (Table 6.3) indicating that for maximum extraction of bismuth with APDC the volume of the aqueous phase should be kept to a minimum. In practice the most suitable volume was 60 ml.

TABLE 6.3

Optimum Aqueous Volume

Aqueous Volume (ml.)	Absorbance
50	0.151
75	0.140
100	0.129
125	0.115
150	0.083
175	0.052
200	0.063

The aqueous phases each contained 100μg. of bismuth before extraction.
The absorbance of the IBMK extracts were measured at 223.1 nm. under the conditions shown in Table 6.1.

In similar experiments the variation in absorbance of the IBMK extracts with the volume of APDC solution used and the time of shaking were ascertained. In each case the optimum volume and time were identical with those found by Lau et al (99). The optimum conditions for the extraction of bismuth with APDC into IBMK are summarised in Table 6.4.

TABLE 6.4

Optimum Extraction Parameters

Aqueous Phase	
Aqueous volume	60 ml.
Concentration of bismuth	0-100µg.
Concentration of masking agent	10 ml.
Concentration of APDC solution	6 ml.
pH	10
Organic Phase	10.0 ml. of IBMK.
Time of Shaking	2 minutes

The IBMK extracts were dried over anhydrous sodium sulphate before spraying into the flame.

6.2.2. The Percentage Extraction of Bismuth

The efficiency of the extraction of 100µg. of bismuth into IBMK with APDC when carried out as described in Table 6.4 was established in a manner similar to that described for lead in chapter 3. The absorbance of each of the three successive IBMK extracts were 0.240, 0 and 0, confirming the quantitative extraction of bismuth in one extraction.

The sensitivity for the determination of bismuth in organic solutions was ascertained again noting a five fold increase in signal for the 223.1 nm. resonance line over the longer wavelength (Table 6.1). The increase in sensitivity when the organic solutions were sprayed, over the determination in water, was approximately four fold.

In subsequent analysis by atomic absorption the 223.1 nm. resonance line was used allowing ample sensitivity for the atomic absorption determination of 1 to 100μg.g.$^{-1}$ of bismuth in steels using a 1 g. sample weight.

6.2.3. Interferences

Lau et al (99) have already discussed the co-extraction of many metals with bismuth using APDC including the metals likely to be found in a steel matrix. The authors described the prior complexation of the majority of these interferents with EDTA. In this study the interference of iron (111) upon the extraction detailed in Table 6.4 was ascertained. EDTA already present in the masking agent used to buffer the pH to between 9 and 11, was omitted from the study here, buffering being accomplihsed by adding sodium citrate and ammonia solutions. Because of the difficulty in maintaining a solution of iron (11) at high pH values the experiment was also carried out at pH 4 where solubility of up to 1 g. of iron was maintained by adding 3 g. of sodium citrate. The variation in the absorbance of 80μg. of bismuth extracted into 10 ml. of IBMK in the presence of 0 to 20 ml. of iron (111) solution (0.05 g.ml^{-1}) is shown in Figure 6.1.

The interference of iron at both pH values was serious, as expected, the colour of the organic extracts were green in the presence of iron instead of the usual pale yellow indicating that extraction of some iron had occurred. In another experiment increasing amounts of EDTA were added to the aqueous solutions containing bismuth and iron (111) to ascertain the minimum amount of EDTA necessary to prevent interference by 1 g. of iron.

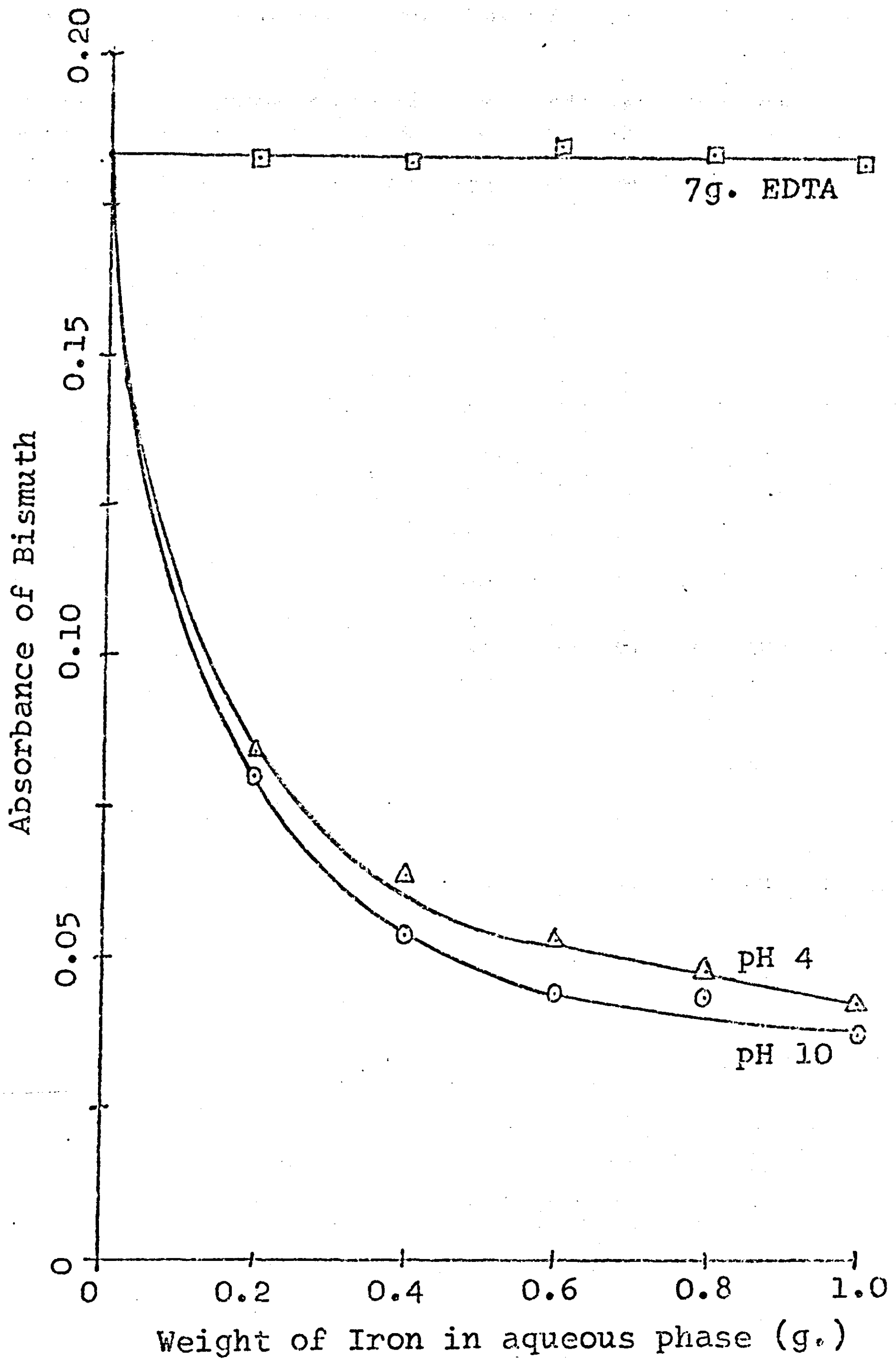


Figure 6.1

The Interference of Iron

The absorbance of Bi was measured at 223.1 nm. under the conditions shown in Table 6.1.

6.2.3.1. The Interference of Iron in the Presence of EDTA

Seven 8.0 ml. aliquots of bismuth solution ($10 \mu g.ml^{-1}$) and 20 ml. aliquots of iron (111) solution ($0.05 g.ml^{-1}$) were transferred to 250 ml. beakers adding 20 to 140 ml. of hot EDTA solution. The pH of the solution was adjusted to 10 by adding concentrated ammonia solution, preventing the precipitation of ferric hydroxide by adding 30%(w/v) sodium citrate from a burrette. The solutions were evaporated to about 40 ml., cooled, the pH readjusted to 10, transferred to 125 ml. separatory funnels, 6 ml. of APDC solution added and the aqueous volume adjusted to 60 ml. before extracting the bismuth into 10.0 ml. of IBMK.

A second series of solutions were prepared in a similar way to that described above, this time adjusting the pH to 4. Unfortunately the insolubility of EDTA in water at this pH restricted the addition of EDTA to less than 2 g. The experiment at the lower pH was discontinued.

The absorbance of the organic phases from the extraction at pH 10 are shown in Table 6.5 and indicate that EDTA additions in excess of 6 g. of the disodium salt are required to prevent interference by 1 g. of iron. 3 g. of sodium citrate were also required to maintain solubility of iron (111). The use of 7 g. of disodium EDTA to prevent the interference of 0 to 1 g. of iron was confirmed in the following experiment.

TABLE 6.5

The Addition of EDTA to the Fe-Bi-APDC Extraction System[a]

Weight of EDTA (disodium salt) added to the aqueous solution (g.)	Volume of 30%(w/v) sodium citrate added to the aqueous solution[b] (ml.)	Absorbance[c]
2	30	0.072
4	20	0.132
6	10	0.180
8	5	0.185
10	2	0.180
12	0	0.178
14	0	0.182

[a] The aqueous phase before extraction contained 1 g. of Fe (as Fe (111)) and 80μg. of Bi.

[b] The amount of sodium citrate added was that found in the experiment to be necessary to prevent precipitation of ferric hydroxide after the addition of EDTA.

[c] The absorbance of the IBMK extracts were measured at 223.1 nm. under the conditions shown in Table 6.1.
The absorbance of 80μg. of Bi extracted into IBMK as described in Table 6.4 was 0.180.

6.2.3.2. The Extraction of Bismuth in the Presence of Iron and EDTA

An aqueous solution was prepared containing 8.0 ml. of bismuth solution (10μg.ml.$^{-1}$) and 10 ml. of 30%(w/v) sodium citrate. Concentrated ammonia solution was added until the solution was alkaline, or hydroxides were precipitated, followed by 70 ml. of hot EDTA solution. The solution was evaporated to about 40 ml., cooled and transferred to a 125 ml. separatory funnel before adjusting the pH to 10. 6 ml. of APDC solution were added and the bismuth was extracted into IBMK as described in Table 6.4.

A further five solutions were treated in the same way this time including 4, 8, 12, 16 and 20 ml. of iron(111) solution (0.05 $g.ml.^{-1}$) in the aqueous solution.

The absorbance of the IBMK extracts in relation to the iron concentration is shown in Figure 6.1, the maximum deviation of 1% from the absorbance obtained in the absence of iron confirmed that interference from iron had been eliminated.

Iron has been shown to interfere with the extraction and subsequent determination of bismuth using APDC by forming an extractable complex with the reagent. Iron also forms a stable complex with EDTA and 7 g. of the disodium salt has been shown to prevent the co-extraction of up to 1 g. of iron. The majority of the other metals present in stainless steel also form complexes with EDTA, their effect upon the extraction of bismuth in the presence of EDTA is discussed in the following section.

6.2.3.3. Interference from Minor Elements

The interference effects of twelve metals present in stainless steels were investigated by preparing solutions containing 8.0 ml. of bismuth solution ($10 \mu g.ml.^{-1}$) and each metal in turn. The solution of the metal was prepared by dissolving the metal or metal compound in a suitable solvent before mixing with the bismuth. 10 ml. each of concentrated nitric and hydrochloric acids were added and the solution was evaporated to ca. 5 ml. before adding 20 ml. of water and 10 ml. of 30%(w/v) sodium citrate. The solutions were then treated as described in section 6.2.3.1 and the organic extracts were sprayed into the flame.

The absorbance of the extracts and the amount of bismuth recovered (Table 6.6) showed little deviation from the calibrant solution for all of the twelve metals except copper. The 11% loss of bismuth in the presence of copper was expected as EDTA has been shown by Lau et al (99) not to mask copper in the extraction of bismuth with APDC. A brown precipitate, formed on adding APDC to the solution containing copper, was soluble in the IBMK, yielding a dark brown solution.

TABLE 6.6

The Interference from Minor Elements

Metal and weight (g.) in the aqueous solution		Metal or metal compound used	Absorbance[c]	Weight of Bi recovered[b] (μg.)
Ni	0.25	Ni	0.179	79
Cr	0.25	Cr	0.180	79
Mn	0.1	Mn	0.181	80
Mo	0.05	MoO_3	0.180	79
V	0.02	NH_4VO_3	0.181	80
Cu	0.005	Cu	0.162	71
Sn	0.005	Sn	0.182	80
Ti	0.01	Ti	0.182	80
W	0.01	W	0.182	80
Al	0.1	Al	0.180	79
Co	0.02	Co	0.182	80
Nb	0.02	Nb_2O_5	0.182	80

[a] The absorbance of the IBMK extracts were measured at 223.1 nm. under the conditions shown in Table 6.1.

[b] The amount of Bi recovered was calculated by relation to the absorbance (0.182) of 80μg. of Bi extracted alone under the conditions shown in Table 6.4.

Numerous methods were tried to prevent the co-extraction of copper including the addition of potassium cyanide found by Lau et al to mask copper. Unfortunately the prevention of interference by 0.005 g. of copper was not complete even when a 50 molar excess of cyanide was present. A precipitation scheme was investigated for the removal of copper as cuprous iodide after the prior reduction of iron(111) to iron(11) with ascorbic acid. This scheme worked well in practice but was found to be tedious, detracting from the simplicity of the analysis procedure so far. With the time of analysis in mind a more suitable method of inhibiting the interference of copper was sought

6.2.3.4. Interference of Copper

The effect of up to 5 mg. of copper (the maximum likely to be found in 1 g. of stainless steel) upon the extraction and determination of 80μg. of bismuth was ascertained in an experiment conducted as described in Table 6.4 in the presence of 0 to 50 ml. aliquots of copper solution (0.5 mg.ml.^{-1}). On examination of the absorbance of the IBMK extracts (Figure 6.2, plot a) the extraction of bismuth was found to decrease inversely with the amount of copper in the aqueous phase before extraction.

Copper was thought to inhibit the extraction of bismuth and not to interfere with the determination by atomic absorption. This was confirmed by repeating the procedure above twice, the first time using the copper solutions alone and the second time on seven 8.0 ml. aliquots of bismuth solution (10$\mu\text{g.ml.}^{-1}$). The IBMK extracts containing only bismuth were mixed together and 5 ml. aliquots were mixed with 5 ml. of each of the seven extracts containing copper. The solutions were

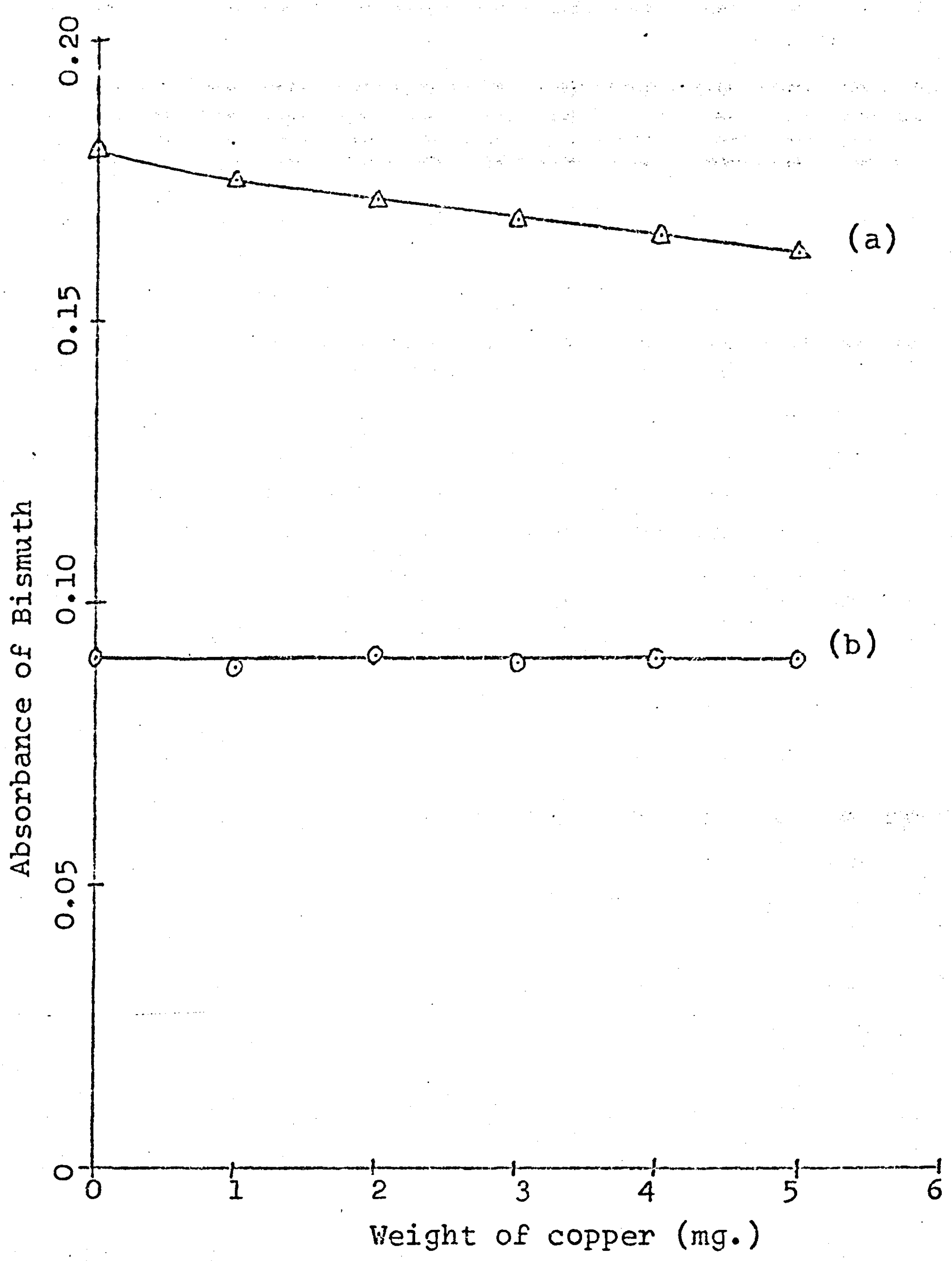


Figure 6.2

The Interference of Copper

The absorbance of Bi was measured at 223.1 nm. under the conditions described in Table 6.1.

(a) The interference of Cu upon the extraction and determination of Bi.

(b) The interference of Cu upon the determination of Bi.

sprayed into the flame and the variation in the absorbance of bismuth with increasing copper concentration is shown in Figure 6.2, plot b. As the deviation in the absorbance represented in plot b. of Figure 6.2 was minimal the presence of copper in the organic phases did not interfere with the determination of bismuth. Interference by copper was, therefore, with the extraction of bismuth by APDC. The amount of copper extracted into IBMK with APDC was the subject of a further investigation involving solution spectrophotometry.

The wavelength of maximum absorption of the copper-APDC complex was ascertained after extracting the copper from 5 ml. of copper solution ($50\mu g.ml.^{-1}$) into 50 ml. of IBMK as described in Table 6.4 for bismuth. The dried IBMK extract was transferred to a 2 cm. silica cell and its absorption measured against IBMK over the range 350 to 700 nm. on the Unicam SP 800 spectrophotometer. Maximum absorption occurred at 430 nm.

A calibration curve was prepared (Figure 6.3) of the absorbance of copper-APDC in IBMK with increasing concentration of copper. 0, 1.0, 2.5, 4.0 and 5.0 ml. of copper solution ($50\mu g.ml.^{-1}$) were transferred to five 125 ml. separatory funnels adding 10 ml. each of masking agent and APDC solution before diluting to 60 ml. with water. Each solution was shaken for 45 secs. with four successive 10 ml. aliquots of IBMK allowing ample time for complete phase separation before transferring the four organic extracts to a 50 ml. graduated flask for dilution to the mark with IBMK. A portion of each mixed extract was placed in a 2 cm. silica cell and its absorbance measured, at 430 nm., on the Unicam SP 500 spectrophotometer, against IBMK.

The amount of copper transferred to the IBMK phase was determined by extracting the copper from 0.5 to 10.0 ml. aliquots of copper solution (0.5 mg.ml^{-1}) into 10.0 ml. of IBMK as described for bismuth in Table 6.4. Suitable aliquots of the IBMK extracts were taken (Table 6.7), diluted with IBMK, transferred to 2 cm. silica cells and the absorbance at 430 nm. measured on the Unicam SP 500 spectrophotometer.

TABLE 6.7

The Extraction of Cu-APDC

Weight of Cu in aqueous Solution before extraction (mg.)	Aliquot of IBMK extract taken (ml.)	For dilution with IBMK to (ml.)	Absorbance at 430 nm.	Amount of Cu extracted (μg.)
0.25	5	100	0.196	126
0.5	2.5	100	0.164	206
1.0	2.5 ml. taken and diluted to 50 ml. with IBMK. 10 ml. of this solution was diluted to 50 ml. with IBMK.		0.105	333
2.0			0.095	300
3.5			0.102	322
5.0			0.098	314

The maximum amount of copper extracted into IBMK with APDC, calculated by relating the absorbance of the IBMK extracts to Figure 6.3, was 320μg. when 1 mg. and over of copper was originally present in the aqueous solution (Table 6.7).

Copper has been shown to co-extract with bismuth into IBMK with 320μg. marking either the maximum extraction of copper into IBMK or the maximum amount of copper complexed by the amount of APDC present (15 x 10^{-5} moles). The former was thought to be the case as the aqueous solution usually contained some precipitate of the copper complex. Furthermore, under these

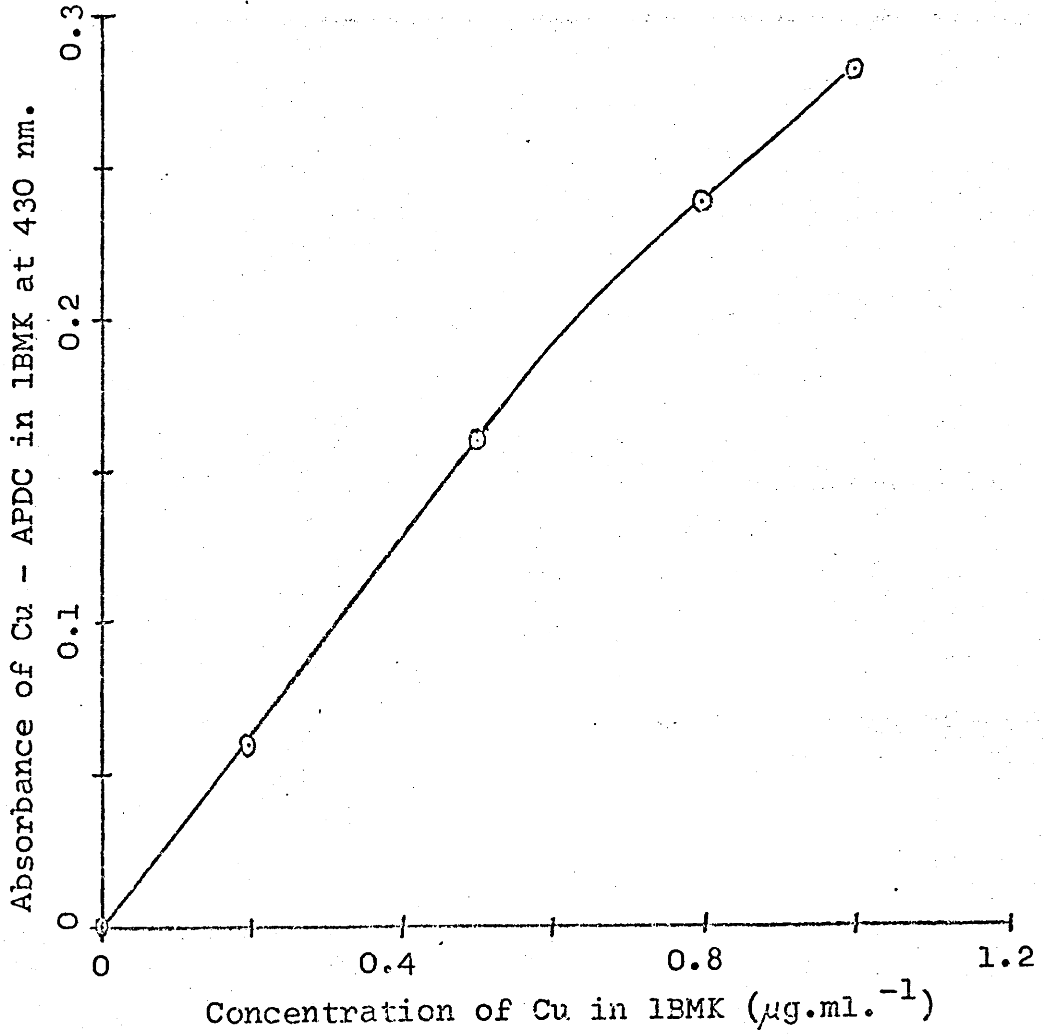


Figure 6.3

Calibration Curve for the Determination of Copper by Solution Spectrophotometry extraction conditions copper is extracted in preference to bismuth principally because of its large excess over bismuth. Using a 6 ml. aliquot of APDC solution, for a copper complex of the type Cu $(C_4H_8\ NCS_2)_2$ then the 15 x 10^{-5} moles of APDC will react with only 0.0048 g. of copper, i.e. there is not enough APDC to react with bismuth in the solutions containing appreciable amounts of copper. The effect of increasing the APDC concentration in the extraction medium was therefore investigated.

A series of solutions was prepared containing 8.0 ml. of bismuth solution ($10 \mu g.ml.^{-1}$), 10 ml. of copper solution ($0.5\ mg.ml.^{-1}$), 10 ml. of masking agent and 0 to 16 ml. of APDC solution. The bismuth was extracted into IBMK as described in Table 6.4.

On spraying the dried organic extracts into the flame the maximum absorbance of bismuth (Table 6.8) in the presence of the maximum amount of copper likely to be found in stainless steels occurred when over 8 ml. of APDC solution were present. The absorbance of the extracts from solutions containing copper and APDC solution in excess of 8 ml. equalled that of bismuth extracted in the absence of copper. In subsequent extractions of bismuth 10 ml. of APDC solution were added to the aqueous phase to provide a sufficient excess of the reagent to react with all the copper and all the bismuth present. In this way interference from copper was deemed to have been resolved.

TABLE 6.8

Optimum Concentration of APDC[a]

Volume of APDC solution (ml.)	Concentration of APDC ($\times 10^{-5}$ moles)	Absorbance[b]
2	5	0.025
4	10	0.051
6	15	0.101
8	20	0.179
10	25	0.181
12	30	0.180
14	35	0.183
16	40	0.179

[a] The aqueous phases contained 50 mg. of Cu and 80μg. of Bi before the extraction.

[b] The absorbance of 80μg. of Bi after extraction into IBMK using 6 ml. of APDC solution was 0.182.

The absorbance of the IBMK extracts were measured at 223.1 nm. under the conditions shown in Table 6.1.

This section has described the determination by atomic absorption of up to 10μg.ml.$^{-1}$ of bismuth after extraction with APDC. The interference of twelve metals found in steels with bismuth was investigated and resolved for all except copper by adding sufficient EDTA to complex the interferents. The interference of copper was prevented by increasing the amount of APDC present in the extraction medium such that there was ample excess of the reagent over both copper and bismuth.

At this stage the extraction procedure was considered sufficiently sensitive and specific to allow an analysis procedure to be recommended for the determination of bismuth in stainless steels.

6.3. Recommended Procedures

6.3.1. Analysis of Stainless Steels

Dissolve 1.0 g. of the steel in 20 ml. of concentrated hydrochloric acid and 10 ml. of concentrated nitric acid. Evaporate the solution to approximately 5 ml. and add 20 ml. of water and 10 ml. of 30%(w/v) sodium citrate. Add concentrated ammonia solution until the solution is alkaline or precipitation occurs, then add 70 ml. of hot EDTA solution and evaporate the solution to about 30 ml. Transfer to a 125 ml. separatory funnel, add 10 ml. of masking agent and 10 ml. of APDC solution, dilute to 60 ml. with water and add 10.0 ml. of IBMK. Shake the solution for 2 min. and allow the layers to separate. Discard the lower aqueous phase and filter the IBMK phase through a Whatman 540 filter paper containing 1 g. of anhydrous sodium sulphate, collecting the solution in a stoppered polythene bottle. Spray the solution into the flame, measure the absorbance of bismuth with the instrumental settings as described in Table 6.1, and read off the bismuth content from the calibration graph.

6.3.2. Preparation of Calibration Graph

Transfer 0, 2.0, 4.0, 6.0, 8.0 and 10.0 ml. of bismuth solution ($10\mu g.ml^{-1}$) into 125 ml. separatory funnels, add 10 ml. of masking agent and 10 ml. of APDC solution to each. Dilute to 60 ml. and continue as described above.

6.4. Atomic Fluorescence

The atomic fluorescence spectrophotometry of bismuth was studied using a modified Jarrell-Ash Spectrometer and a bismuth EDL. The spectrometer may be used to detect and measure atomic fluorescence under two modes of operation, i.e. where the source light is modulated at 50 Hz., in tune with the amplifier, and where the light is continuous, i.e. an unmodulated source.

The microwave power required for the maximum intensity of light from the bismuth EDL at a given wavelength was dependent upon whether the EDL was operated in the modulated or unmodulated mode. The optimum power was ascertained by placing the EDL about 6 cm. from the entrance slit of the monochromator and measuring the emission at 306.8 nm. at various microwave powers (Figure 6.4). The optimum were 55 w. (unmodulated) and 40 w. (modulated). An explanation for this difference in the optimum power requirements has been presented by Dagnall et al(103)

The Jarrell-Ash Spectrometer was designed primarily for atomic absorption and emission analysis. It is, however, very easily adaptable for the study of fluorescence, allowing maximum freedom in the selection of sites for the installation of the optical equipment etc. In this study fluorescence was measured with the burner situated in two positions. In the first the burner was fixed in the position normally chosen in atomic absorption where the fluorescence achieved was some 30% lower than when the burner was sited as near as possible (5 cm.) to the entrance slit. In this position light focusing was not possible. This position was used in all the determinations by atomic fluorescence described in this chapter.

The EDL was placed at 90° to the optical axis of the spectrometer and as near as possible to the flame. An

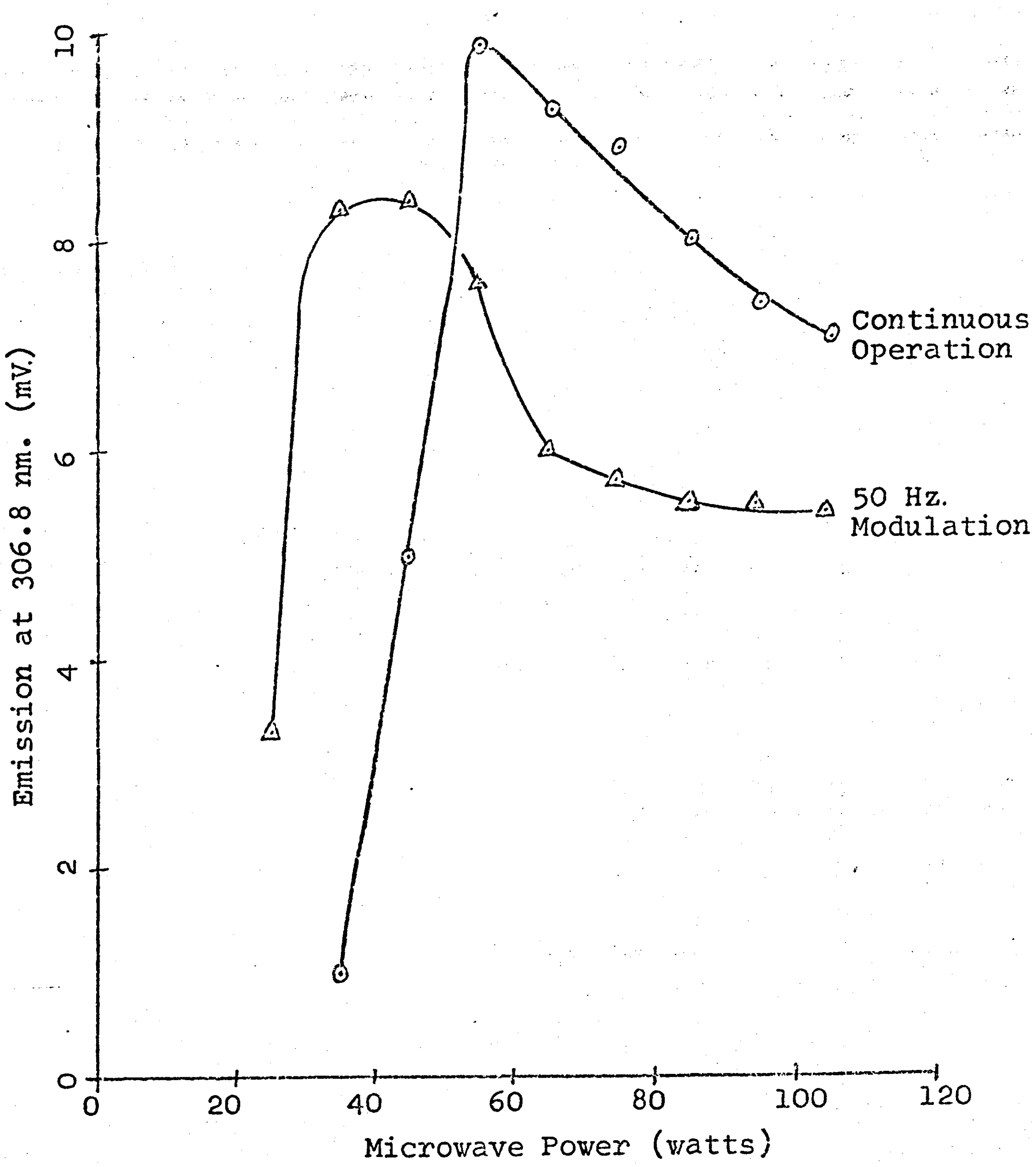


Figure 6.4

Emission Growth Curves for a Bismuth Electrodeless Discharge Lamp asbestos shield was placed between the EDL, the flame and the monochromator slits, which effectively prevented stray light from reaching the monochromator. Experiments were conducted whereby mirrors or lenses were strategically placed -

(a) behind the flame to repass the source light through the flame,

(b) behind the flame to allow more fluorescence to reach the monochromator, and

(c) between the EDL and the flame.

A satisfactory improvement in fluorescence was not achieved by the use of lenses or mirrors in any of the positions.

Three flames were used in this study; hydrogen diffusion, argon-hydrogen and argon-oxygen-hydrogen; each being supported on the Hetco total consumption burner. The flames were selected because of their low flame background (104) and their low quenching characteristics (104,105). Of the three flames argon-hydrogen gave the lowest flame background. Nitrogen was also used as a replacement for argon in this flame but the greater quenching of this diatomic gas decreased the fluorescence by about 10%.

6.4.1. Preliminary Study

The initial atomic fluorescence studies of bismuth were carried out to ascertain the optimum instrumental conditions for the determination in aqueous solutions. These conditions (Table 6.9) were measured in the unmodulated mode at 306.8 nm. for both the hydrogen diffusion and argon-hydrogen flames in a manner similar to that described previously in the atomic absorption determination of lead (chapter 3). The flow rates of hydrogen and argon in the two flames respectively were not varied as they controlled the rate of uptake of the solution. In the latter flame the hydrogen flow rate had very little effect upon the fluorescence signal and was therefore kept to a minimum to minimise the flame background.

TABLE 6.9

Optimum Instrumental Parameters - Atomic Fluorescence

Parameter		Flame		
		H_2	$A-H_2$	$A-H_2-O_2$
EDL power[a]	watt	55	55	55
Slit: entrance	mm.	0.1	0.1	0.1
exit	mm.	0.15	0.15	0.15
Burner height	cm.	6.4	6.9	6.5
Argon pressure	p.s.i.	-	20	20
Argon flow rate	$l.min.^{-1}$	-	8	8
Hydrogen pressure	p.s.i.	10	10	10
Hydrogen flow rate	$l.min.^{-1}$	2	2	2
Oxygen pressure	p.s.i.	-	-	10
Oxygen flow rate	$ml.min.^{-1}$	-	-	500

[a] The EDL was operated in the continuous (unmodulated) mode.

The unmodulated mode of operation was selected for this investigation as maximum fluorescence occurred in this mode and the EDL was much more stable. The EDL under modulation was particularly susceptible to draughts although a shield designed in this laboratory by Hubbard and Michel (106) was helpful in its relief.

6.4.2. Detection Limits

The detection limits for the determination of bismuth in aqueous solution by atomic fluorescence were ascertained in the argon-hydrogen and diffusion flames at a number of wavelengths (Table 6.10). The equipment was operated under the conditions shown in Table 6.9.

TABLE 6.10

Detection Limits

Wavelength (nm.)	Flame[b]:-	Detection Limit[a] (μg.ml.$^{-1}$) H_2	A-H_2	A-H_2-O_2
306.8		0.78	0.03	0.01
302.5		14.3	1.75	
269.7		[c]	18.8	
223.1		13.6	6.80	
206.2		25.0	5.55	

[a] The detection limits are quoted for S:N = 1.

[b] The detection limits quoted in the H_2 and A-H_2 flames were obtained for Bi in aqueous solution whilst that in the A-H_2-O_2 flame was obtained after the extraction of Bi into IBMK.

[c] A detection limit for Bi was not obtained at this wavelength.

In these studies, designed to achieve the maximum fluorescence signal and the minimum noise, it became apparent that in the argon-hydrogen flame the biggest contribution to the background emission came from the photomultiplier tube (HTV, type R 106). Using this flame the background emission at a hydrogen flow rate of 8 l.min.$^{-1}$ was much less than the dark current emission of the tube operated at high voltages. Furthermore the zero control circuitry of the Jarrell-Ash amplifier was incapable of 'backing off' this emission resulting in the use of a much lower photomultiplier tube voltage thereby achieving higher detection limits. The problem was resolved by incorporating a 10 kΩ. variable resistance in series with the potentiometer used for 'zero control' in the amplifier. Using this resistance the emission could be 'backed-off' so that the improved fluorescence measured at the high photomultiplier tube voltages could be facilitated.

The best detection limit attained, i.e. at 306.8 nm. (Table 6.10) was a little better than that quoted by West et al (97) in the same flame at 302.5 nm. using an iodine EDL.

6.4.3. The Determination of Bismuth in Organic Solution

The optimum instrumental conditions for the determination of bismuth in IBMK were established after the extraction of 50μg. of bismuth with APDC as described in Table 6.4. These conditions, shown in Table 6.9 for the argon-hydrogen flame were used to assess the effect of allowing oxygen into the system to assist in the combustion of the organic solvent. In the study the oxygen was premixed with the argon before introduction into the Hetco burner. The flow of argon was initially set at 8.5 $1.min^{-1}$ when the rate of uptake of solution was 2.5 $ml.min^{-1}$. This uptake rate was maintained when the oxygen was introduced by reducing the flow of argon. The experiment was conducted at hydrogen flow rates of 2, 2.5 and 3 $1.min^{-1}$.

In general the background emission from the flame increased in proportion with the flow of oxygen into the flame. The maximum enhancement of signal (Figure 6.5) occurred with an oxygen flow rate of 500 $ml.min^{-1}$ and a hydrogen flow rate of 2 $1.min^{-1}$. Under these conditions the flame background was also minimal.

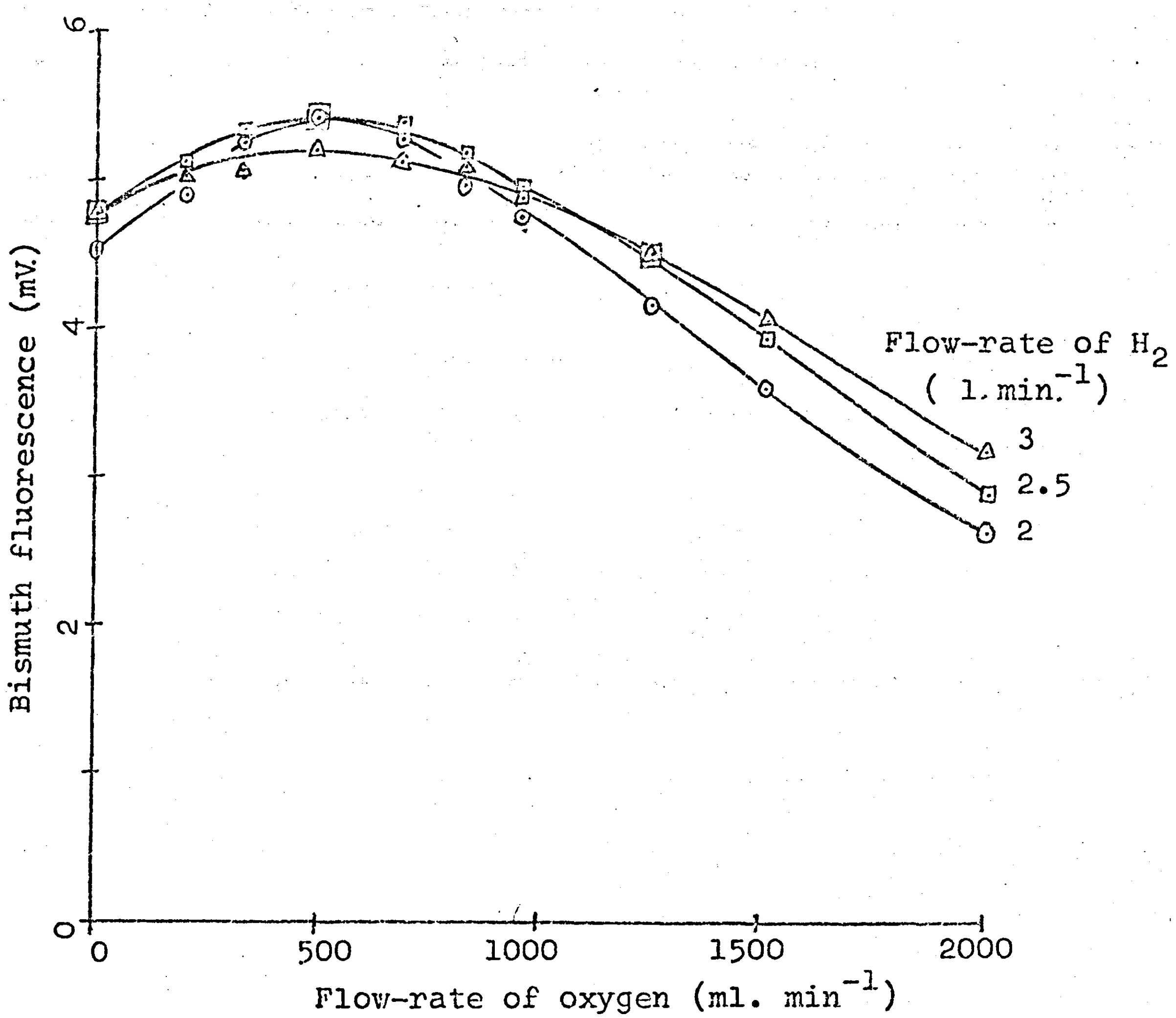


Figure 6.5

The Addition of Oxygen to the Argon-Hydrogen Flame

The fluorescence of 5µg.ml.$^{-1}$ of Bismuth in IBMK was measured under the conditions shown in Table 6.9.

Sensitivity data for the determination of bismuth in IBMK by atomic fluorescence is shown in Table 6.10 and when compared with that for aqueous solution a three fold decrease in the limit of detection is apparent. A comparison of the detection limits of the two techniques, atomic absorption and fluorescence, shows that the latter is six times more sensitive than the former for bismuth in organic solutions.

6.4.3.1. Interference Study

The determination of bismuth by atomic fluorescence has been shown to offer ample sensitivity for the determination of bismuth in steels, possibly in amounts less than those specified in the atomic absorption investigation.

The non-interference by the matrix elements in steels was ascertained by repeating the experiment described in section 6.2.3.3, measuring the fluorescence of the IBMK extracts after including 10 ml. of APDC solution in the extraction medium instead of the 6 ml. originally used. The fluorescence of the twelve IBMK extracts differed by less than 4% from that where bismuth alone was extracted, indicating that the recommended procedures outlined in section 6.3 were readily adaptable for the atomic fluorescence determinations of bismuth in steels.

6.5. Calibration and Analysis of Alloys

Calibration of both the atomic absorption and fluorescence procedures was carried out as recommended in section 6.3.2. The plots were both linear between 0 to 100 $\mu g.g^{-1}$ of bismuth in steel (Figure 6.6).

An experiment designed to test the recovery of bismuth added to steels and to compare the precision of the determinations by atomic absorption and fluorescence was conducted

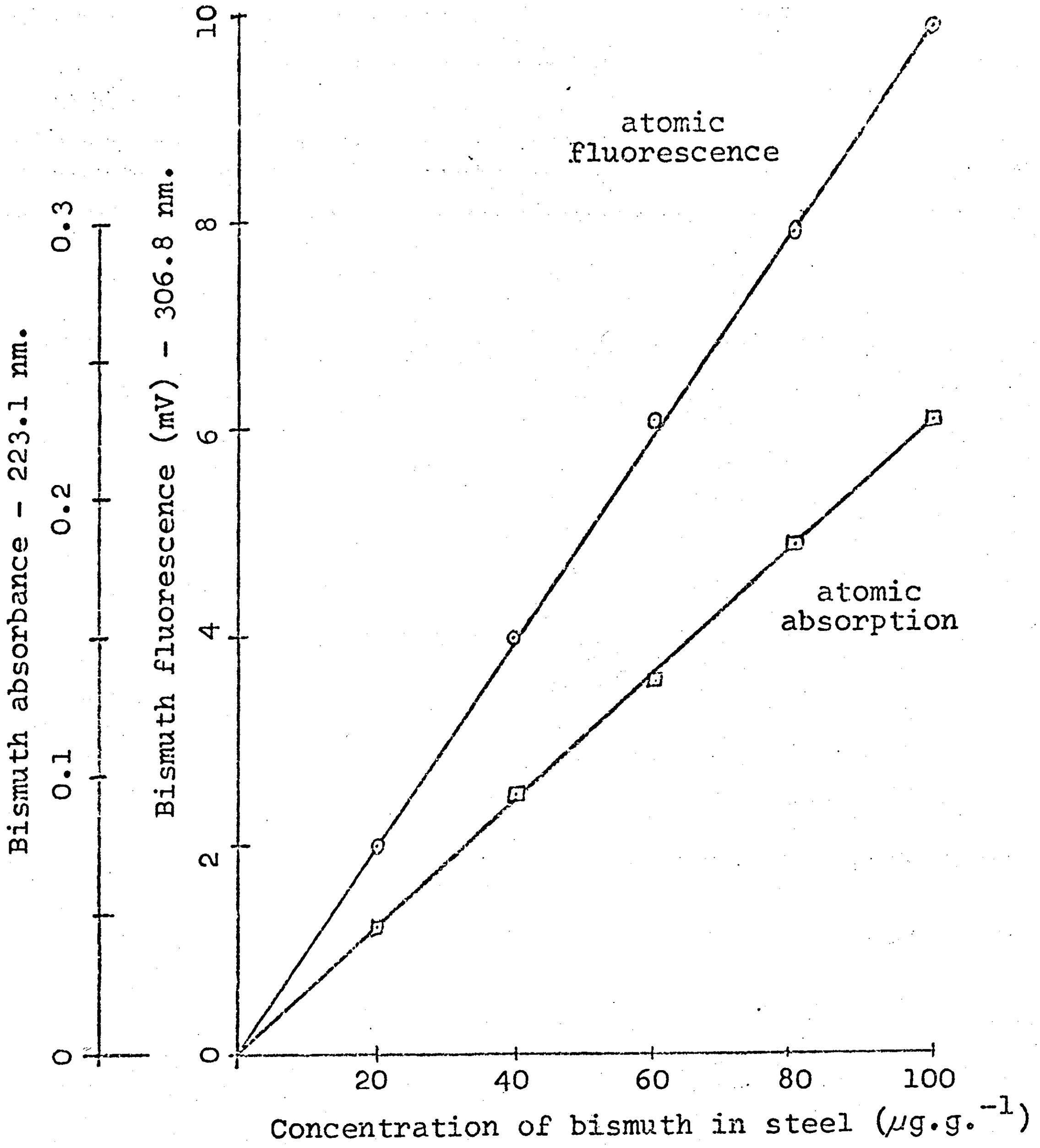


Figure 6.6

Calibration Graphs for Bismuth by Atomic Absorption and Fluorescence

The absorbance and fluorescence of Bi were measured as described in Tables 6.1 and 6.9 respectively.

after adding 0 to 30μg. of bismuth to seven stainless steels known not to contain bismuth. The amount of bismuth recovered (Table 6.11) was ascertained by relation of the fluorescence or absorbance of bismuth to Figure 6.6.

TABLE 6.11

Recovery of Bismuth Added to Steels

Composition of Steel, % of element					Amount of bismuth added (μg.)	Amount of bismuth recovered (μg.)	
Ni	Cr	Mo	Cu	Mn		a.a.s.	a.f.s.
12	17	2	0.15	1.5	30	31	31
-	1	-	0.10	0.5	10	9	11
10	18	0.5	0.25	1	5	5	5
-	1	-	0.20	1	30	30	31
10	18	1	0.30	1	10	9	10
10	18	1	0.20	1	5	5	5
10	18	1	0.20	1	10	9	10

The standard deviation of the errors of the two techniques for the seven alloys was 0.82 and 0.71μg. of bismuth for atomic absorption and fluorescence respectively indicating virtual equality in the precision of the techniques.

Four stainless steel alloys of known bismuth content were analysed twice by each technique (Table 6.12). The analysis compared very favourably with the average analysis quoted by British Steel Corporation, who used a variety of techniques which included square-wave polarography and solution spectrophotometry after extraction of the bismuth with dithizone and iodide.

TABLE 6.12

The Determination of Bismuth in Steels

Alloy No.	Bismuth Content	Analysis by proposed methods ($\mu g.g.^{-1}$)	
		a.a.s.	a.f.s.
1	1	1, 1	15, 1.5
2	50	51, 51	50, 51
3	68	70, 70	68, 70
4	105	107, 106	104, 106

6.6. Conclusion

A solvent extraction system for bismuth has been adapted so that the metal can be determined in stainless steel within the concentration range 1 to 100$\mu g.g.^{-1}$ by either atomic absorption or atomic fluorescence spectrophotometry.

The system based upon APDC is shown to increase the atomic absorption sensitivity four fold over water and when the bismuth is extracted in the presence of EDTA the system is specific for bismuth and copper. None of the other metals commonly found in steels have been shown to cause interference with the extraction and determination by atomic absorption. The problems associated with copper were the subject of an investigation in which it was established that up to 320μg. of copper were extracted with the reagent into IBMK. This amount of copper is shown to interfere with the extraction of bismuth and not with the determination. The study also disclosed that the recommended amount of APDC did not complex all the bismuth and all the copper, hence inhibiting the extraction of bismuth by providing competition for extraction. In the presence of a sufficient amount of APDC to complex both copper and bismuth then bismuth is quantitatively extracted even in the presence of a 50 fold excess of copper. Thus the presence of EDTA and a large excess of APDC was sufficient to prevent interference with the extraction and determination of bismuth by atomic absorption. A method was then postulated for the determination of trace amounts of bismuth in steels.

Of the two flames studied in the determination of bismuth in aqueous solution by atomic fluorescence the argon-hydrogen flame was found to impart the better detection limit, a value far superior to that in atomic absorption. In the determination in organic solutions a six fold decrease in detection limit over similar atomic absorption studies was achieved by bleeding oxygen into the argon-hydrogen flame.

No interference from twelve metals present in steel with bismuth was encountered upon its determination in organic solution by atomic fluorescence and hence the recommended analysis procedures were found to be equally viable for both atomic fluorescence and absorption.

In a comparison of the analysis of four alloys by the two techniques virtually equal precision was found at the levels of bismuth studied. However the determination by atomic fluorescence was carried out under conditions not optimum for the best sensitivity. Under optimum conditions it should be possible to determine bismuth in steels down to 0.1μg.g.$^{-1}$.

Finally the method offers an alternative procedure for the determination of bismuth in steels of at least equal merit to those being investigated by the BISRA committee. The method describes has the additional advantage in that it is not as lengthy since it does not require any preliminary removal of iron.

CHAPTER SEVEN

AN INVESTIGATION INTO LOCK-IN AMPLIFICIATION IN ATOMIC SPECTROSCOPY

7.1. Introduction

The problem of detecting and measuring a very small signal in the midst of a sea of noise has for a long time worried scientists and may be likened to the proverbial search for 'a needle in a haystack'. The greatest contribution to this noise in atomic spectroscopy has come from the flame. Since the flame noise increases with flame temperature then the choice of flame used in the flame technique plays a large part in establishing the lower limit at which a metal can be detected and measured.

The position is most acute in atomic emission as relatively high flame temperatures are required in the initial excitation process. In atomic absorption and fluorescence the intensity of absorption or fluorescence is not governed by the flame provided it is hot enough to allow ground state atoms to form. Thus, in atomic fluorescence, the flame background signal can be minimised by using very cool flames, e.g. argon-hydrogen, and by use of modulation. Indeed this thesis has shown that the detection limit for the fluorescence of bismuth in the argon-hydrogen flame is governed by random emissions from the photomultiplier tube cathode rather than from the flame (section 6.4.2).

Modulation is useful in minimising the effect of the flame background on atomic absorption and fluorescence. In flame spectroscopy the measurement equipment usually utilises alternating current (ac.) amplification such that the direct current (dc.) emission from flames is not measured. Thus, without some form of modulation atomic emission cannot be measured. In atomic emission modulation is usually achieved by placing a mechanical 'chopper' between the flame and the detector so that the dc. signal from the flame is pulsed. In this form the emission signal from both the flame and metal is measured.

In atomic fluorescence and absorption the light from the source is pulsed rather than the light from the flame allowing only the absorption and fluorescence signals to be measured. This subject is dealt with more fully by Ramirez-Munoz (13).

The frequency of modulation in atomic absorption is usually low, 50-400 Hz, but in atomic fluorescence more successful modulation has been achieved at 20 kHz (103). The application of modulation to hollow cathode lamps is usually achieved by leaking alternating current through the rectification equipment feeding the lamp or by pulsing of the current to the lamp.

Modulation of EDLs is achieved in numerous ways (e.g. 103,107,108). In the modulation equipment used in the studies detailed in the last two chapters of this thesis modulation of the microwave power supplied to the EDLs was achieved by transformer coupling a 12v. ac. waveform to the dc. of the magnetron circuit (108). The use of a transformer, however, restricts the modulation to a low frequency sinnsoidal waveform, in the case of the studies described in chapters 6 and 7 the frequency was 50 Hz.

Until recently the problems associated in obtaining very low limits of detection for metals by atomic fluorescence in the presence of a large noise component have appeared insurmountable in instruments which are normally equipped with ac. amplifiers as the increase in signal intensity after amplification is always accompanied by an equal increase in noise.

With the advent of 'lock-in' amplifiers all this has changed for, at a price, it is possible to obtain limits of detection far superior to those obtained using a conventional ac. amplifier. A lock-in amplifier is basically an instrument for the measurement of the amplitude of ac. signals in the presence of noise and consists of a high gain ac. amplifier followed by a synchronous detector and low pass filter. The secret of the lock-in amplifier is the synchronous detector.

A detector rectifies the ac. output of the amplifier to dc., enabling the signal to be measured on a meter or recorder. In a normal ac. amplifier detection is asynchronous, that is to say an ac. signal of any frequency would be converted to dc. without discrimination. In such amplifiers the output signal would consist of a signal, whose voltage is to be measured, superimposed upon a signal resulting from rectification of the noise. A synchronous detector or lock-in detector is a reference operated device in which a signal is only rectified if it is synchronised to the waveform of a reference source.

Thus a lock-in amplifier will only measure an ac. signal in phase with a reference source. Any noise which is not in phase with the reference signal will be rejected and not measured. The major component of noise in atomic fluorescence is of this type, i.e. flame noise. However any noise in phase with the reference signal, e.g. source intensity fluctuations, will be detected and measured. This type of noise, including low frequency, mains-borne noise, can be eliminated by incorporating some type of filter into the circuitry. The use of lock-in amplifiers allows the use of relatively high modulation frequencies which avoids the low frequency noise associated with normal amplifiers tuned to around 50 Hz.

This picture represents an idealised lock-in system as elimination of noise is never complete. The noise which is measured, however, appears as an ac. ripple superimposed upon the dc. output signal and as such does not constitute a background signal which needs 'backing off' before measurements can be taken. This is the case in a normal ac. amplifier.

In atomic fluorescence spectroscopy utilising microwave powered EDLs the reference signal is usually derived from the signal generator used to apply modulation to the EDL. In this way it is assured that both reference and source are in phase. Numerous papers have been published recently using lock-in amplifiers in both atomic fluorescence (e.g. 35,109) and absorption (e.g. 110,111) in a variety of aspects.

The high cost of good quality lock-in amplifiers compared with the conventional type has prohibited the general use of such systems in many laboratories although some commercially available atomic spectrometers do incorporate some form of lock-in amplifier.

Caplan and Stern (112) have described the construction of an inexpensive lock-in amplifier whose performance is claimed to surpass that of many commercial products. An amplifier of similar design to that of Caplan and Stern was constructed and its use is described here in terms of a comparison with a normal ac. amplifier in both atomic absorption and fluorescence.

Argon and nitrogen separation of flames has been shown to lower the detection limits for many metals in both atomic absorption and fluorescence (96,113,114) especially when the measurements are being taken at wavelengths where there is high emission or absorption by the flame. The effects of argon separation on the air-acetylene flame in atomic fluorescence are also discussed in this chapter with particular reference to its use with both types of amplificiation systems.

The detection limits achieved by other workers for lead, silver and bismuth in atomic fluorescence in air-acetylene flames using conventional amplifiers are shown in Table 7.1. The use of separation has decreased the detection limit by between four and ten fold, the decrease being similar whether the source is modulated or run continuously.

The aims of the work described in this chapter are to justify the use of a lock-in amplification system in both atomic absorption and fluorescence, whilst at the same time investigating the need for flame separation in lock-in-systems.

TABLE 7.1

Detection Limits in Atomic Fluorescence

Metal	Wavelength (nm.)	Detection Limit (μg.ml^{-1})		S:N Ratio	Reference	Comments[a]
		Modulated	Continuous			
Bi	306.8	0.3/0.7[b]	0.04/0.5	1:1	96	Air-C_2H_2
	223.1	0.6/2.5	0.2/2			Either U or
	302.5	0.1/0.15	0.3/1.5			argon-S
Bi	306.8	55/220	-	2:1	113	Air-C_2H_2
Ag	328.1	0.02/0.08	-			Either U o
Pb	283.3	3/6	-			argon-S
	405.7	1/2.3	-			
Bi	206.2	0.4	2.0	2:1	115	U
	302.5	1.0	-			Air-C_2H_2
Pb	405.8	0.20	-	2:1	116	Air-C_2H_2
	283.3	0.15	-			Nitrogen S
	217.0	0.12	-			

---

[a] U = Unseparated, conventional flame.

S = Separated flame, using either argon or nitrogen.

[b] These values refer to the detection limit achieved in the separated/unseparated flames.

7.2. Experimental

7.2.1. Apparatus

A Jarrell-Ash 82-529 Spectrometer was used as the basic instrument for both atomic absorption and fluorescence. This instrument is equipped with a 0.5 metre Ebert Monochromator, a HTV type R106 Photomultiplier tube and a wide band ac. amplifier tuned to respond to the 50 Hz modulation applied to the hollow cathode lamps used in atomic absorption studies.

In atomic absorption nebulization and air-acetylene flame support equipment was supplied by Pye-Unicam. Both the normal and argon separated flames in the atomic fluorescence investigation were supported on the Beckman-R.I.I.C. atomic emission burner whilst the Unicam atomizer and cloud chamber were used for solution nebulization. The support gases were all supplied by Air-Products Ltd.

The EDLs for bismuth and lead were supplied by E.M.I. Ltd. whilst the silver EDL was prepared in the laboratory in a method similar to that described by Zacha et al (46). The EDLs were powered at 2450 MHz. using a Microtron 200, Mk.II microwave generator with associated stabilizer and modulator for 50 Hz. A $\frac{1}{4}$ wave cavity (type 214L) was used as microwave coupler to the EDL. These units were supplied by Electromedical Supplies Ltd.

The lock-in amplifier was built in the laboratory to the specifications described by Caplan et al (112), a 'block' circuit diagram of which is shown in Figure 7.1.

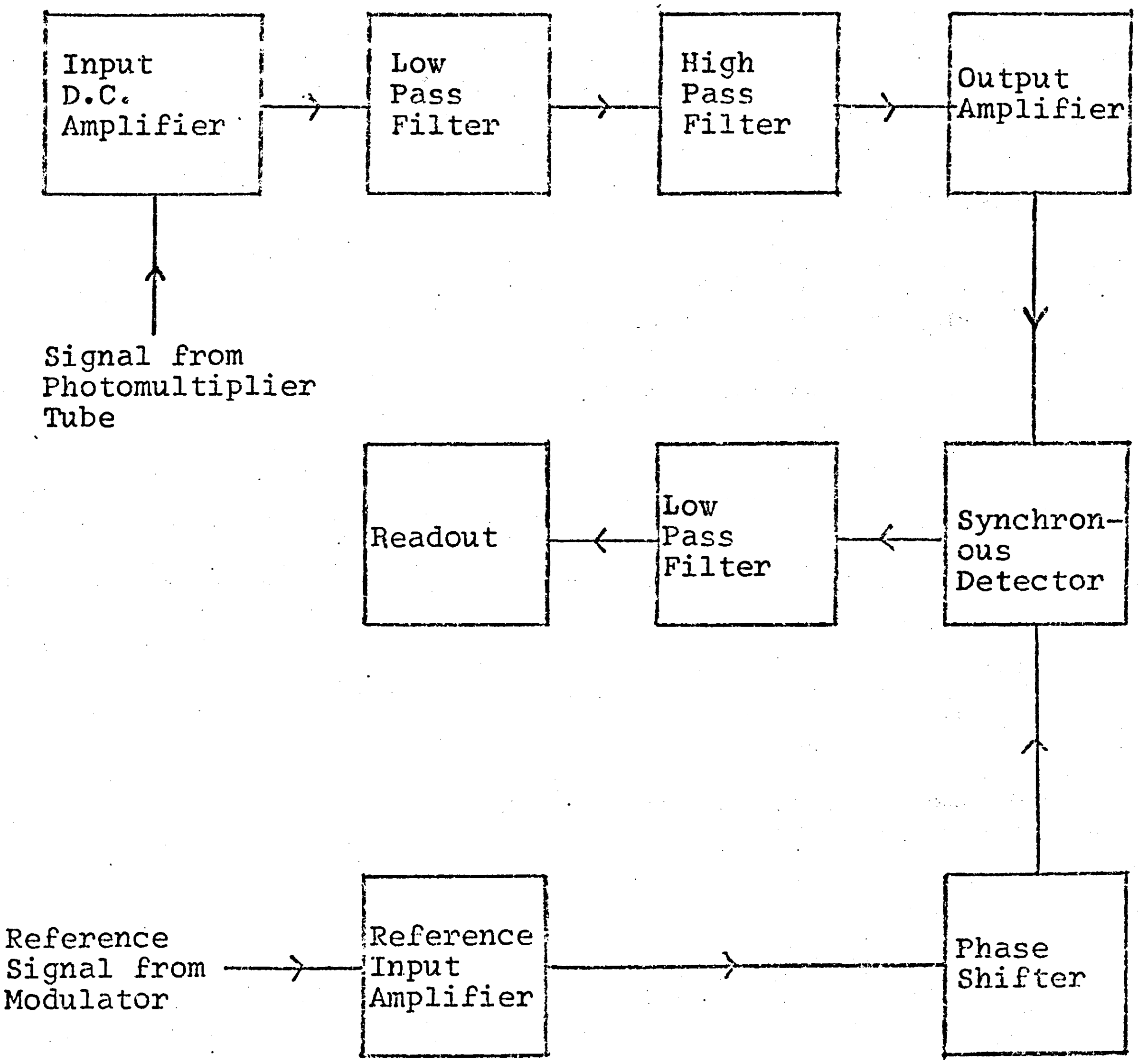


Figure 7.1

The Lock-In Amplifier

7.2.2. Atomic Absorption

The detection limits for the determination of lead, silver and bismuth in aqueous solution by atomic absorption were measured in the conventional air-acetylene flame. The Jarrell-Ash Spectrometer was operated in the mode normally selected for atomic absorption with hollow cathode lamps being used as light sources for the metals.

The detection limits achieved for the metals were comparable to those quoted elsewhere (46) when measured using the conventional asynchronous amplification equipment.

A five fold decrease in the detection limit of each metal was achieved when the signal from the photomultiplier tube was applied to the lock-in amplifier. However extreme difficulty was experienced in both optimising the instrumental parameters for atomic absorption and in establishing the positions of 0 and 100% transmission on the recorder scale. Further experiments with lock-in amplification were abandoned in favour of an investigation into atomic fluorescence.

7.2.3. Atomic Fluorescence

7.2.3.1. Optimisation of Microwave Power

The optimisation of the spectral intensity with microwave power for the lead and silver EDLs was accomplished in a manner identical to that described for bismuth in chapter 6. The emission growth curves (Figure 7.2) for lead and silver at their main resonance lines were compiled when the EDLs were operated both in the continuous (unmodulated) mode and under modulation at 50 Hz.

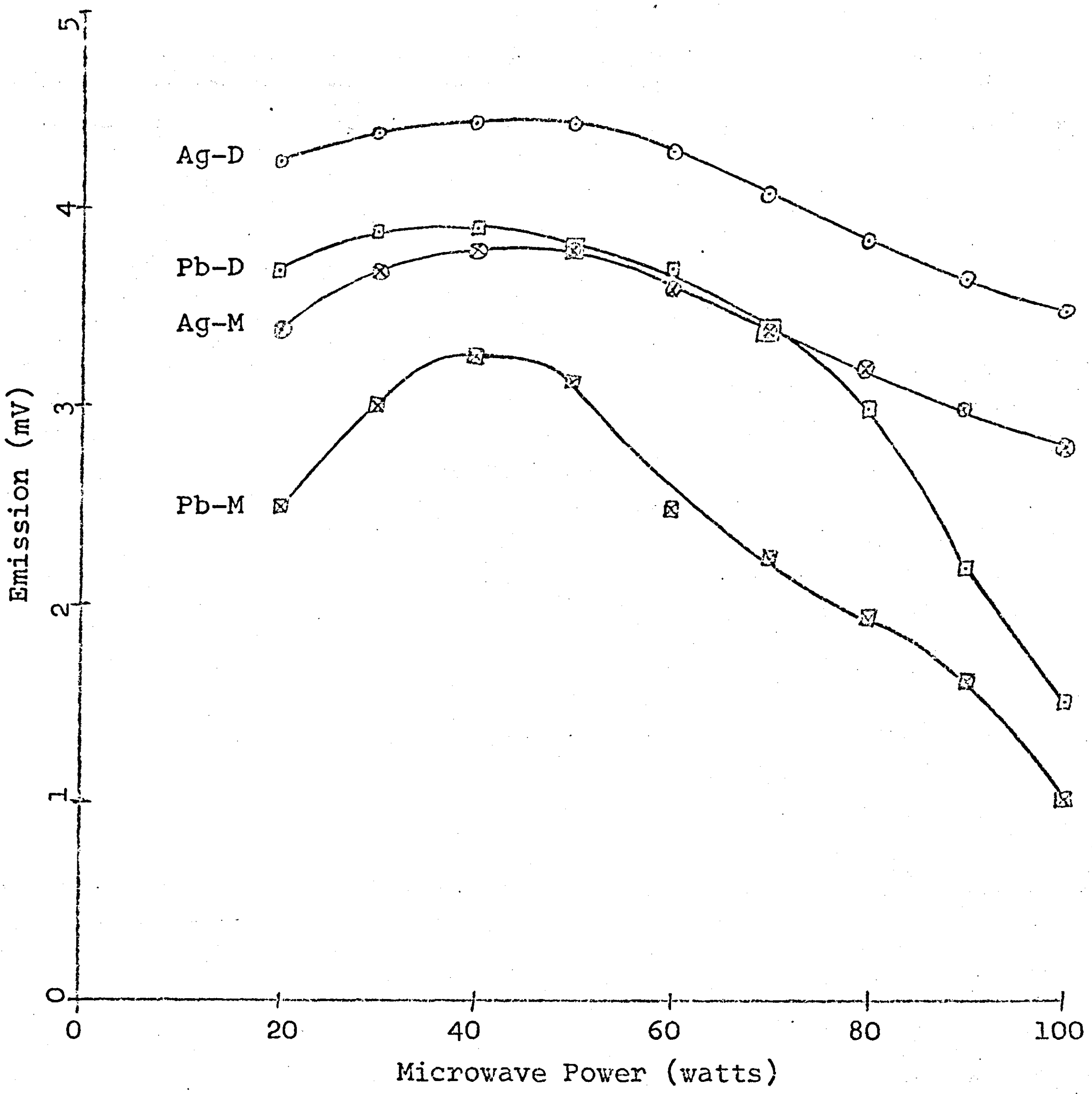


Figure 7.2

Emission Growth Curves for Lead and Silver Electrodeless Discharge Lamps

Legend:-

Ag-D	Silver EDL operated continuously - 328.1 nm.
Ag-M	Silver EDL operated with 50 Hz. modulation - 328.1 n
Pb-D	Lead EDL operated continuously -- 217.0 nm.
Pb-M	Lead EDL operated with 50 Hz modulation - 217.0 nm.

7.2.3.2. Measurement of Fluorescence

The burner was positioned as near as possible to the monochromator entrance slit as this position has already been shown to produce maximum fluorescence for bismuth (chapter 6). As flame separation was to be used in this study then the EDL was moved away from the flame making the use of a lens (focal length: 5 cm.) necessary to focus the source light onto the centre of the flame. An asbestos baffle was carefully arranged to prevent stray light from the EDL reaching the monochromator slit. In common with the previous study a mirror placed behind the flame to increase the fluorescence reaching the monochromator was not effective using the Jarrell-Ash amplifier as the background radiation increased proportionately.

7.2.3.3. Influence of Burner Height

The influence of the position of the optical light path through the flame on the fluorescence of bismuth, the scatter of source light and the flame background was ascertained.

The photomultiplier tube voltage was set at 600 while water and a solution of 200μg.ml^{-1} of bismuth were sprayed alternately into the normal air-acetylene flame, measuring the signal at various burner heights.

The fluorescence observed from bismuth and the flame background when water was being sprayed were measured and the true fluorescence was calculated by subtraction of the background emission from the observed fluorescence. The variation in both the true fluorescence and the background emission with burner height is shown in Figure 7.3, plots a and b respectively. As these measurements were collected whilst the EDL was in operation the background emission, therefore, included

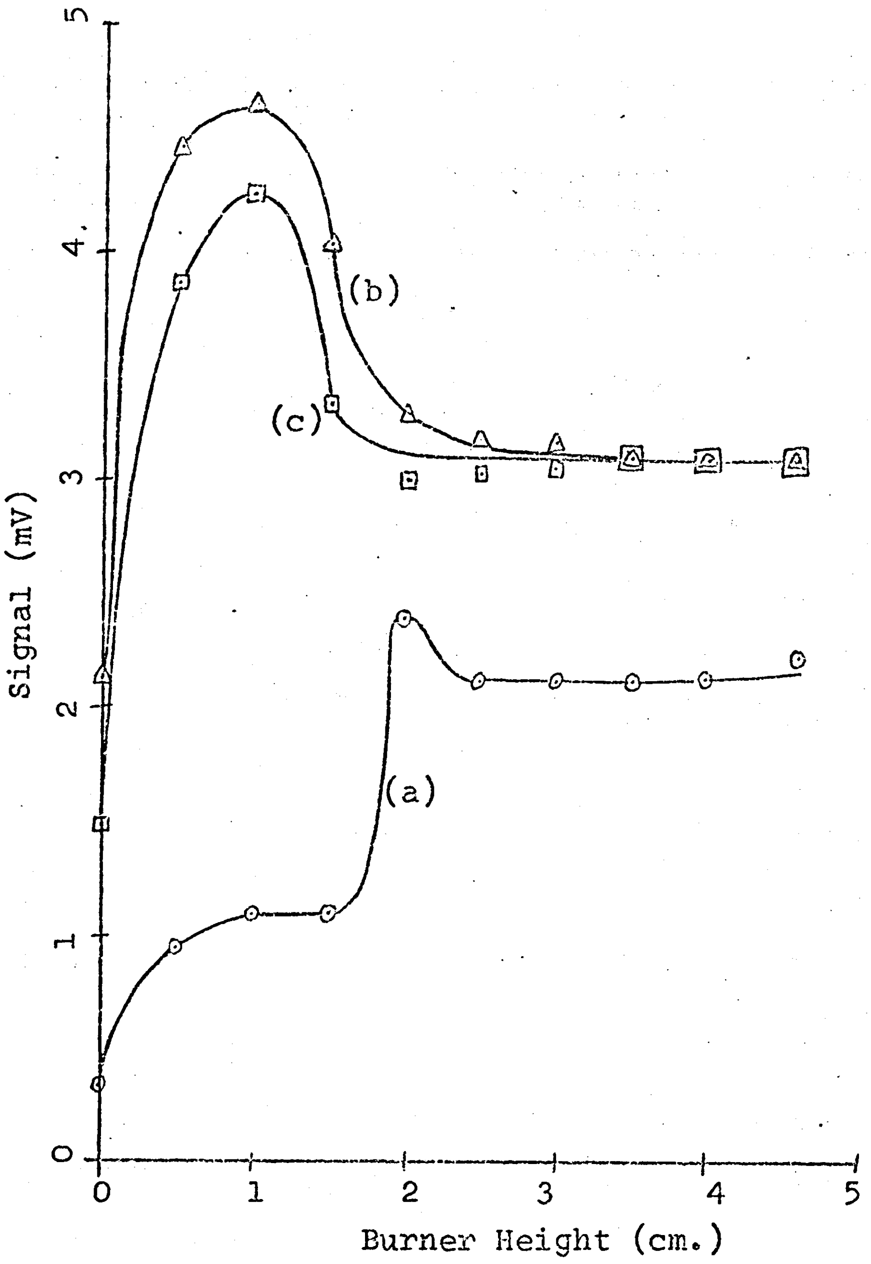


Figure 7.3

Influence of Burner Height on the Fluorescence of Bismuth-Unseparated Air-Acetylene Flame

(a) True fluorescence from 200µg.ml.$^{-1}$ Bi.

(b) Background emission from flame + source light scatter.

(c) Background emission from flame (EDL switched off).

a contribution from source light scatter. The presence of any atomic emission from bismuth and the true flame background, devoid from any scatter problems were ascertained by repeating the above experiment whilst the EDL was switched off. No atomic emission from bismuth at this concentration was observed, the emission measured when the bismuth solution was sprayed being identical with that of water. The variation in the true flame background with burner height is shown in curve c of Figure 7.3.

These experiments were repeated using the argon separated air-acetylene flame spraying a 1μg.ml.$^{-1}$ solution of bismuth, the influence of the burner height being represented in Figure 7.4.

Scattering of the source light was found to be particularly serious at low burner heights (Figures 7,3, 7.4). When the optical light path was higher than 3 cm. above the burner top scattering was virtually non-existent and, subsequently, a burner height of 3.5 cm. was used in this study.

A summary of the optimum instrumental parameters is shown in Table 7.2. These conditions, optimised using an ac. amplifier, were used to ascertain the detection limits for the determination of lead, silver and bismuth by atomic fluorescence using both the asynchronous and synchronous amplifiers. A 'block' diagram showing the atomic fluorescence spectrometer used in this investigation is shown in Figure 7.5.

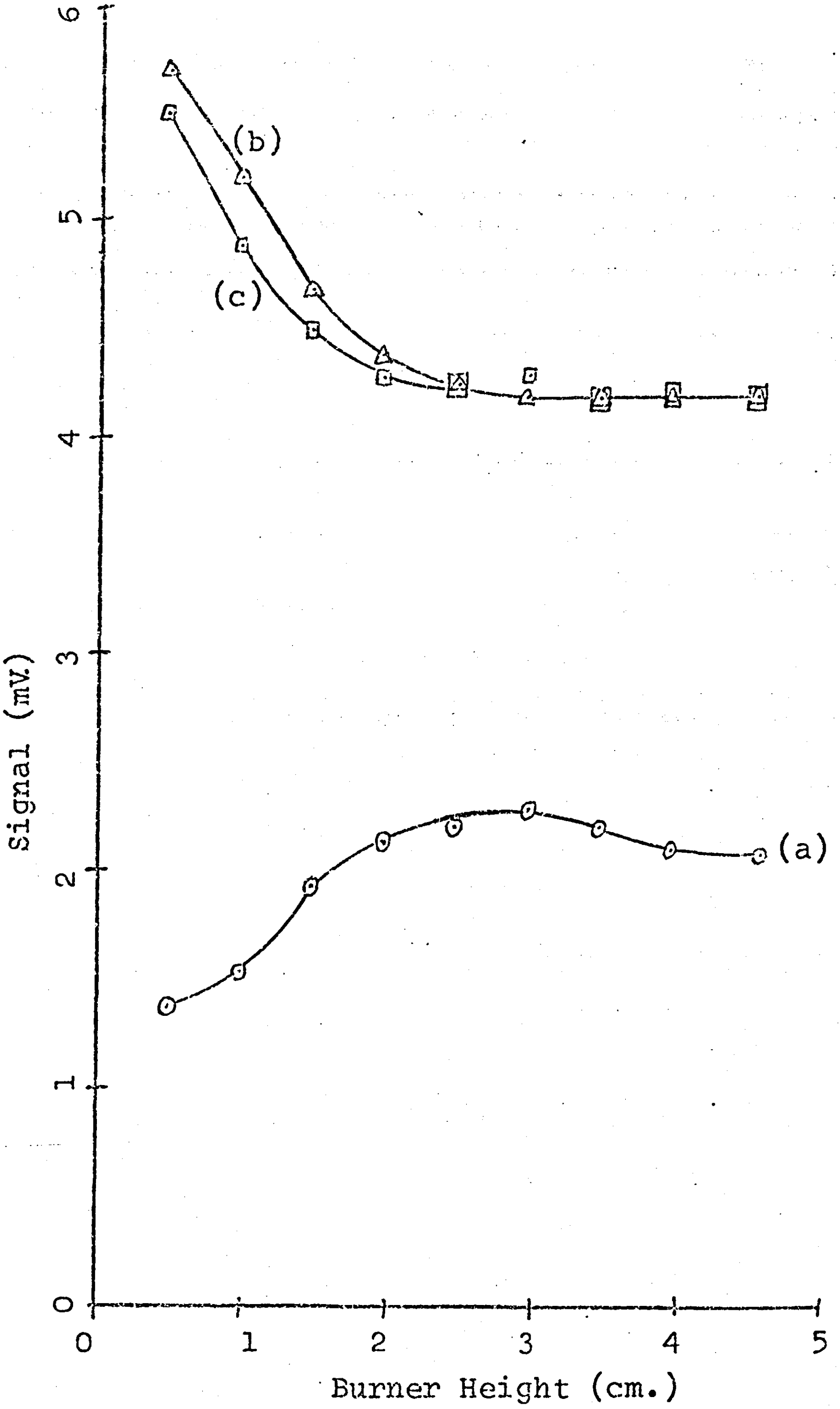


Figure 7.4

Influence of Burner Height on the Fluorescence of Bismuth-Argon Separated Air-Acetylene Flame

(a) True fluorescence from 1μg.ml.$^{-1}$ Bi.

(b) Background emission from flame + source light scatter.

(c) Background emission from flame. (EDL switched off).

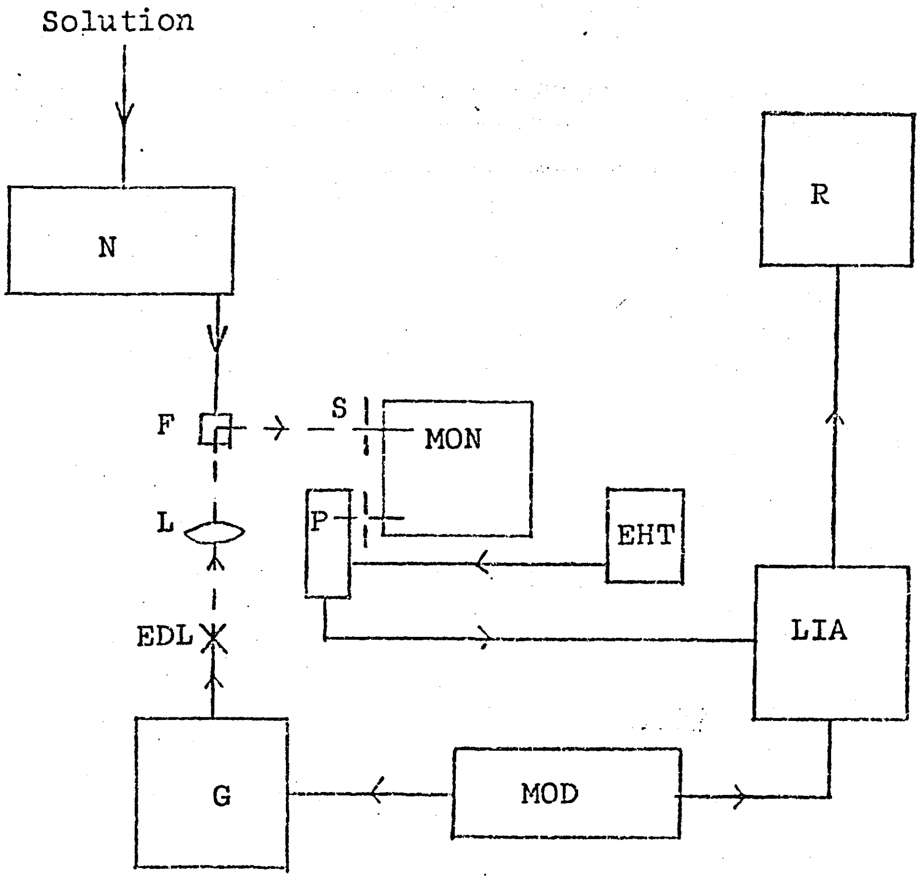


Figure 7.5

Atomic Fluorescence Spectrophotometer

Legend:-

EDL	Electrodeless Discharge Lamp	MOD	Modulator
EHT	E.H.T. Power Supply	MON	Monochromator
F	Flame	N	Nebulizer
G	Microwave Generator	P	Photomultiplier Tube
L	Lens	R	Recorder
LIA	Lock In Amplifier	S	Slits

TABLE 7.2

Optimum Instrumental Conditions

Slit: entrance	mm.	0.100
exit	mm.	0.150
Burner height	cm.	3.5
Air pressure	p.s.i.	30
Air flow rate	$l.min.^{-1}$	5
Acetylene pressure	p.s.i.	10
Acetylene flow rate	$ml.min.^{-1}$	800
Argon pressure	p.s.i.	30
Argon flow rate		Not measured

EDL microwave power:-		50 Hz. Modulation	Unmodulated
Bi	watt	40	55
Pb	watt	40	40
Ag	watt	45	45

Filters - Lock-In Amplifier:-		
Low pass	Hz.	80
High pass	Hz.	1

7.2.3.4. Detection Limits

The limits of detection for the atomic fluorescence determination of bismuth, lead and silver in aqueous solution are shown for the Jarrell-Ash amplifier in Table 7.3 and for the lock-in amplifier in Table 7.4. Those for the former amplifier are quoted in both the modulated and unmodulated modes of operation while those for the lock-in amplifier are, by necessity, under modulation. In order to justify the comparison the modulation frequency was 50 Hz. in both amplifiers. The detection limits were obtained by spraying the metal solutions at suitable concentrations to give fluorescence within the range 1 to 8 mV. The standard deviation of the average signal from seven successive sprayings of the solutions are shown in Tables 7.5 and 7.6. for the two amplifiers. The metal concentration of the solutions sprayed was arranged to give a fluorescence signal of between 5 and 6 mV. when determined under the optimum instrumental conditions shown in Table 7.2.

7.3. Discussion

7.3.1. Atomic Absorption

In atomic absorption absorbance growth curves are usually linear particularly at low analyte concentrations of 10 to 20 times the detection limit. Such plots obey Beer's Law from which the relationship

$$A = \log_{10} \frac{Io}{I}$$

can be derived where A, the absorbance, is proportional to a ratio of the intensities of the source light entering the flame, Io, and the emerging beam, I. In atomic absorption the ratio Io:I is constant and is dependent upon the number of atoms in the flame capable of absorption, i.e. the metal concentration, and not on the degree or quality of amplification available. Thus a lock-in amplifier would not be expected to produce a significant increase in

TABLE 7.3

Limits of Detection using an Alternating Current Amplifier

Element	Wavelength (nm.)	Detection Limit[a] ($\mu g.ml.^{-1}$) Unseparated flame Continuous	Unseparated flame 50 Hz	Argon Separation Continuous	Argon Separation 50 Hz
Bismuth	306.8	0.524	0.676	0.029	0.043
	302.5	1.33	1.67	0.106	0.400
	223.1	1.69	2.09	0.130	0.428
Lead	405.8	0.617	0.702	0.089	0.121
	283.3	0.249	0.273	0.081	0.097
	217.0	0.100	0.107	0.075	0.082
Silver	328.1	0.026	0.037	0.007	0.009

[a] The detection limits are quoted for a S:N ration of 1.

TABLE 7.4

Limits of Detection using the Lock-In Amplifier

Element	Wavelength (nm.)	Detection Limit[a] (μg.ml.$^{-1}$) 50 Hz. Modulation Unseparated flame	Detection Limit[a] (μg.ml.$^{-1}$) 50 Hz. Modulation Argon Separation
Bismuth	306.8	0.0067	0.0062
	302.5	0.0196	0.0207
	223.1	0.0196	0.0205
Lead	405.8	0.0071	0.0078
	283.3	0.0055	0.0063
	217.0	0.0042	0.0041
Silver	328.1	0.0016	0.0019

[a] The detection limits are quoted for a S:N ratio of 1.

TABLE 7.5

Standard Deviation of Fluorescence Measurements using an AC. Amplifier

		Standard Deviation (mV.)			
		Unseparated Flame		Argon Separation	
Element	Wavelength (nm.)	Continuous	50 Hz	Continuous	50 Hz
Bismuth	306.8	0.044	0.027	0.067	0.043
	302.5	0.042	0.069	0.098	0.054
	223.1	0.040	0.038	0.034	0.057
Lead	405.8	0.071	0.082	0.076	0.067
	283.3	0.065	0.069	0.047	0.057
	217.0	0.038	0.038	0.054	0.039
Silver	328.1	0.036	0.024	0.025	0.039

TABLE 7.6

Standard Deviation of the Fluorescence Measurements using the Lock-In Amplifier

Element	Wavelength (nm.)	Standard Deviation (mV.) 50 Hz. Modulation	
		Unseparated Flame	Argon Separation
Bismuth	306.8	0.181	0.153
	302.5	0.137	0.095
	223.1	0.112	0.132
Lead	405.8	0.120	0.119
	283.3	0.101	0.065
	217.0	0.088	0.072
Silver	328.1	0.108	0.118

The detection limit, D, is given by the relationship

$$D = \frac{pcn}{s}$$

where 'p' is the signal:noise ratio, 'c' the concentration, 'n' the average peak to peak noise and 's' the signal intensity. In atomic absorption 's' has equality with the absorbance, A, and the equation therefore becomes -

$$D = \frac{pcn}{A}$$

At constant 'c' and 'p' a decrease in the detection limit will be brought about by either an increase in 'A' or a decrease in 'n' or both. In atomic absorption 'A' is at its maximum value when all the metals atoms are absorbing energy and a better detection limit will only be achieved, therefore, if the noise can be reduced.

This was found to be the case in the atomic absorption investigation using a lock-in amplifier as a decrease in the limit of detection of about five fold was achieved over a conventional amplifier for bismuth, lead and silver by a substantial reduction in noise and not by an increase in signal strength. It was felt, however, that this small increase in sensitivity was not justified by the difficulties involved in the measurement of absorption signals using a lock-in amplifier. Too many variables such as lamp current, photomultiplier tube voltage and amplifier band pass, needed to be inter-related before reproducible absorbance measurements could be taken. The time constants involved in the amplifier were too long for practical analysis and it was difficult to 'back off' the large signal from the hollow cathode lamp even at the lowest possible lamp currents and low photomultiplier tube voltages. Lock-in amplification did, however, have one advantage over a normal ac. amplifier in that it was possible to reduce the noise from the hollow cathode lamp and the photomultiplier tube by the use of much lower lamp currents or photomultiplier tube voltages.

7.3.2. Atomic Fluorescence

Winefordner et al (36) have shown that the intensity of fluorescence of a particular metal at low concentrations is proportional to the radiance of the light source as well as to the metal atom concentration in the flame. As powerful spectral sources are not always available the degree of fluorescence achieved is limited and there exists, therefore, a definite need for lock-in amplification to make the best use of the fluorescence signal available.

A comparison of the detection limits obtained in atomic fluorescence with the ac. amplifier (Table 7.3) revealed values comparable with those achieved by other authors (Table 7.1) even though the instrumental conditions (Table 7.2) were optimum only for bismuth. A better detection limit was obtained in every case when the EDL and amplifier were operated in the continuous (dc.) mode. This is because part of the signal is always lost by the 'chopping' action of the modulator.

Table 7.3 also compares the detection limits for the three metals in both the conventional and argon separated flames and shows approximately a 10 fold decrease in the limits of detection for the metals in both the continuous and modulated modes under separation. The figure quoted for bismuth in the unseparated air-acetylene flame in the continuous operating mode is comparable to that achieved in the argon-hydrogen flame discussed in the preceding chapter. On separating the air-acetylene flame the chief source of background signal and noise became the photomultiplier tube making it possible to use the highest tube voltages available in order to achieve a large increase in the signal measured.

On repeating the experiment with a lock-in amplifier an increase in fluorescence of the order of 100 was obtained in the conventional flames over the detection limits achieved in the normal amplifier (Table 7.4). Under argon separation, however, a far smaller decrease in detection limit was apparent using lock-in amplification, the values being of the same order as those obtained in the unseparated flame. Thus the use of a separated flame in conjunction with a synchronous amplifier was not justified. This was expected as it has already been shown earlier in this chapter that any signal out of phase with the synchronous detector would be rejected and not measured. The flame background falls into this category as it consists of an almost continuous signal source and only a small fraction of it will be modulated at 50 Hz, in phase with the EDL and detector.

Tables 7.5 and 7.6 compare the standard deviation of the fluorescence signal from each of the metals in both the conventional and lock-in amplifiers respectively. The standard deviations whilst larger for the lock-in amplifier should not be viewed in isolation as, although they predict that the lock-in amplifier is more prone to drift and instability, it should not be forgotten that they represent the signals from metals whose concentration is up to 100 times smaller than those used in the conventional amplifier.

7.4. Conclusion

Lock-in amplification has been shown to be of limited value in atomic absorption spectroscopy as a decrease in the limit of detection becomes apparent only if there is a considerable reduction in the noise. The small decrease in the detection limits achieved, approximately five fold, were not justified by the long spraying times involved before steady signals were obtained.

The effects of lock-in amplification in atomic fluorescence spectroscopy are much more advantageous. A two orders of magnitude of ten decrease in the detection limits for bismuth, lead and silver in the air-acetylene flame was achieved over the conventional amplifier using the lock-in system. Separated flames, however, showed little advantage over the normal air-acetylene flame using the lock-in amplifier although a significant improvement in detection limit was shown under separation using the ansynchronous detector.

The main disadvantage of the lock-in system of amplification used in this study was the lengthy time constant inherent with the high degree of low pass filtering used in the amplifier. This, although detracting from the practical use of a lock-in system, may be overcome by a compromise between the efficiency of the low pass filter and the time constant.

No mirrors were used in this investigation as their use with the ac. amplifier did not improve the fluorescence signal without increasing the flame background. However a further decrease in the detection limits should be possible with the lock-in amplifier if mirrors are used as the detector will not rectify the signal from the flame background. Similarly the use of high modulation frequencies has not been investigated and a significant improvement in the sensitivity should be possible at frequencies in the kilohertz range.

With regard to the use of atomic fluorescence spectrometers equipped with lock-in amplifiers in the determination of trace amounts of metals in steels, these amplifiers should be of benefit both in lowering the limit at which the metal can be determined and in decreasing the amount of sample required for the analysis. This may be especially advantageous where the amount of sample available for analysis is limited. Where the determination of trace metals in steel by atomic fluorescence using a conventional amplifier often requires a preliminary solvent extraction then, it may be possible to determine the same amount of the metal without recourse to solvent extraction if a lock-in system is used.

In atomic fluorescence studies where the achievement of very low limits of detection is of prime importance then the use of a lock-in system of amplification is of benefit. Although this lock-in amplifier has not been compared with commercial instruments it is thought to compare very favourably. As its cost is roughly comparable with commercially built asynchronous amplifiers then some sort of lock-in system is well within the scope of any laboratory considering atomic fluorescence spectroscopy.

CONCLUSION

This thesis has investigated the atomic spectroscopy of four metals; bismuth, lanthanum, lead and silver, with particular reference to their determination in trace amounts in steels.

Of the three associated techniques, ~~atomic~~ flame emission, whilst having the requirements with regard to sensitivity for the determination of these trace metals, suffers serious inter-element interference problems which render both the direct determination in aqueous solution and the determination after prior solvent extraction extremely difficult.

On the other hand atomic absorption suffers far less from these problems, ample sensitivity being available especially when the metal is extracted into an organic solvent. Many of the problems associated with the determination of trace metals in steel, after a preliminary solvent extraction, occur in the extraction system and not in the actual determination, as the extraction of the metal of interest is often inhibited by the co-extraction of other matrix elements.

The applications of atomic fluorescence are limited but as the technique becomes available in more and more laboratories through the introduction of commercial instruments, the applications will flourish. The stage is rapidly approaching where the sensitivities available for atomic fluorescence are better or comparable to those for atomic absorption for a large number of metals. As more intense spectral sources become available and instrumentation continues to improve the sensitivity and precision will also show further improvement so that, in the future, atomic fluorescence may even surpass the role of atomic absorption in the determination of trace amounts of metals. As the advancement of instrumentation proceeds, e.g. in lock-in amplification systems, it will become possible to determine trace amounts of metals in steels directly, by atomic fluorescence without recourse to a preliminary solvent extraction separation.

Of the three atomic spectroscopic techniques, atomic absorption will, however, continue to be in the forefront of the techniques available for the determination of metals in intermediate concentrations in steels and also in many other materials.

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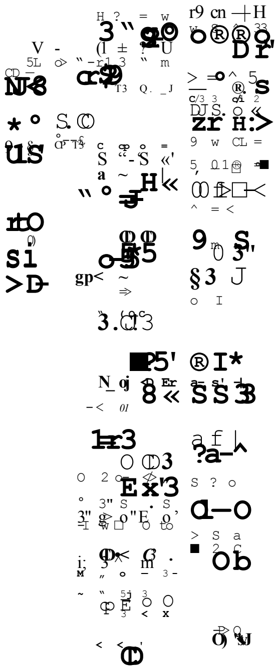

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